THERMAL & STATISTICAL PHYSICS SSP3133

MAXWELL'S RELATIONS

DR WAN NURULHUDA WAN SHAMSURI

Acknowledgement : PROFESSOR DR RAMLI ABU HASSAN

So far … parameters used to describe physical systems
U, T, S, P, V, μ, N

Now, add 3 more
F, G and H

$F = U - TS$	; Helmholtz free energy
$H = U + PV$	; Enthalpy
$G = U - TS + PV$	; Gibbs free energy

Diff. form (using $dU = TdS - PdV + \mu\, dN$)

$$dF = -SdT - PdV + \mu\, dN$$

$$dH = TdS + VdP + \mu\, dN$$

$$dG = -SdT + VdP + \mu\, dN$$

The 2nd law: a means of determining whether a process is ***reversible*** **,** ***irreversible***, or ***impossible*.**

If it is irreversible, then it is said to occur *spontaneously*,

The difficulty →need the *total* entropy, i.e., that of the system and its surroundings.

-preferable to have a state function that depended only on the system → in order to determine whether a process is spontaneous, reversible or nonspontaneous.

Such a state function exists and is given the name *free energy*.

There are various kinds of free energies.

At constant V and T: *Helmholtz free energy*,

At constant T and P: *Gibbs free energy*,

All together; …. 10 parameters

U, T, S, P, V, μ, N, F, G, H

All are exact diff, eq.

dU, dT, dS, dP, dV, dμ, dN, dF, dG, dH

Note: for exact diff. eq.

$$dz = ydx + w\,dv + u\,dt$$

Partial Differential Relations (revision)

$$dz = M\,dx + N\,dy$$

$$M = \left(\frac{\partial z}{\partial x}\right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y}\right)_x$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x\,\partial y} \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial y\,\partial x}$$

The order of differentiation is immaterial for properties since they are continuous point functions and have exact differentials. Thus,

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Demonstration of the reciprocity relation for the function $z + 2xy - 3y^2z = 0$.

$$Find \left(\frac{\partial z}{\partial x}\right)_y, \left(\frac{\partial z}{\partial y}\right)_x$$

$$\left(\frac{\partial x}{\partial z}\right)_y$$

Function: $z + 2xy - 3y^2z = 0$

1) $z = \dfrac{2xy}{3y^2 - 1} \rightarrow \left(\dfrac{\partial z}{\partial x}\right)_y = \dfrac{2y}{3y^2 - 1}$

2) $x = \dfrac{3y^2z - z}{2y} \rightarrow \left(\dfrac{\partial x}{\partial z}\right)_y = \dfrac{3y^2 - 1}{2y}$

Thus, $\left(\dfrac{\partial z}{\partial x}\right)_y = \dfrac{1}{\left(\dfrac{\partial x}{\partial z}\right)_y}$

Reciprocity relation

$$\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y = 1 \rightarrow \left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{(\partial z/\partial x)_y}$$

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial y}\right)_x \rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Cyclic relation

Note: for exact diff. eq.

$$dz = y\,dx + w\,dv + u\,dt$$

and

$$\left(\frac{\partial z}{\partial x}\right)_{v,t} = y, \quad \left(\frac{\partial z}{\partial v}\right)_{x,t} = w, \quad \left(\frac{\partial z}{\partial t}\right)_{x,v} = u$$

$$\left(\frac{\partial y}{\partial v}\right)_{x,t} = \left(\frac{\partial w}{\partial x}\right)_{v,t}, \quad \left(\frac{\partial y}{\partial t}\right)_{x,v} = \left(\frac{\partial u}{\partial x}\right)_{v,t}, \quad \left(\frac{\partial w}{\partial t}\right)_{x,v} = \left(\frac{\partial u}{\partial v}\right)_{x,t}$$

$$\left(\frac{\partial^2 z}{\partial v \partial x}\right) = \frac{\partial^2 z}{\partial x \partial v}, \quad \left(\frac{\partial^2 z}{\partial t \partial v}\right) = \frac{\partial^2 z}{\partial v \partial t}, \quad \left(\frac{\partial^2 z}{\partial t \partial x}\right) = \frac{\partial^2 z}{\partial x \partial t}$$

4 equations

1. $dU = TdS - PdV + \mu dN$

2. $dF = - SdT - PdV + \mu dN$

3. $dH = TdS + VdP + \mu dN$

4. $dG = - SdT + VdP + \mu dN$

Let's take equation 1,

$$dU = TdS - PdV + \mu dN \; \ldots\ldots\ldots\ldots\ldots(*)$$

rearranging

or $$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

Or $$dV = -\frac{1}{P}dU + \frac{T}{P}dS + \frac{\mu}{P}dN$$

Or $$dN = \frac{1}{\mu}dU - \frac{T}{\mu}dS + \frac{P}{\mu}dV$$

Take the first eq. (*)

$$dU = TdS - PdV + \mu dN$$

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T, \quad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -P, \quad \left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu$$

note: from above

$$\left(\frac{\partial^2 z}{\partial v \partial x}\right) = \frac{\partial^2 z}{\partial x \partial v}, \quad \left(\frac{\partial^2 z}{\partial t \partial v}\right) = \frac{\partial^2 z}{\partial v \partial t}, \quad \left(\frac{\partial^2 z}{\partial t \partial x}\right) = \frac{\partial^2 z}{\partial x \partial t}$$

Can write: $$\left(\frac{\partial^2 U}{\partial S \partial V}\right) = \left(\frac{\partial^2 U}{\partial V \partial S}\right)$$

Or $$\left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)\right) = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)\right)$$

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

$$-\left(\frac{\partial P}{\partial S}\right)_{V,N} = \left(\frac{\partial T}{\partial V}\right)_{S,N} \qquad (*)$$

and so on……

$$-\left(\frac{\partial P}{\partial S}\right)_{V,N} = \left(\frac{\partial T}{\partial V}\right)_{S,N} \qquad (*)$$

$$\left(\frac{\partial \mu}{\partial S}\right)_{V,N} = \left(\frac{\partial T}{\partial N}\right)_{S,V} \text{..........}(**)$$

$$\left(\frac{\partial \mu}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial N}\right)_{S,V} \text{..........}(***)$$

eqs. (*), (**), (***) are known as Maxwell's relations.

2. $dF = -SdT - PdV + \mu dN$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S, \quad \left(\frac{\partial F}{\partial V}\right)_{T,N} = -P, \quad \left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu$$

….continue to derive MR (Maxwell Relation)

3. $dH = TdS + VdP + \mu\, dN$

$$\left(\frac{\partial H}{\partial S}\right)_{V,P} = T, \quad \left(\frac{\partial H}{\partial P}\right)_{S,N} = V, \quad \left(\frac{\partial H}{\partial N}\right)_{P,S} = \mu$$

….continue to derive MR (Maxwell Relation)

4. dG = - SdT + VdP + μ dN

$$\left(\frac{\partial G}{\partial T}\right)_{N,P} = -S, \quad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V, \quad \left(\frac{\partial G}{\partial N}\right)_{P,T} = \mu$$

(Maxwell Relation)

….continue to derive MR

All together there are 48 Maxwell's relations !!!

