Second Law of Thermodynamics

Syllabus: Reversible and irreversible process with examples. Interconversion of work and heat. Heat engines. Carnot’s cycle, Carnot engine & efficiency. Refrigerator & coefficient of performance, Kelvin-Planck and Clausius statements for the second law and their equivalence. Carnot’s Theorem. Applications of second law of Thermodynamics: Thermodynamic scale of temperature and its equivalence to perfect gas scale.

Thermodynamic Processes

- **Reversible process:**

- Infinitesimal change in the conditions of the surroundings leads to a ‘reversal’ of the process
- System is very close to equilibrium and infinitesimal changes can restore the system and surroundings to the original state
- *Any reversible process is necessarily a quasi-static one*
- During a reversible process, the system is in thermodynamic equilibrium with its surroundings throughout the entire process
- Since it would take an infinite amount of time for the reversible process to finish, perfectly reversible processes are impossible

Thermodynamic Processes

Reversible process is quasi-static but the reverse not necessarily true

Quasi-static process are those processes in which a system is taken from one state to other in infinitesimal steps (slowly) such that there is always an equilibrium maintained between system and surrounding. For a process which is not quasi-static, it would allow the system an infinite number of pathways to return to its initial state and thus make the process irreversible. Hence, a reversible process must be quasi-static.

However, if a process is quasi-static, it doesn't mean that the process is reversible. For example, during the compression of a gas present in cylinder using a piston such that there is friction between the cylinder and piston, in this case there will be generation of dissipative entropy which will make the process irreversible even though it is performed quasi-statically.

Thermodynamic Processes

- **Irreversible process:**

- A thermodynamic process which is not reversible, is called an irreversible process
- A change in the thermodynamic state of a system and all of its surroundings cannot be precisely restored to its initial state by infinitesimal changes in some properties of the system
- A system that undergoes an irreversible process may still be capable of returning to its initial state; however, the impossibility occurs in restoring the environment to its own initial conditions
- **All natural processes are irreversible**

Second Law of Thermodynamics

Heat Reservoir/Bath/Source/Sink

- A system at some temperature T throughout and is conditioned in such a way that it can exchange heat but no work with its surroundings

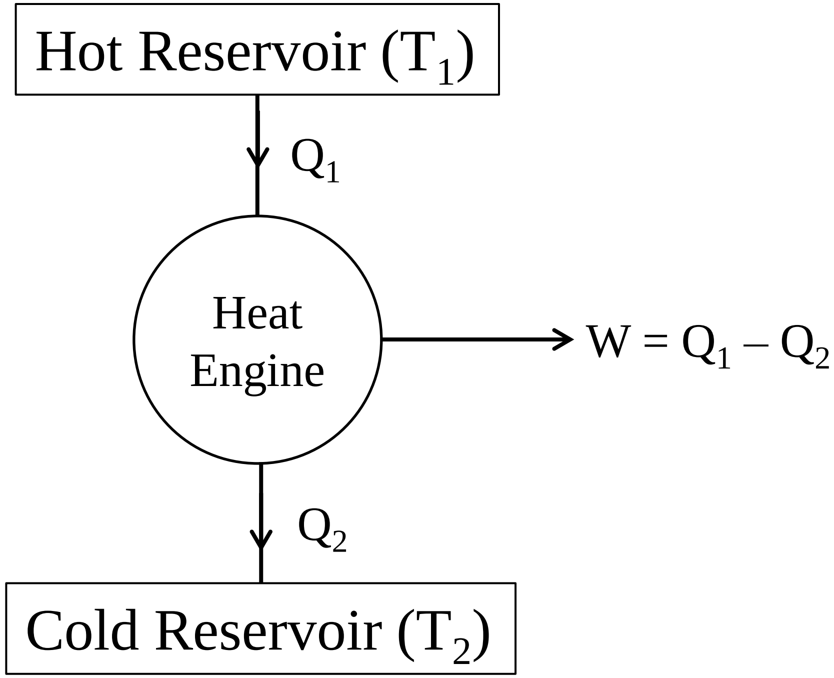
  For example, a mass of water at temperature T throughout – its volume remains practically constant

- It is an effectively infinite pool of thermal energy at a given, constant temperature. The temperature of the reservoir does not change when heat is added or extracted because of the infinite heat capacity.

- As it can act as a source and sink of heat, it is often also referred to as a heat reservoir or heat bath

Second Law of Thermodynamics

Conversion of heat into work: Heat Engine



Hot Reservoir (T_1)

Q_1

Heat Engine

$W = Q_1 - Q_2$

Q_2

Cold Reservoir (T_2)

Efficiency: $\eta = \dfrac{\text{work output}}{\text{heat input}} = \dfrac{W}{Q_1} = \dfrac{Q_1 - Q_2}{Q_1}$

$$= 1 - \frac{Q_2}{Q_1}$$

Second Law of Thermodynamics

- ❑ Is it possible to design a heat engine that yields $\eta = 1$ (100% efficiency)? $Q_2 = 0$!!!
- ❖ Well, even an ideal heat engine can not deliver 100% efficiency
- ❑ What is an ideal heat engine?
- ❖ Idea of ideal heat engine was introduced by Carnot, a French engineer, in 1824 which realizes a cyclic process called the Carnot cycle.
  - Comprises two isothermal and two adiabatic processes
  - All processes are reversible – an ideal case

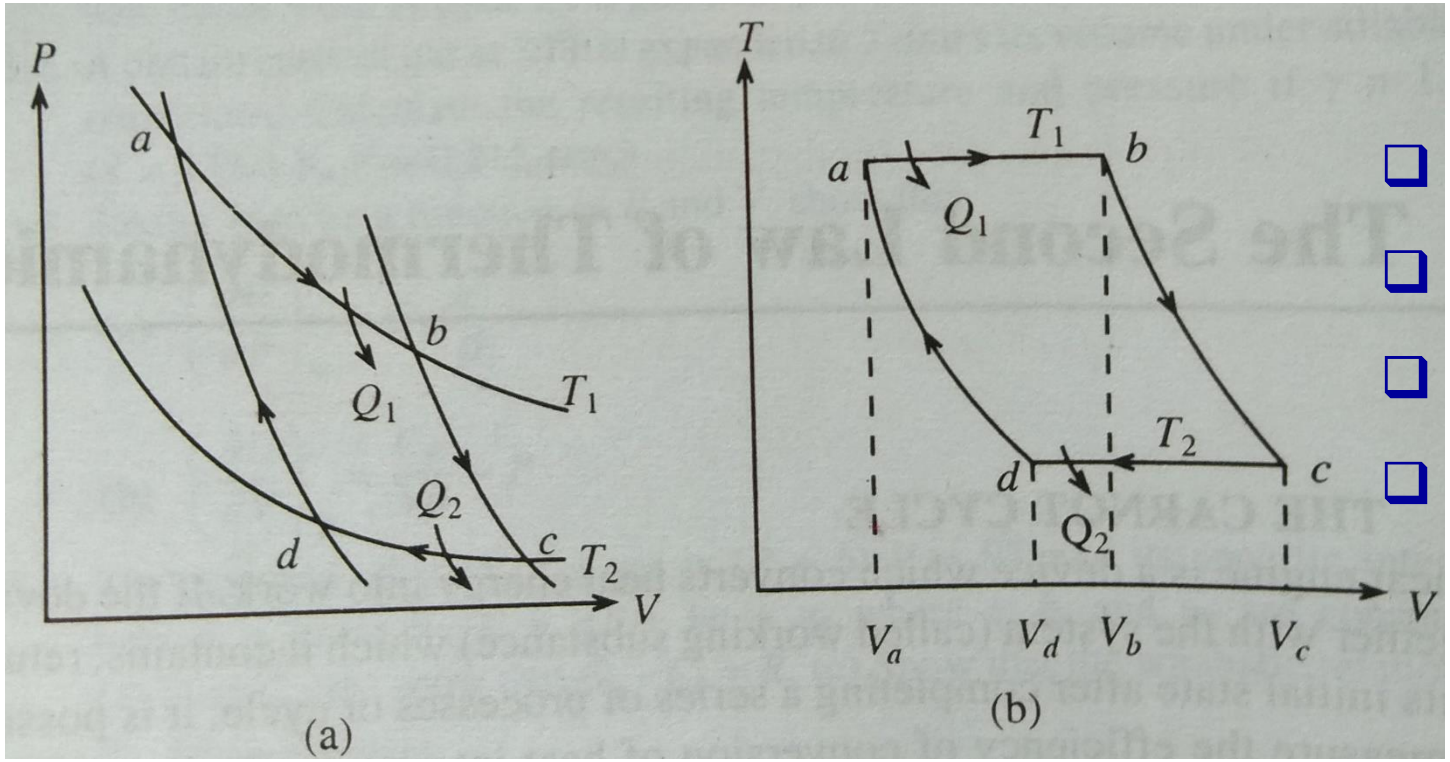
Carnot cycle may be performed by any nature of working substance – solid, liquid, gas, paramagnetic substance etc.

Second Law of Thermodynamics

- Heat transfer takes place only in two isothermal processes: Q_1 amount of heat is absorbed by the working substance from the hot reservoir at temperature T_1 and Q_2 amount of heat is rejected by the substance to the cold reservoir at temperature T_2
- The processes are reversible – temperature of the working substance is equal to the temperature of the reservoir during the heat transfer
- Cyclic process: No change in internal energy

Second Law of Thermodynamics

Carnot cycle with simple compressible system



- ☐ a → b: Reversible isothermal expansion
- ☐ b → c: Reversible adiabatic expansion
- ☐ c → d: Reversible isothermal compression
- ☐ d → a: Reversible adiabatic compression

Second Law of Thermodynamics

Carnot cycle of an ideal gas

$$Q_1 = W_1 = \int_{V_a}^{V_b} p\,dV = nRT_1 \int_{V_a}^{V_b} \frac{dV}{V} = nRT_1 \ln\left(\frac{V_b}{V_a}\right)$$

$$Q_2 = W_3 = -\int_{V_c}^{V_d} p\,dV = nRT_2 \int_{V_c}^{V_d} \frac{dV}{V} = nRT_2 \ln\left(\frac{V_c}{V_d}\right)$$

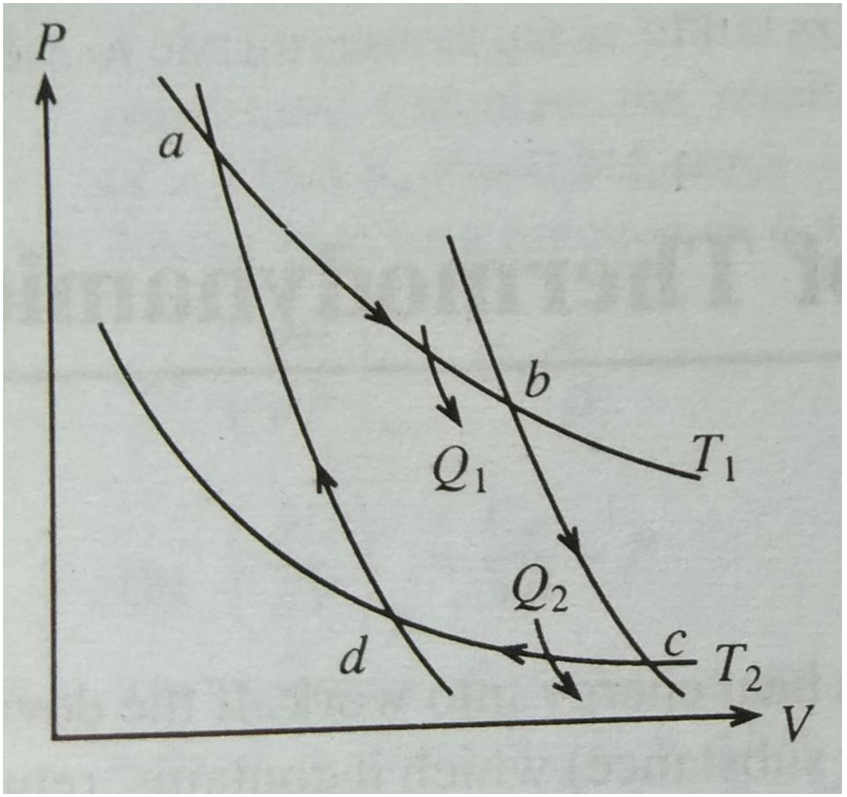
adiabatic process b → c: $T_1 V_b^{\gamma-1} = T_2 V_c^{\gamma-1}$