Most commonly used (12 eqs)

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N} \quad ....(MR-1) \qquad ....(*)$$

$$-\left(\frac{\partial P}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial V}\right)_{S,N} \quad \ldots\ldots\ldots\ldots\ldots(MR-2)$$

$$\left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \quad \ldots\ldots\ldots\ldots\ldots(MR-3)$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N} \quad \ldots\ldots\ldots\ldots\ldots(MR-4) \quad \ldots\ldots\ldots(*)$$

$$-\left(\frac{\partial P}{\partial N}\right)_{T,V} = \left(\frac{\partial \mu}{\partial V}\right)_{T,N} \quad \ldots\ldots\ldots\ldots\ldots(MR-5)$$

$$-\left(\frac{\partial S}{\partial N}\right)_{T,V} = \left(\frac{\partial \mu}{\partial T}\right)_{V,N} \quad \ldots\ldots\ldots\ldots\ldots(MR-6)$$

$$\left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,N} \quad \ldots\ldots\ldots\ldots\ldots(MR-7) \quad \ldots\ldots\ldots(*)$$

$$\left(\frac{\partial V}{\partial N}\right)_{S,P} = \left(\frac{\partial \mu}{\partial P}\right)_{S,N} \quad \ldots\ldots\ldots\ldots(MR-8)$$

$$\left(\frac{\partial T}{\partial N}\right)_{S,P} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \quad \ldots\ldots\ldots\ldots(MR-9)$$

$$-\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{P,N} \quad \ldots\ldots\ldots\ldots(MR-10) \quad \ldots\ldots\ldots(*)$$

$$\left(\frac{\partial V}{\partial N}\right)_{T,P} = \left(\frac{\partial \mu}{\partial P}\right)_{T,N} \quad \ldots\ldots\ldots\ldots(MR-11)$$

$$-\left(\frac{\partial S}{\partial N}\right)_{T,P} = \left(\frac{\partial \mu}{\partial T}\right)_{P,N} \quad \ldots\ldots\ldots\ldots(MR-12)$$

Note: eqs. MR-1, 4, 7 & 10 with (*) ---- for nondifusive interactions

Some applications --- non diffusive system

Note:

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

1. $\Delta U(T,P)$

To determine the change in system internal energy (1st law)

$$\Delta U(S,V) = T\,\Delta S - P\Delta V \quad \ldots\ldots(*)$$

Easy to measure changes in T & P, rather than in S & V

Need to transform eq (*) from

$\Delta U(S, V)$ to $\Delta U(T, P)$

$$\Delta S(T,P) = \left(\frac{\partial S}{\partial T}\right)_P \Delta T + \left(\frac{\partial S}{\partial P}\right)_T \Delta P$$

$$\Delta V(T,P) = \left(\frac{\partial V}{\partial T}\right)_P \Delta T + \left(\frac{\partial V}{\partial P}\right)_T \Delta P$$

from (*)

$$\begin{aligned}\Delta U(T,P) &= T[\left(\frac{\partial S}{\partial T}\right)_P \Delta T + \left(\frac{\partial S}{\partial P}\right)_T \Delta P] - \\ &\quad P[\left(\frac{\partial V}{\partial T}\right)_P \Delta T + \left(\frac{\partial V}{\partial P}\right)_T \Delta P] \\ &= \left[T\left(\frac{\partial S}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial T}\right)_P\right]\Delta T + \\ &\quad \left[T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T\right]\Delta P\end{aligned}$$

But, $T\left(\frac{\partial S}{\partial T}\right)_P = C_P$, $\left(\frac{\partial V}{\partial T}\right)_P = V\beta$, $\left(\frac{\partial V}{\partial P}\right)_T = V\kappa$

And using MR-10

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

Therefore,

$$\Delta U(T,P) = (C_P - PV\beta)\,\Delta T - (T\beta - P\kappa)\,V\,\Delta P$$

Can determine the change in internal energy in terms of (ΔT, ΔP) and easily measurable properties of the system.

Thermodynamic processes

Note:

1. State Variables: P, V and T

   the variables: pressure, volume and temperature, or P, V and T --- define the *state* of a system.

2. Functions:

   A function: f(x, y, z) is defined at a single point (x,y,z).

   e.g: internal energy U, which is a function of P, V and T. ideal gas U = (3/2)kT;

   Functions are path independent.

3. Processes:

   Heat flow, Q, and work, W are *processes*.

   Q and W are quantities defined in terms of two states (i.e., two sets of state variables).

Q flows between two states.

W is performed between two states.

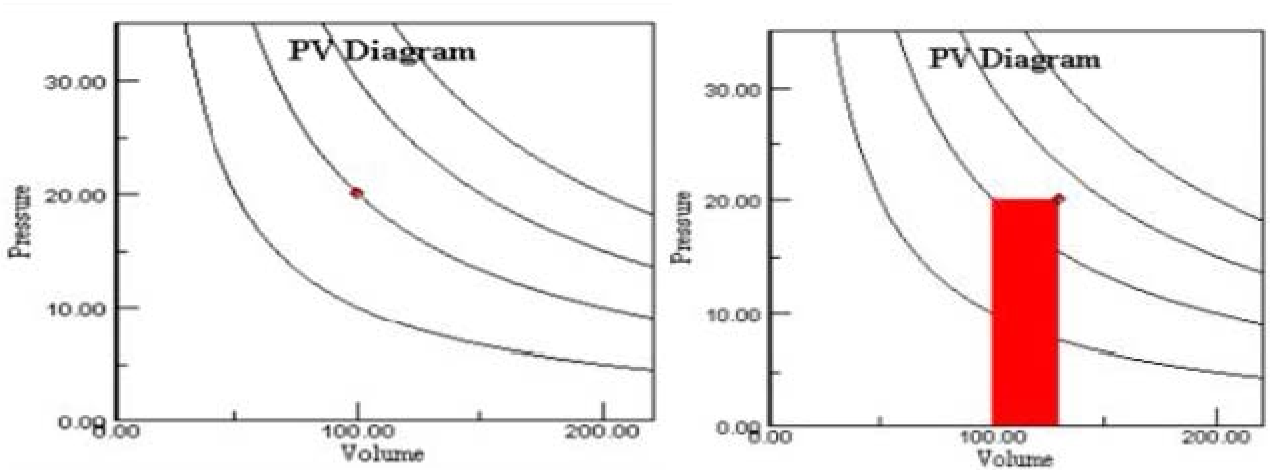
W and Q cannot be defined at a single state of the system.

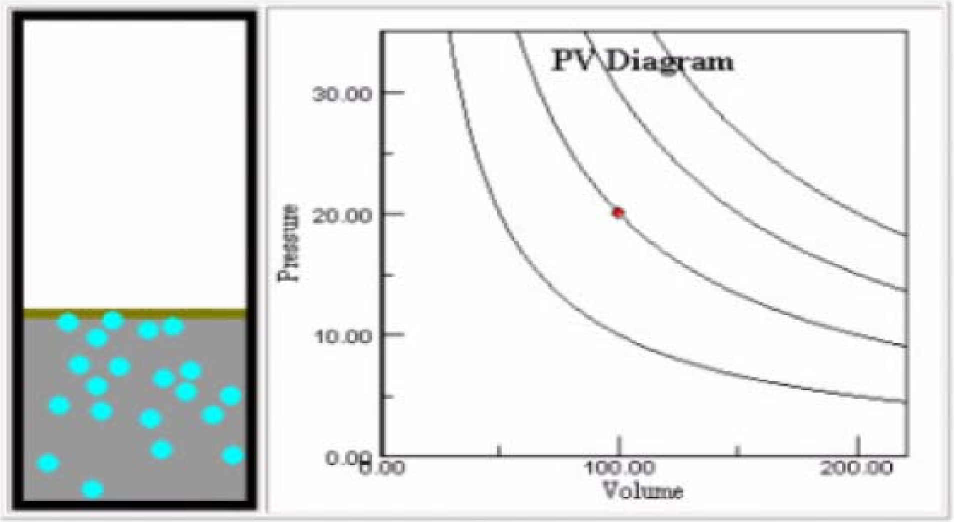
Thus, Q and W are *processes* rather than functions.

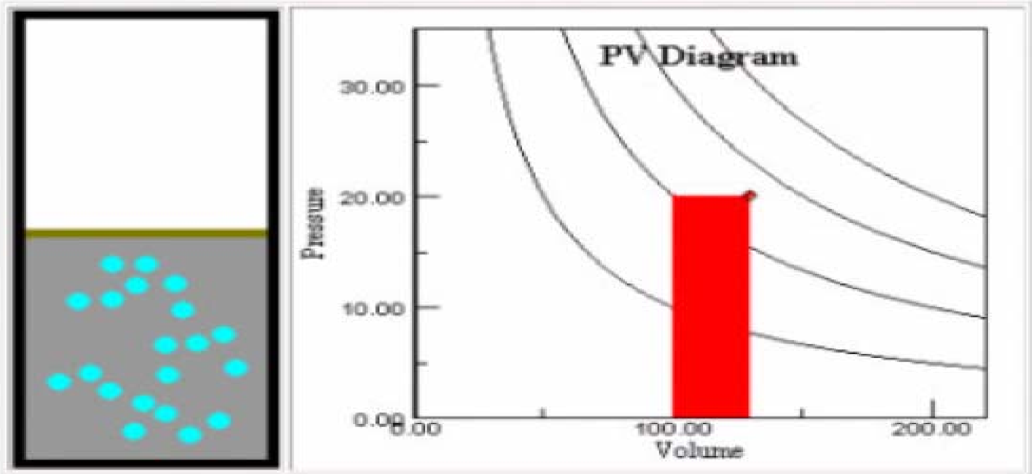
Types of thermodynamic processes

1. **Isobaric** - the pressure is kept constant.

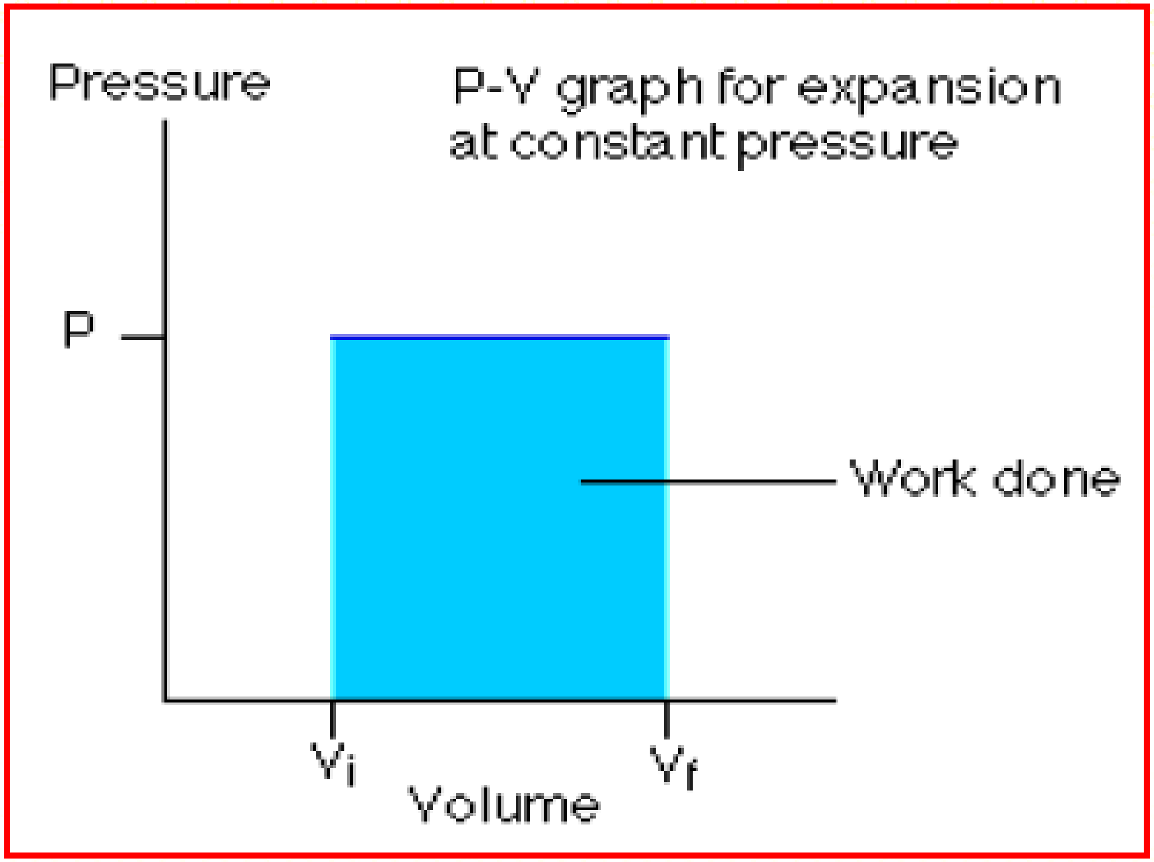
The work done by the system: the pressure multiplied by the change in volume