adiabatic process d → a: $T_1 V_a^{\gamma-1} = T_2 V_d^{\gamma-1}$

$$\boxed{\Rightarrow \frac{V_b}{V_a} = \frac{V_c}{V_d}}$$

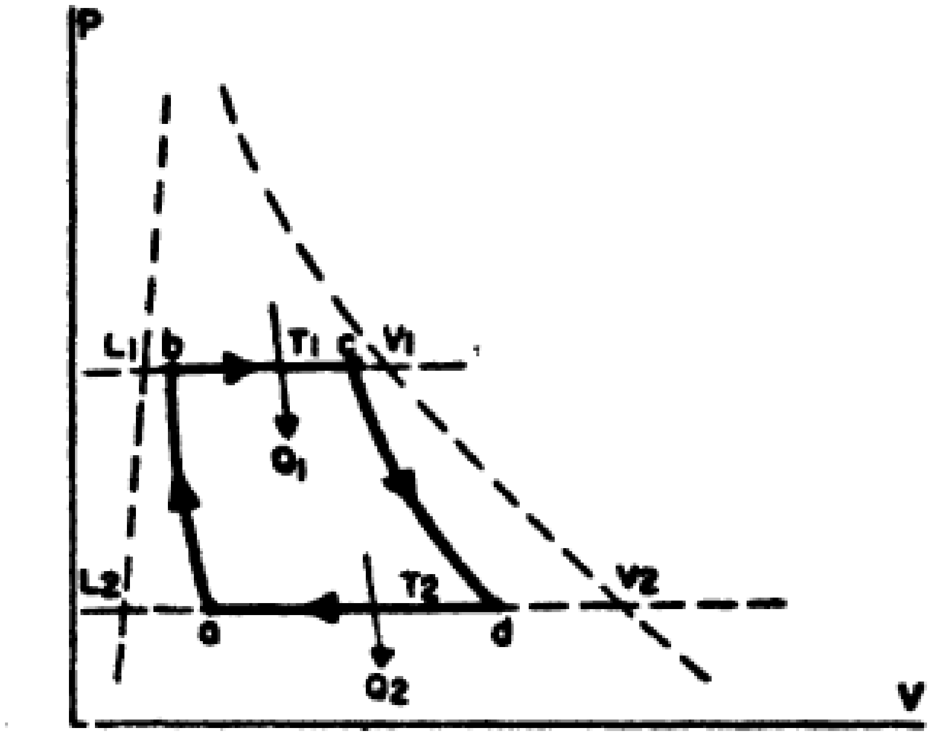
$$\boxed{\Rightarrow \frac{Q_2}{Q_1} = \frac{T_2 \ln(V_c/V_d)}{T_1 \ln(V_b/V_a)} = \frac{T_2}{T_1}}$$

$$\boxed{\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}}$$



Second Law of Thermodynamics

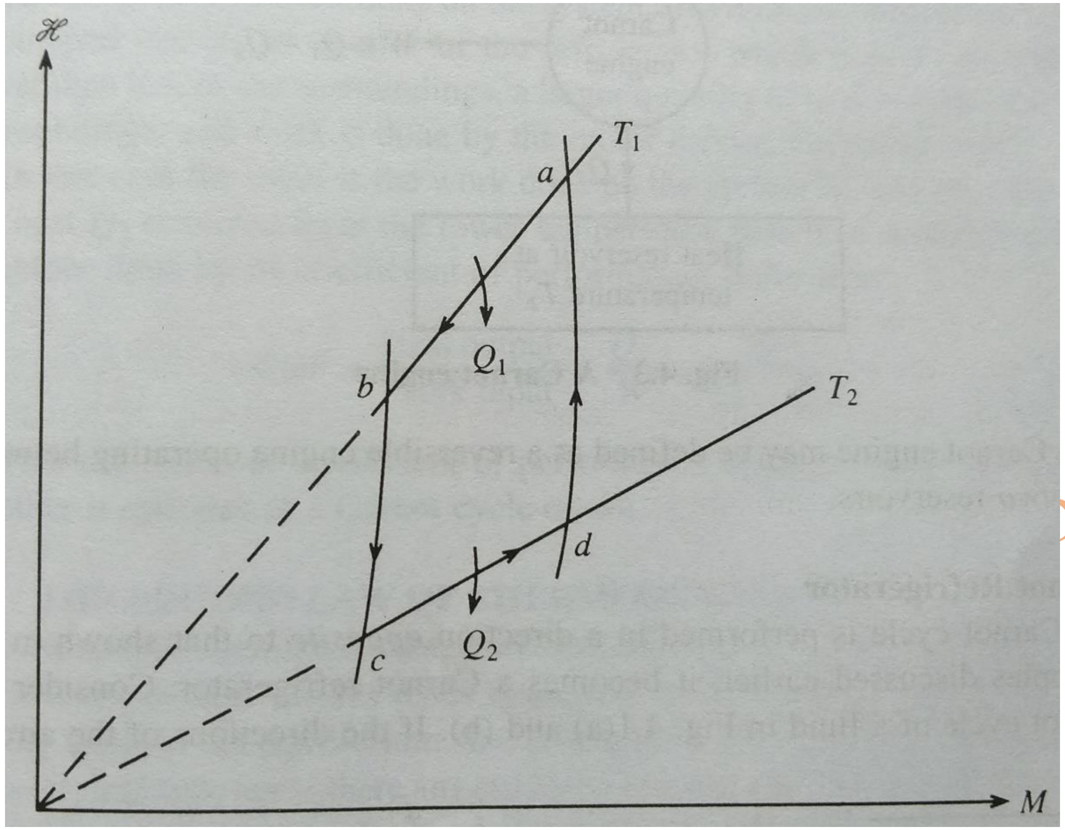
Carnot cycle of a liquid-vapour mixture



- a → b: Reversible adiabatic compression
- b → c: Reversible vaporization at fixed pressure and temperature
- c → d: Reversible adiabatic expansion
- d → a: Reversible condensation at fixed pressure and temperature

Second Law of Thermodynamics

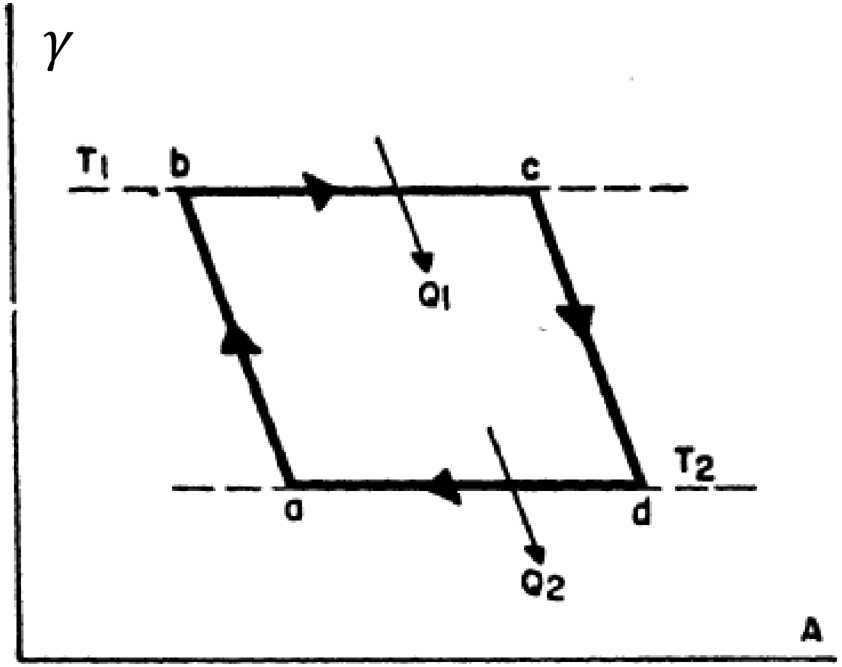
Carnot cycle of a paramagnet



- a → b: Reversible isothermal demagnetization
- b → c: Reversible adiabatic demagnetization
- c → d: Reversible isothermal magnetization
- d → a: Reversible adiabatic magnetization

Second Law of Thermodynamics

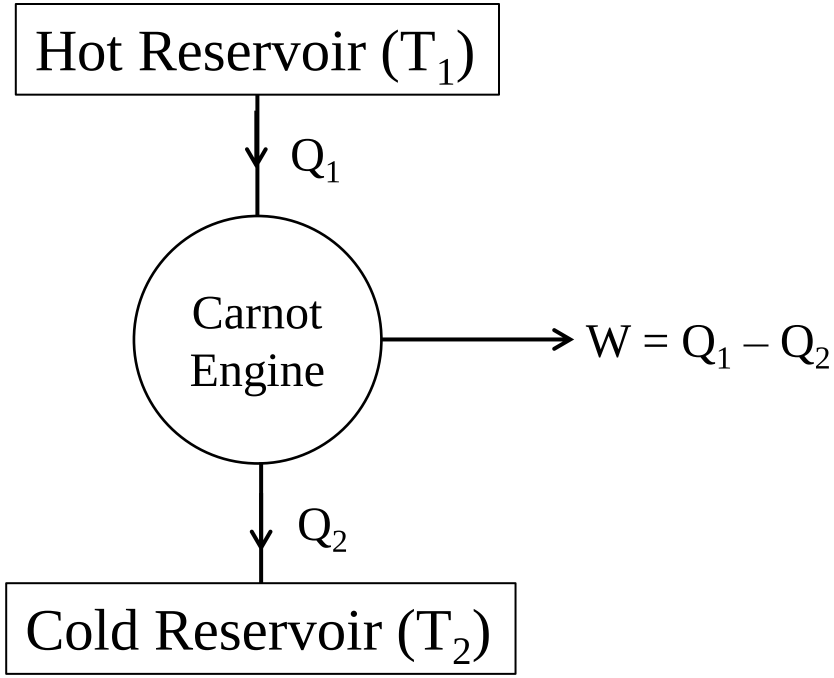
Carnot cycle of a surface film



- ❑ a → b: Reversible adiabatic compression
- ❑ b → c: Reversible isothermal expansion
- ❑ c → d: Reversible adiabatic expansion
- ❑ d → a: Reversible isothermal compression

Second Law of Thermodynamics

Carnot Engine: Reversible engine



Hot Reservoir (T_1)

Q_1

Carnot Engine

$W = Q_1 - Q_2$

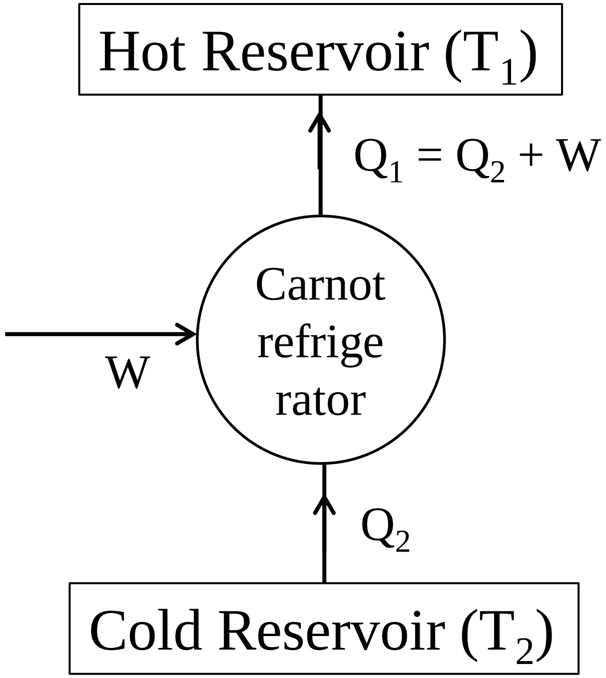
Q_2

Cold Reservoir (T_2)

Efficiency: $\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$

Second Law of Thermodynamics

Carnot Refrigerator: Reversible heat pump



Hot Reservoir (T_1)

$Q_1 = Q_2 + W$

Carnot refrigerator

W

Q_2

Cold Reservoir (T_2)

Coefficient of Performance (CoP):

$$= \frac{\text{heat output}}{\text{work input}} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

$$= \frac{T_2}{T_1 - T_2} \quad (\because Q_1/Q_2 = T_1/T_2)$$

Second Law of Thermodynamics

A Carnot engine is operated between two heat reservoirs at temperature 27 °C and 327 °C. Find the efficiency of the engine. The engine releases 50 cal heat per cycle into the cold reservoir. How much heat does it absorb per cycle from the hot reservoir? What is the work output per cycle? What is the coefficient of performance of a heat pump operated between the same two reservoirs?

$$\boxed{\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{27+273}{327+273} = 0.5 = 50\%}$$

$$\boxed{\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \Rightarrow Q_1 = Q_2 \frac{T_1}{T_2} = 50 \times \frac{327+273}{27+273}\ \text{cal} = 100\ \text{cal}}$$