The work done by the system: the pressure multiplied by the change in volume


Pressure
P-V graph for expansion at constant pressure
P
Work done
Vi
Vf
Volume

Note: 1. $dU = TdS - PdV + \mu dN$

2. $dF = -SdT - PdV + \mu dN$

3. $dH = TdS + VdP + \mu dN$

4. $dG = -SdT + VdP + \mu dN$

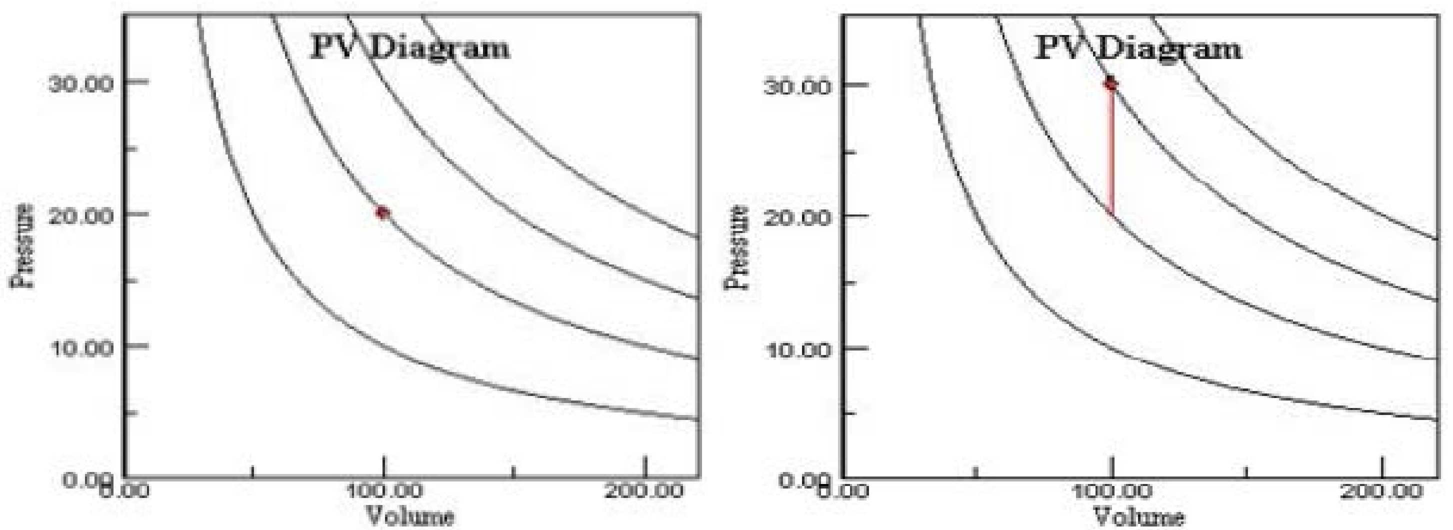
Using eq (3)

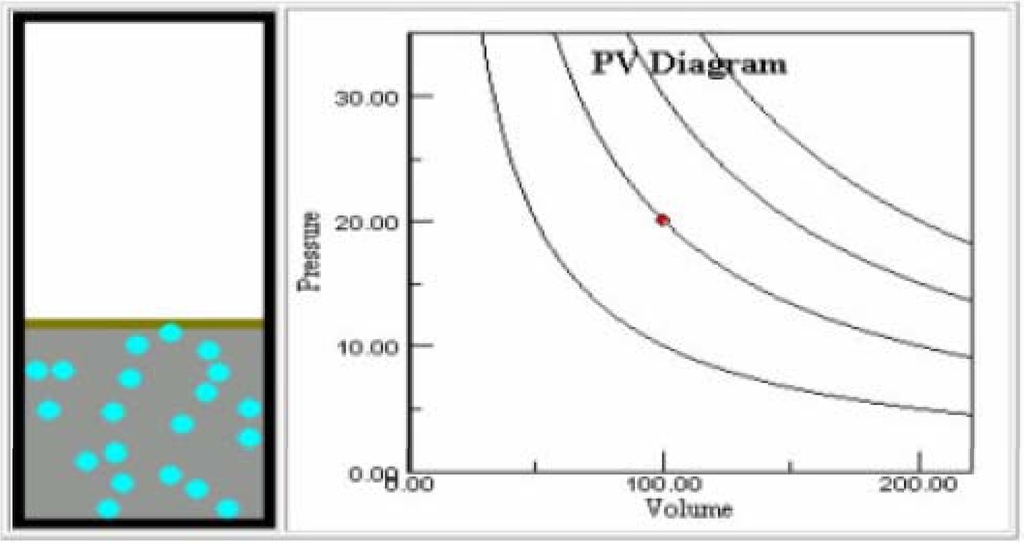
for nondiffusive isobaric process

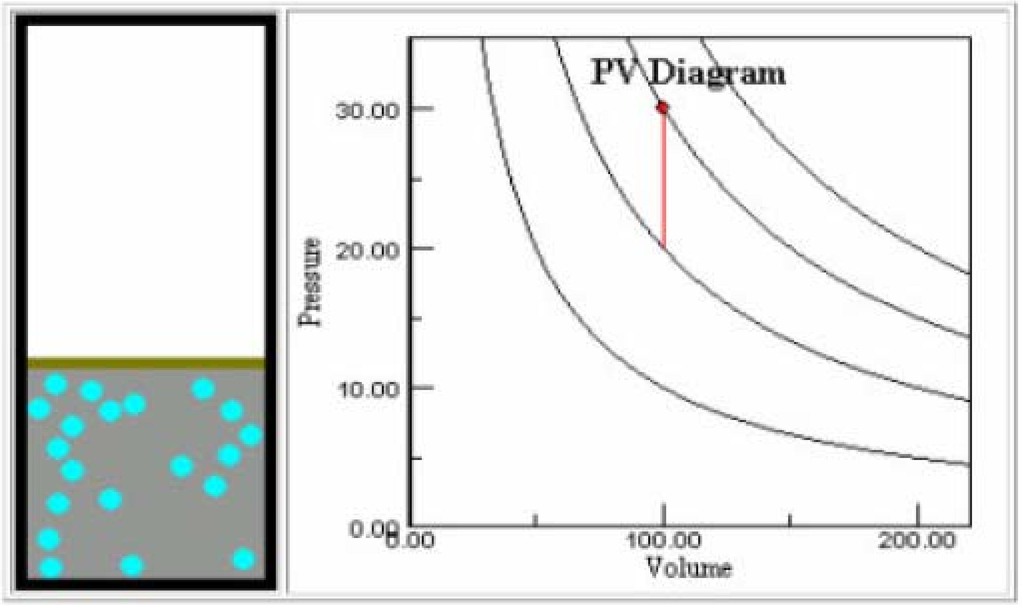
$$dH = TdS + 0 + 0 \quad \text{or} \quad dH = TdS$$

Change in enthalpy is equaled to amount of heat added or removed.

2. **Isochoric** - the volume is kept constant. The work done is zero

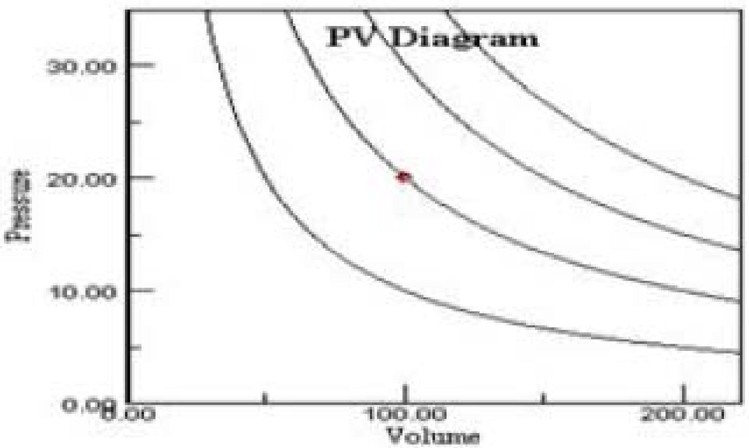


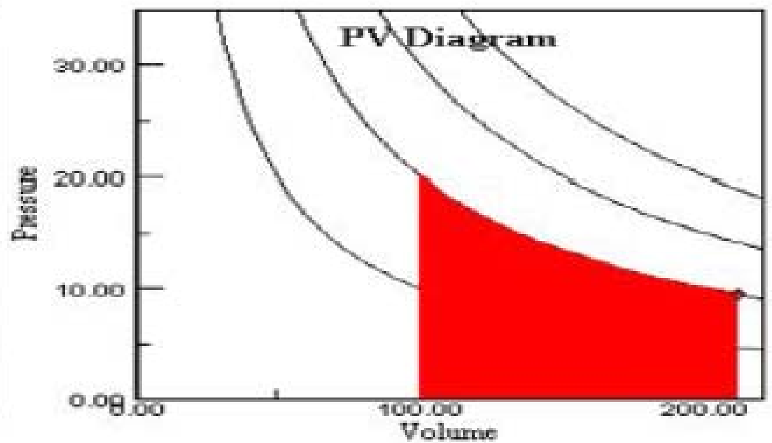

PV Diagram
Pressure
30.00
20.00
10.00
0.00
0.00
100.00
200.00
Volume

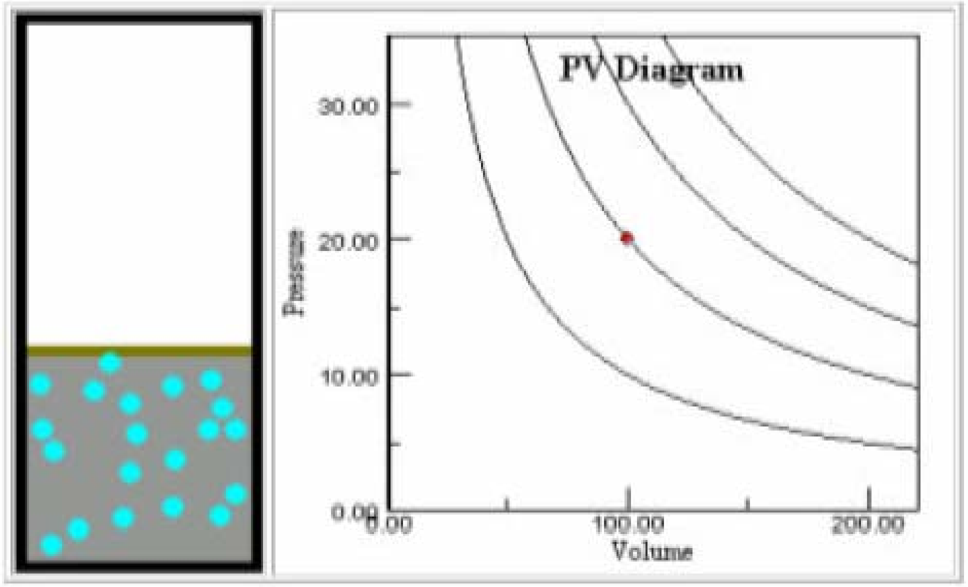

PV Diagram
Pressure
30.00
20.00
10.00
0.00
0.00
100.00
200.00
Volume

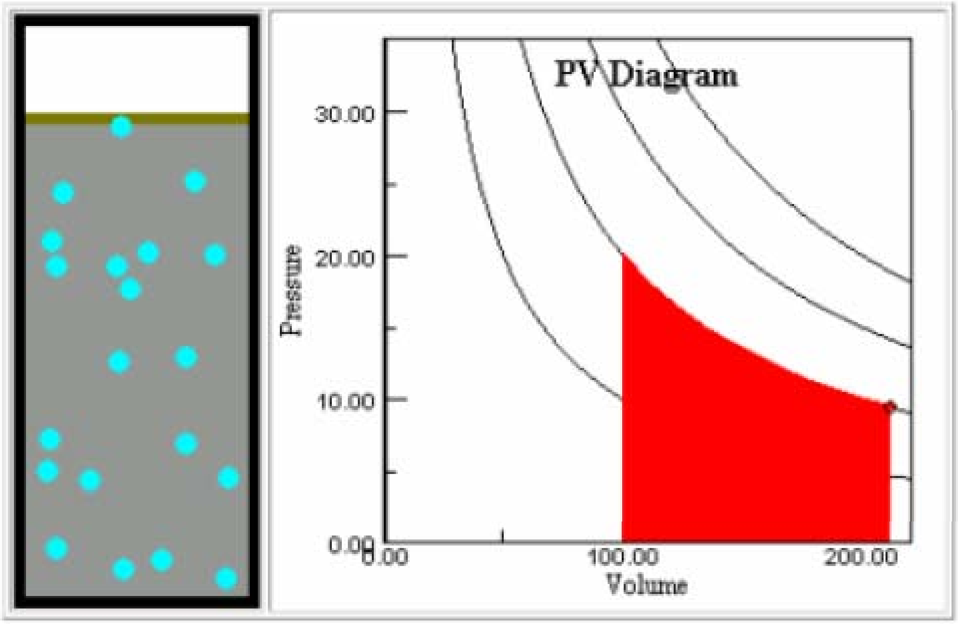
3. **Isothermal** - the temperature is kept constant.

If the V increases while the T is constant, the P must decrease, and if the V decreases the P must increase.






PV Diagram
30.00
20.00
10.00
0.00
0.00
100.00
200.00
Pressure
Volume

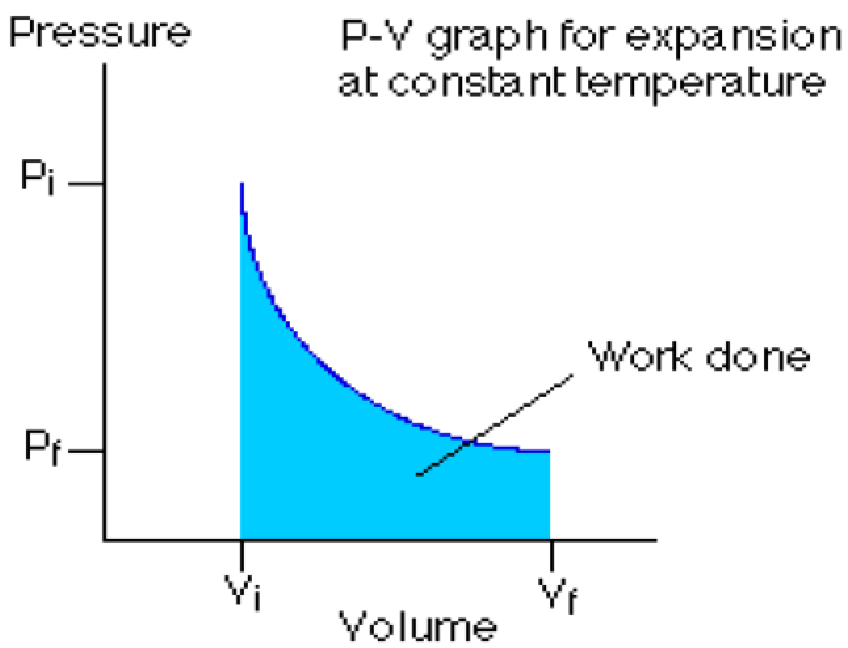

PV Diagram
30.00
20.00
10.00
0.00
0.00
100.00
200.00
Pressure
Volume

OPENCOURSEWARE

Using eq (2) $dF = -SdT - PdV + \mu dN$

$$dF = 0 - PdV + 0 \quad \text{or} \quad dF = PdV$$

The Helmholtz free energy is a measure of the work done on a system, or of the potential energy stored.