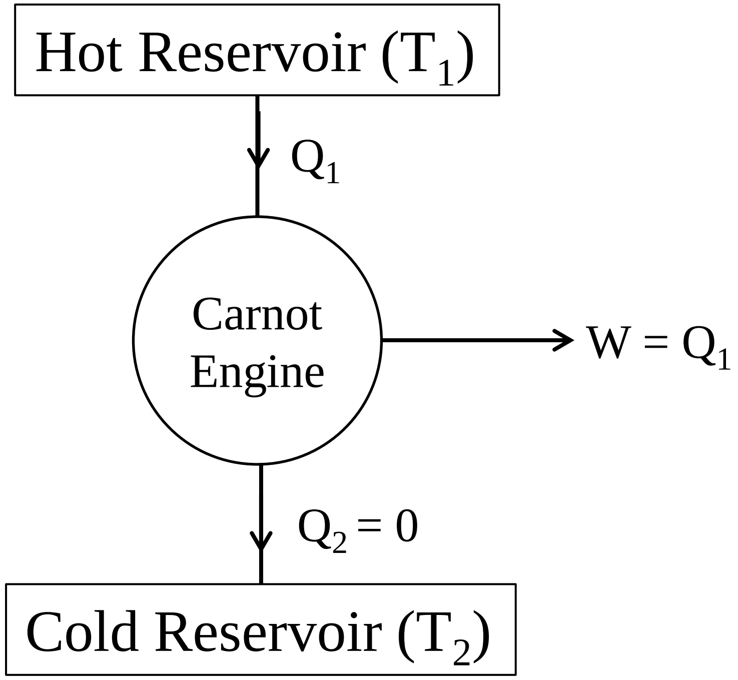
$$\boxed{\eta = \frac{W}{Q_1} \Rightarrow W = \eta Q_1 = 0.5 \times 100\ \text{cal} = 50\ \text{cal}}$$

$$\boxed{\text{CoP} = \frac{T_2}{T_1 - T_2} = \frac{27+273}{327-27} = 1 = 100\%}$$

Second Law of Thermodynamics

- Is it possible to design a heat engine that yields η = 100% ?

- Is it possible to design a heat pump that yields CoP = ∞?



Hot Reservoir (T_1)

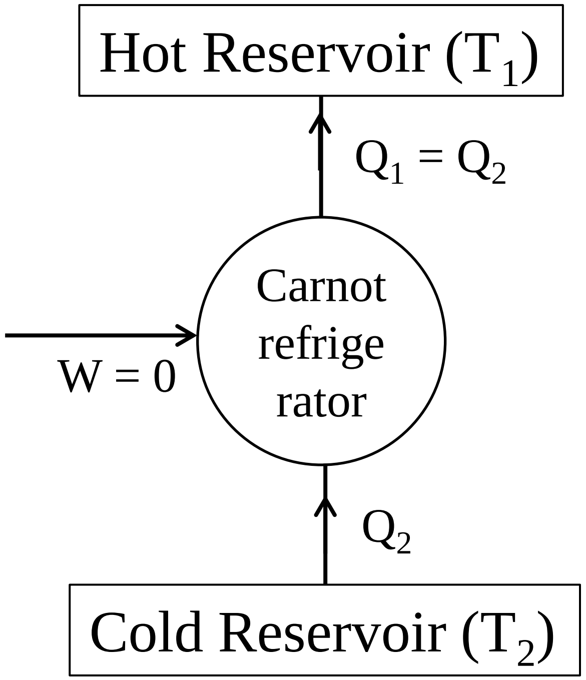
Q_1

Carnot Engine

$W = Q_1$

$Q_2 = 0$

Cold Reservoir (T_2)



Hot Reservoir (T_1)

$Q_1 = Q_2$

Carnot refrigerator

$W = 0$

Q_2

Cold Reservoir (T_2)

First law allows both devices in principle, not possible to implement!

Second Law of Thermodynamics

- The first law of thermodynamics arose as the result of the impossibility of constructing a machine which could create energy.
- It places no limitations on the possibility of transforming energy from one form into another.
- What we just have realized that, on the basis of first law alone, the possibility of transforming heat into work or work into heat always exists provided the total amount of heat is equivalent to the total amount of work. However, there are very definite limitations to the possibility of transforming heat into work.
- We need to introduce the SECOND LAW to rule out the possibility of constructing a perpetuum mobile of the second kind! (Note that, the FIRST LAW rules out the possibility of constructing a perpetuum mobile of the first kind – constructing a self-operating machine).

Second Law of Thermodynamics

Original statement of Lord Kelvin: It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects

Original statement of Max Planck: It is impossible to construct an engine which, working in a complete cycle, will produce no effect other than the raising of weight and cooling of a heat reservoir

Kelvin-Planck statement: *It is impossible to construct an engine that, operating in a cycle, will produce <u>no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work</u>*

Heat does not flow spontaneously from a cold body to a hot body

Second Law of Thermodynamics

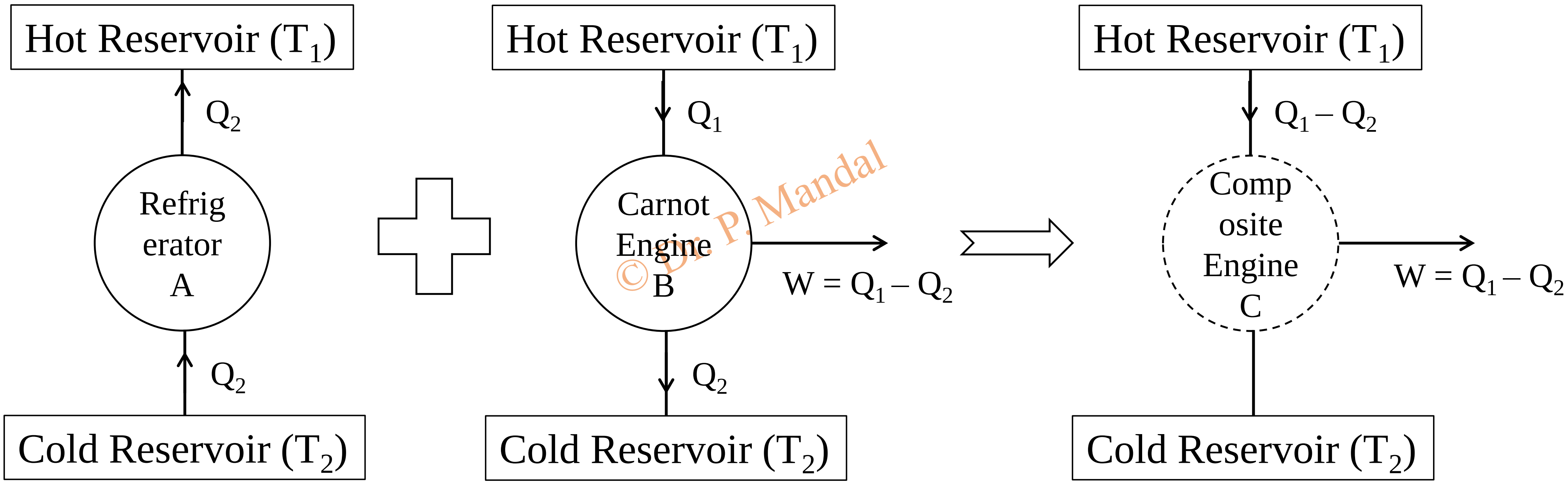
Clausius statement: *It is impossible to construct a refrigerator that, operating in a cycle, will produce* <u>*no effect other than the transfer of heat*</u> *from a lower-temperature reservoir to a higher-temperature reservoir*