$$W = nRT\ln(V_f/V_i)$$

$$U \propto T$$

1st law

$$0 = Q - W, \quad \text{so} \quad Q = W$$

The work done by the system is still the area under the P-V curve,

$$W = nRT\ln(V_f/V_i)$$

$$U \propto T$$

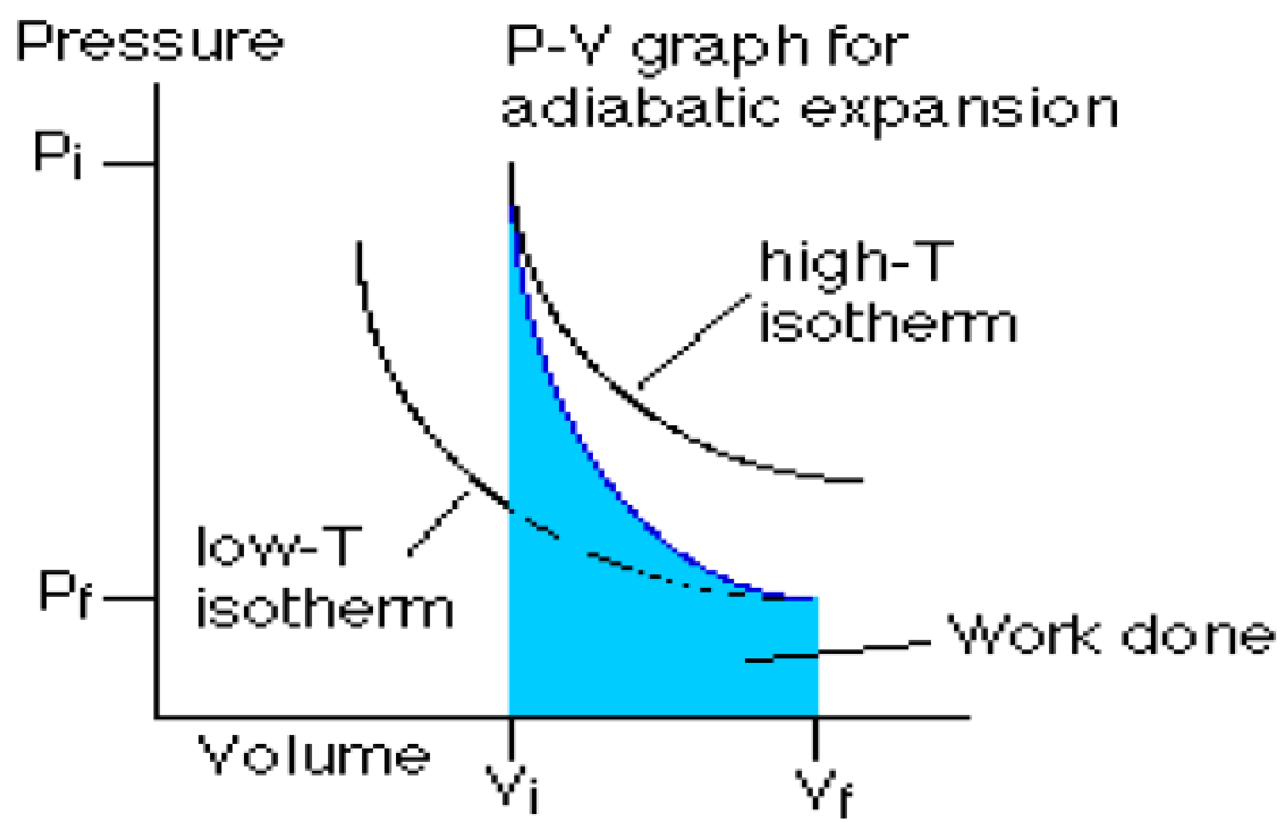
1st law $\quad 0 = Q - W, \quad$ so $\quad Q = W$

If the system does work, the energy comes from heat flowing into the system from the reservoir;

If work is done on the system, heat flows out of the system to the reservoir.

4. **Adiabatic** - in an adiabatic process, no heat is added or removed from the system.

1st law $\quad W = -\Delta U$



Adiabatic processes in gases

For ideal gas

$$U = \frac{\upsilon}{2} NkT \quad ; \upsilon\text{: degrees of freedom}$$

$$PV = NkT \quad ; N\text{: number of molecules}$$

Diff. form
$$dU = \frac{\upsilon}{2} Nk \, dT \quad \ldots(*)$$

$$PdV + VdP = Nk\, dT \quad \ldots(**)$$

$$dU = -P\, dV \quad \ldots\ldots\ldots\ldots\ldots(***)$$

(1^{st} law for adiabatic process --- $\delta Q = 0$)

From (*) & (***)

$$\frac{\upsilon}{2} Nk \quad dT = -PdV$$

And using (**)

$$\frac{\upsilon}{2}(PdV + VdP) = -PdV$$

$$\left(\frac{\upsilon + 2}{\upsilon}\right)\left(\frac{dV}{V}\right) + \frac{dP}{P} = 0$$

Integerate: $\left(\frac{\upsilon + 2}{\upsilon}\right) \ln V + \ln P = 0$

or

$$PV^{\frac{\upsilon+2}{\upsilon}} = const.$$

with $\frac{\upsilon + 2}{\upsilon} = \gamma$

From the definition of C_v & C_P

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \& \quad C_P = \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + \left(P\frac{\partial V}{\partial T}\right)_P$$

From (*) & (**)

$$\left(\frac{\partial U}{\partial T}\right) = \frac{\upsilon}{2}Nk = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_P$$

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

Therefore

$$C_V = \frac{\upsilon}{2} Nk$$

$$C_P = \frac{\upsilon}{2} Nk + Nk = \left(\frac{\upsilon + 2}{2}\right) Nk$$

The ratio

$$\frac{C_P}{C_V} = \left(\frac{\upsilon + 2}{\upsilon}\right) = \gamma$$

Carnot Cycle, Heat Engine & Refrigerator

Reversible processes

Definition : ***a process that, once having taken place, can be reversed, and in so doing leaves no change in either the system or surroundings.***

In other word the system and surroundings are returned to their original condition before the process took place.

Irreversible process

Definition : ***a process that cannot return both the system and the surroundings to their original condition.***

Cyclic process or cycle

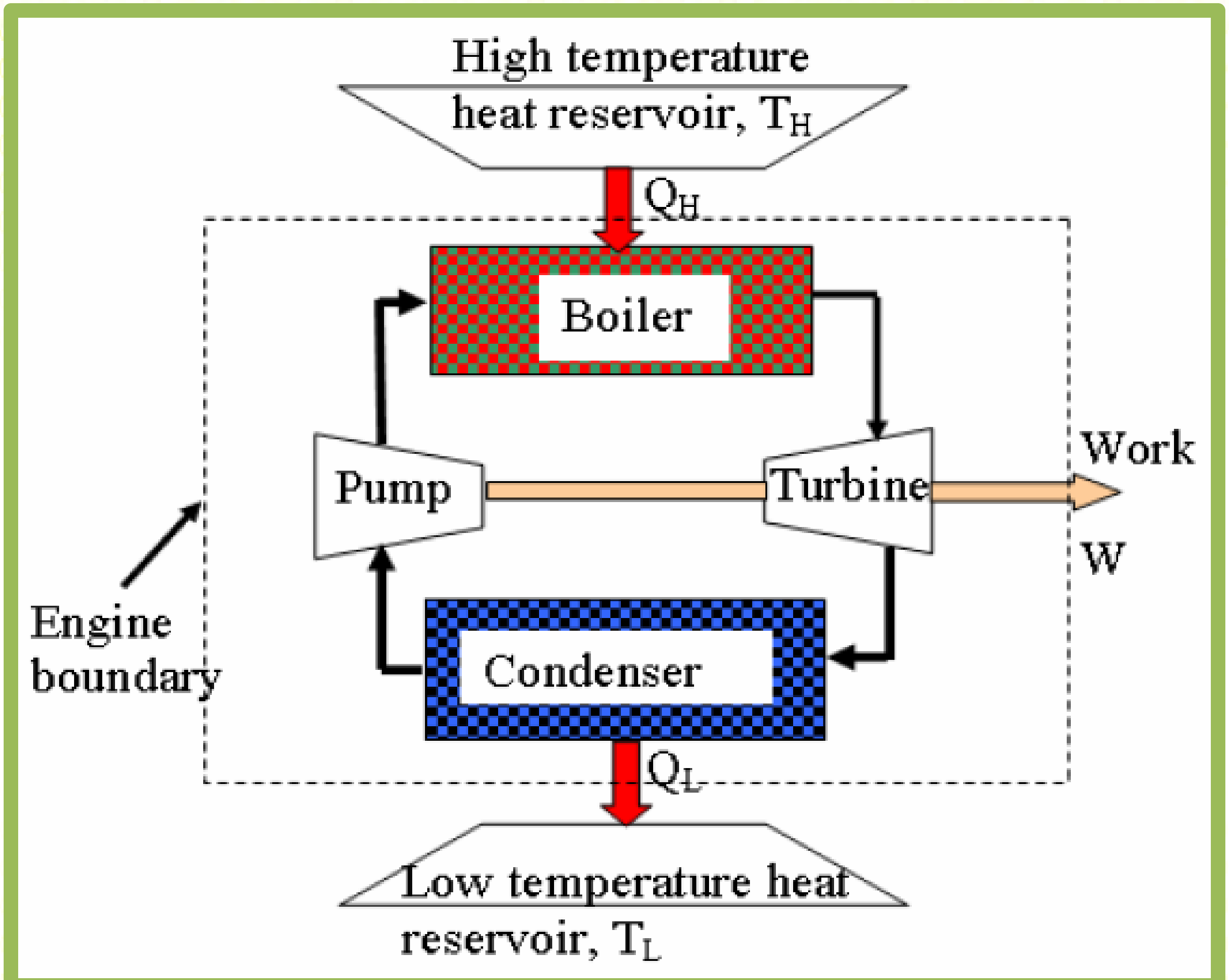
When a system in a given initial state goes through a number of different changes in state (going through various processes) and finally returns to its initial state.

Heat engines

Heat engine is defined as a device that converts heat energy into mechanical energy.

or

more exactly a system which operates continuously and only heat and work may pass across its boundaries.


High temperature
heat reservoir, T_H
Q_H
Boiler
Pump
Turbine
Work
W
Engine
boundary
Condenser
Q_L
Low temperature heat
reservoir, T_L

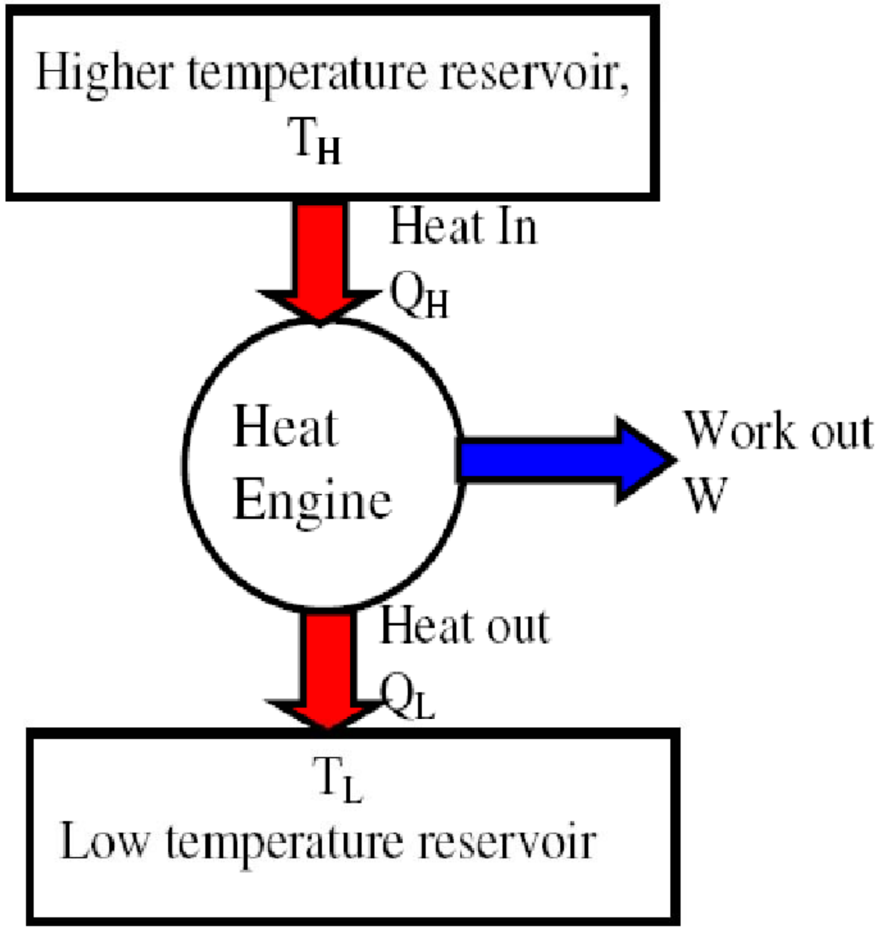
In a full cycle of a heat engine, three things happen:

1. Heat is added. (at high temperature); Q_H.

2. Some of the energy from that input heat is used to perform work (W).
3. The rest of the heat is removed at a relatively cold temperature (Q_C).

Cons. Of energy: $Q_H = W + Q_C$

Heat engine diagram



An important measure of a heat engine is its **efficiency**:

A ratio of how much of the input energy ends up doing useful work

Efficiency: η = (work done) / (input heat) = W / Q_H

Work is just the input heat minus the rejected heat, so:

$$\eta = (Q_H - Q_C) / Q_H = 1 - Q_C/Q_H$$

Note: this is the maximum possible efficiency for an engine.

Carnot cycles

The processes that HE undergoes are highly irreversible.