Experimental evidence in support of this law consists mainly in the failure of all efforts that have been made to construct a perpetuum mobile of the second kind

Kelvin-Planck statement and Clausius statement are equivalent. If we assume one statement is violated, it will lead to the violation of other statement

Second Law of Thermodynamics

Let, Clausius statement is invalid! We can have a refrigerator, whose only final result is to transfer heat from cold reservoir to hot reservoir!

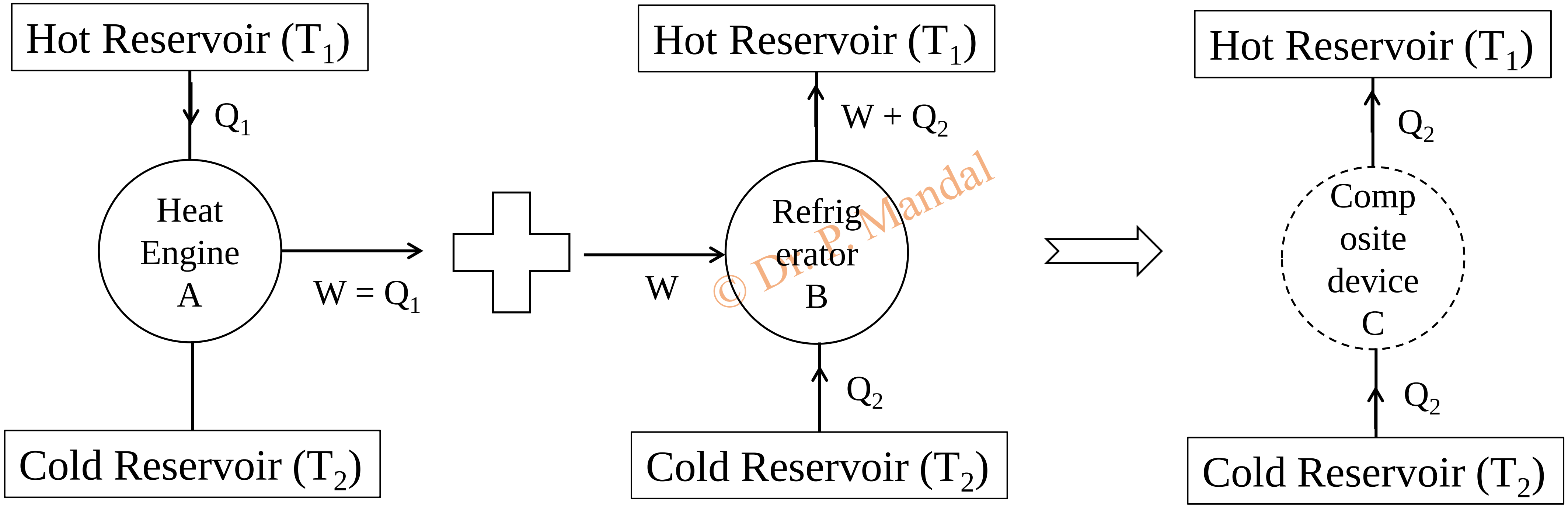


Violates Clausius statement

Violates Kelvin-Planck statement

Second Law of Thermodynamics

Let, Kelvin-Planck statement is invalid! We can have a heat engine, whose only final result is to transform heat absorbed from a reservoir into work



Hot Reservoir (T_1)

Q_1

Heat Engine A

$W = Q_1$

Cold Reservoir (T_2)

Hot Reservoir (T_1)

$W + Q_2$

W

Refrigerator B

Q_2

Cold Reservoir (T_2)

Hot Reservoir (T_1)

Q_2

Composite device C

Q_2

Cold Reservoir (T_2)

Violates Kelvin-Planck statement

Violates Clausius statement

Second Law of Thermodynamics

Carnot’s Theorem and corollary:

Direct consequences of the second law of thermodynamics:

- **The Theorem:** No heat engine can be more efficient than a reversible heat engine operating between the same two reservoirs
- **The Corollary:** All reversible heat engines operating between the same two reservoirs have the same efficiency

Second Law of Thermodynamics

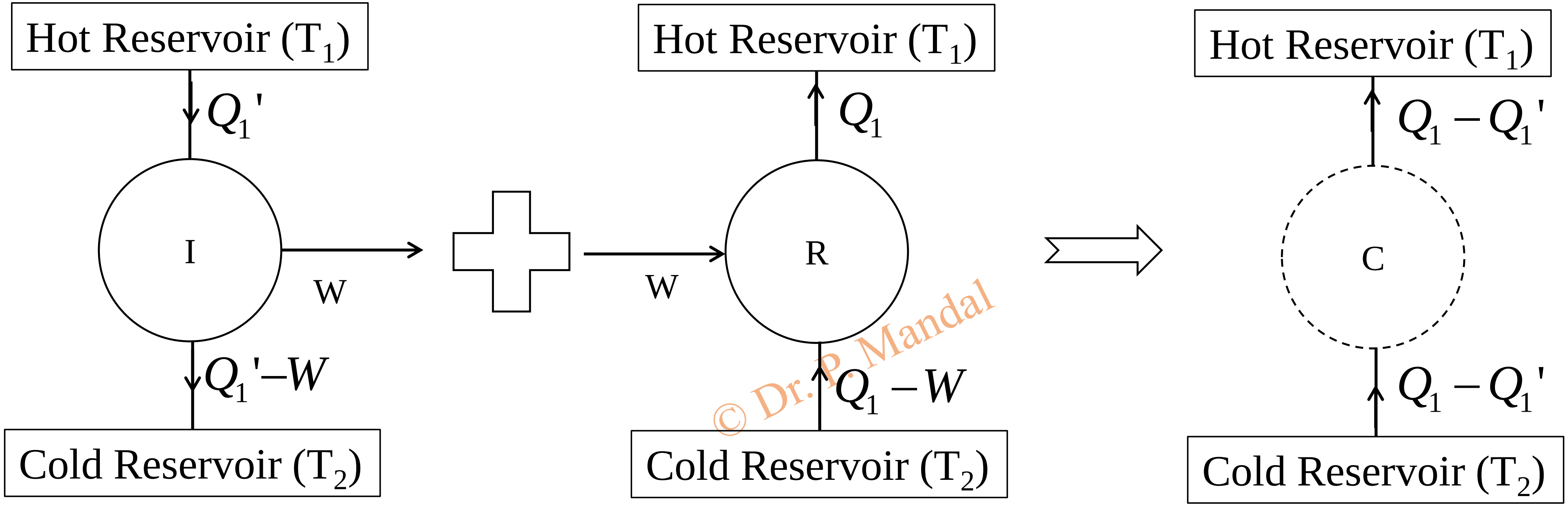
Carnot's Theorem: Proof

	Reversible Engine (R)	Any other Engine (I)
Work delivered	W	W
Heat absorbed from source	Q_1	Q_1'
Heat released at sink	$Q_1 - W$	$Q_1' - W$
Efficiency	$\eta_R = W/Q_1$	$\eta_I = W/Q_1'$

$$\text{assume} \quad \eta_I > \eta_R \quad \text{or} \quad \frac{W}{Q_1'} > \frac{W}{Q_1}$$

$$\Rightarrow Q_1 > Q_1'$$

Second Law of Thermodynamics



$$\boxed{\Rightarrow \eta_I \leq \eta_R}$$

Violates Clausius statement

Second Law of Thermodynamics

Corollary: Proof

- Consider two reversible engines R_1 and R_2 operating between the same two reservoirs and assume $\eta_{R1} > \eta_{R2}$
- Engine R_1 drives engine R_2 backwards so that it becomes a reversible refrigerator
- Following the same procedure we conclude $\eta_{R1} \leq \eta_{R2}$
- Next, assume $\eta_{R2} > \eta_{R1}$ and Engine R_2 drives engine R_1 backwards so that it becomes a reversible refrigerator: $\eta_{R2} \leq \eta_{R1}$

$$\boxed{\boldsymbol{\eta_{R2} = \eta_{R1}}}$$

Second Law of Thermodynamics

Thermodynamic Scale of Temperature:

- Mercury & Alcohol Thermometers: Volume increases with increase in temperature
- Resistance Thermometer: Resistance changes as the temperature changes
- Thermocouple Thermometer: Thermo-emf is a function of the temperature difference between the junctions

Rate of change of physical property depends on the system. Thus, different scales of temperature are used in these thermometers.

Second Law of Thermodynamics

Thermodynamic Scale of Temperature:

❖ Perfect Gas Thermometer:

- ❑ Based on the principle that at constant pressure, volume increases with increase in temperature while at constant volume, pressure increases with increase in temperature.
- ❑ Examples: Hydrogen gas scale, Oxygen gas scale
- ❑ There are very small differences between the various real gas scales – small difference is due to deviation of real gas behaviors from that of perfect gas. After correction, one gets the perfect gas scale from real gas scale.
- ❑ At low pressure ($P \rightarrow 0$), all real gases behave like a perfect gas (follows the equation of state $PV = RT$) – perfect gas scale is considered to be independent of the thermometric substance as compared to other scales.

Second Law of Thermodynamics

Thermodynamic Scale of Temperature:

- Perfect Gas Thermometer:

- ☐ In practice, perfect gas scale is not independent of the thermometric substance. Moreover, real gas behaviours widely deviate from that of perfect gas at low temperature and concept of perfect gas scale becomes irrelevant.
- ☐ Thus, we need a scale of temperature which is independent of the system –thermodynamic scale of temperature, introduced by Kelvin based on second law of thermodynamics.

Second Law of Thermodynamics

Thermodynamic Scale of Temperature:

- The fundamental theorem is that the ratio Q_2/Q_1 has the same value for all reversible engines that operate between the same temperatures t_1 and t_2 - the ratio is independent of the working substance provided it is reversible.

$$\frac{Q_2}{Q_1} = f(t_1, t_2)$$

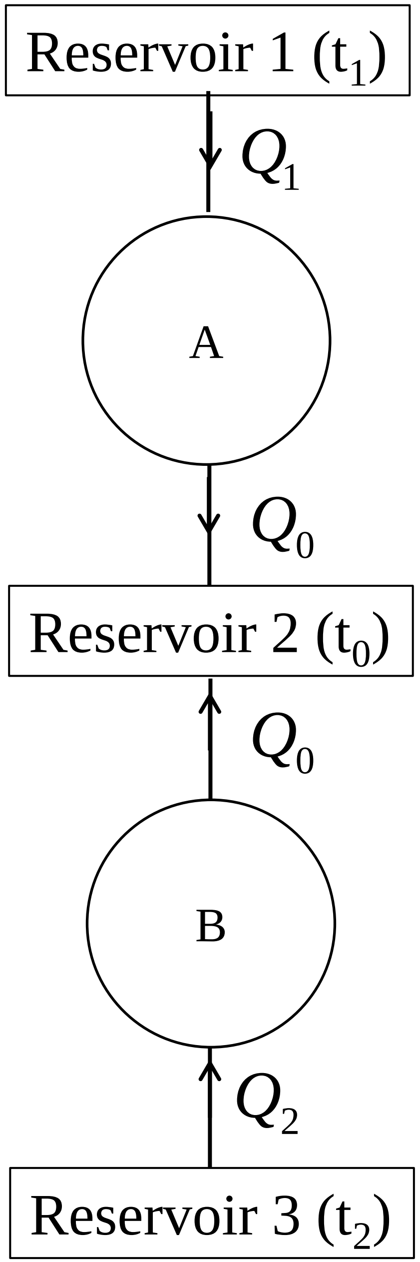
- $f(t_1, t_2)$ is a universal function of t_1 and t_2 and we shall prove that it satisfies the following property:

$$f(t_1, t_2) = \frac{f(t_0, t_2)}{f(t_0, t_1)}$$

t_0, t_1 and t_2 are arbitrary temperatures

Second Law of Thermodynamics

Thermodynamic Scale of Temperature:



$$\frac{Q_1}{Q_0} = f(t_0, t_1)$$

$$\frac{Q_2}{Q_0} = f(t_0, t_2)$$

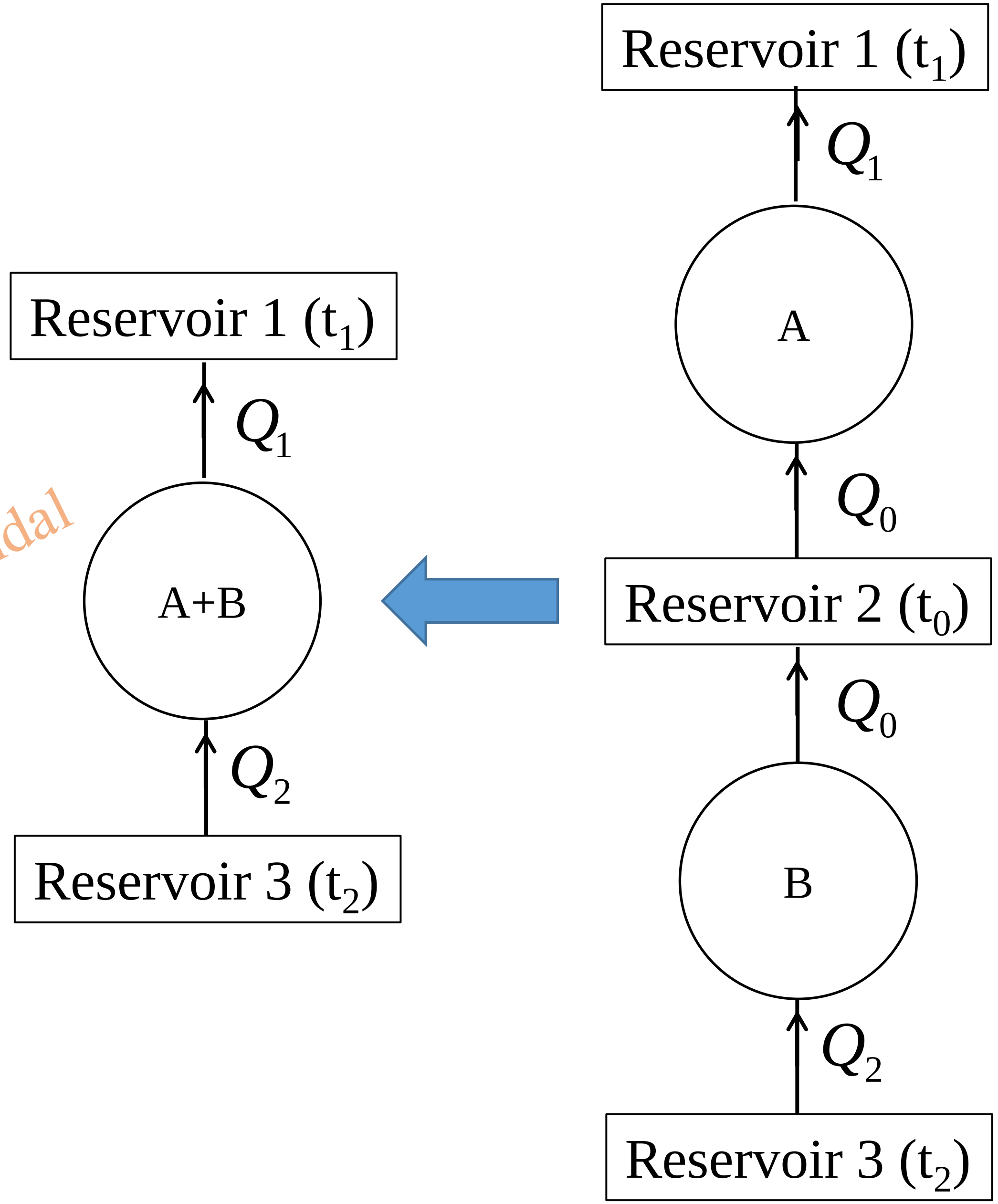
$$\boxed{\frac{Q_2}{Q_1} = \frac{Q_2}{Q_0} \times \frac{Q_0}{Q_1} = \frac{f(t_0, t_2)}{f(t_0, t_1)}}$$

Second Law of Thermodynamics

Thermodynamic Scale of Temperature:

$$\frac{Q_2}{Q_1} = f(t_1, t_2)$$

$$\boxed{f(t_1, t_2) = \frac{f(t_0, t_2)}{f(t_0, t_1)}}$$



Second Law of Thermodynamics

Thermodynamic Scale of Temperature:

- t_0 is arbitrary, keep it constant in all equations: $cf(t_0, t) = \theta(t)$ where c is constant.

$$\frac{Q_2}{Q_1} = f(t_1, t_2) = \frac{f(t_0, t_2)}{f(t_0, t_1)} = \frac{\theta(t_2)}{\theta(t_1)}$$

- $f(t_1, t_2)$ is the ratio of a function of the argument t_2 to the same function of the argument t_1
- Since t is empirical temperature, it is impossible to determine analytic form of $\theta(t)$.
- This scale of temperature is arbitrary one, we can conveniently introduce a new temperature scale using θ itself as the temperature instead of t.

Second Law of Thermodynamics

Thermodynamic Scale of Temperature:

- ❑ However, $\theta(t)$ is not quite uniquely defined as it is indeterminate to the extent of an arbitrary multiplicative constant factor c.
- ❑ We are thus free to choose the unit of new temperature scale θ in any way we see fit. The usual choice is made by placing the difference between the boiling and freezing temperatures of water at one atmospheric pressure equal to 100 degrees – Absolute thermodynamic scale of temperature. It is independent of the special properties of any thermometric substance, and all the thermodynamic laws take on a simple form in this scale.

Second Law of Thermodynamics

Thermodynamic Scale of Temperature:

Equivalence to Perfect Gas Scale:

- ☐ In perfect gas scale $Q_2/Q_1 = T_2/T_1$ where T_1 and T_2 are the temperatures of the reservoirs measured with perfect gas thermometer scale of temperature.
- ☐ Here we show $Q_2/Q_1 = \theta_2/\theta_1$ where θ_1 and θ_2 are the temperatures of the same reservoirs but defined in absolute thermodynamic scale.
- ☐ Thus, the ratio of two temperatures in absolute thermodynamic scale is same as the ratio on the perfect gas thermometer scale i.e., two temperature scales are proportional.
- ☐ The units of temperature for both scales have been chosen equal, we conclude that the two scales themselves are equal i.e., $\theta = T$.