Idealization: engine which operates reversibly between its initial, intermediate and final states – **Carnot engine**

The **Carnot heat engine** uses a particular thermodynamic cycle studied by Nicolas Léonard Sadi Carnot in the 1820s.

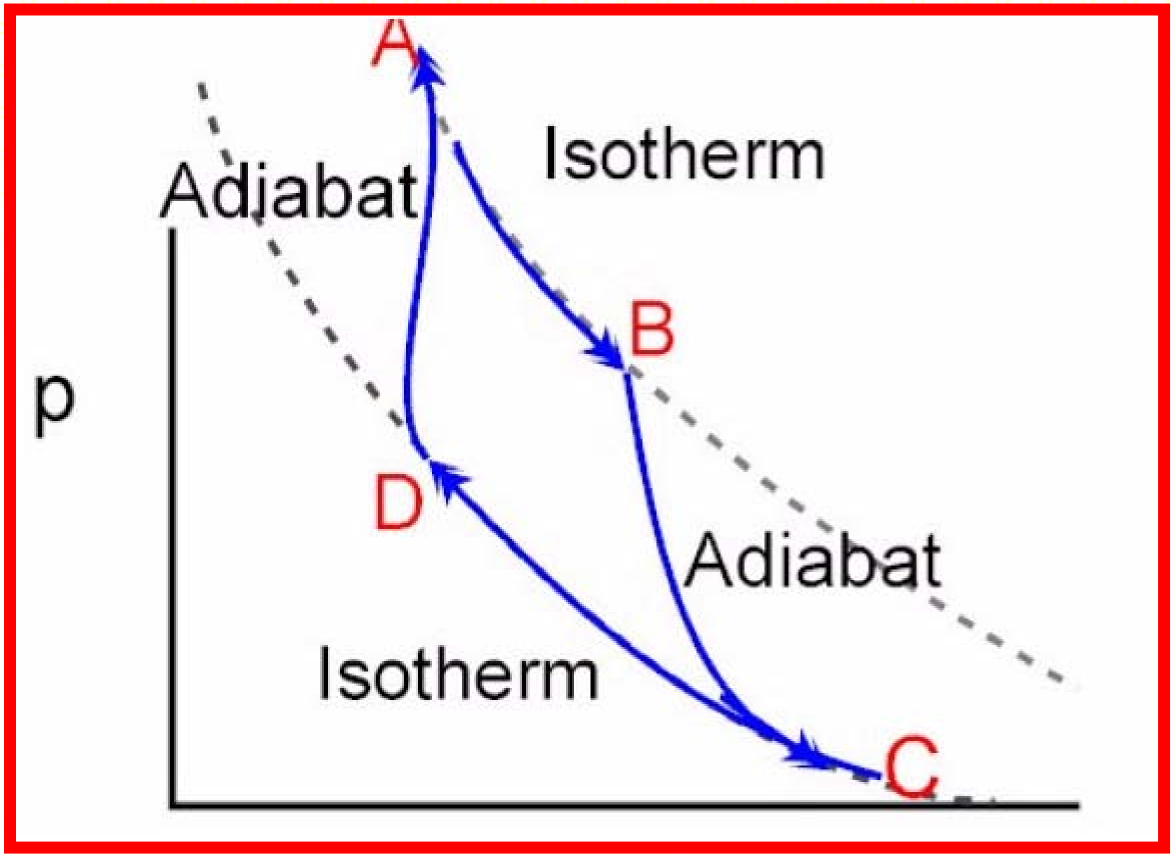
The **Carnot cycle** consists of the following steps:

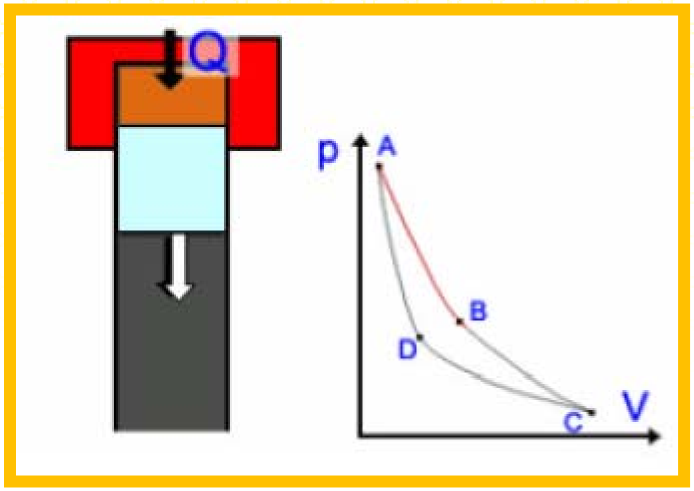
1. **Reversible isothermal expansion of the gas at the "hot" temperature, T_H.** The gas expansion is driven by absorption of heat –gas doing work

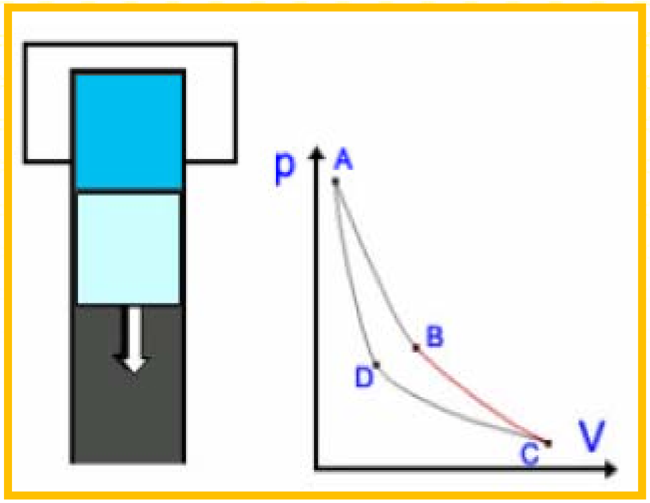
2. **Reversible adiabatic expansion of the gas.** The gas continues to expand, gas doing work -- cool to the "cold" temperature, T_C.

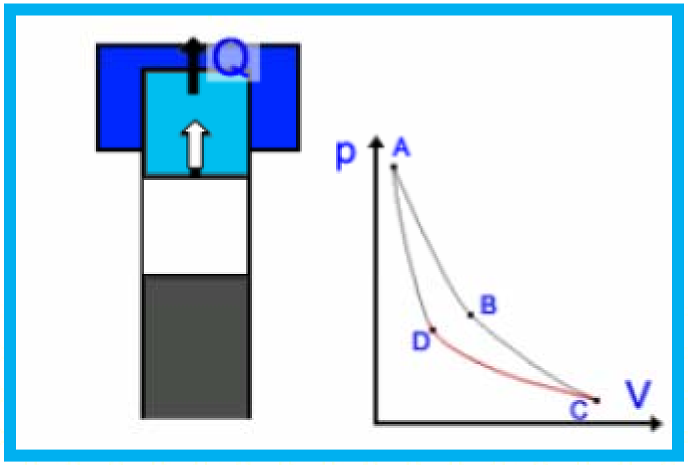
3. **Reversible isothermal compression of the gas at the "cold" temperature, T_C.** work done on the gas, causing heat to flow out of the gas to the low temperature reservoir.

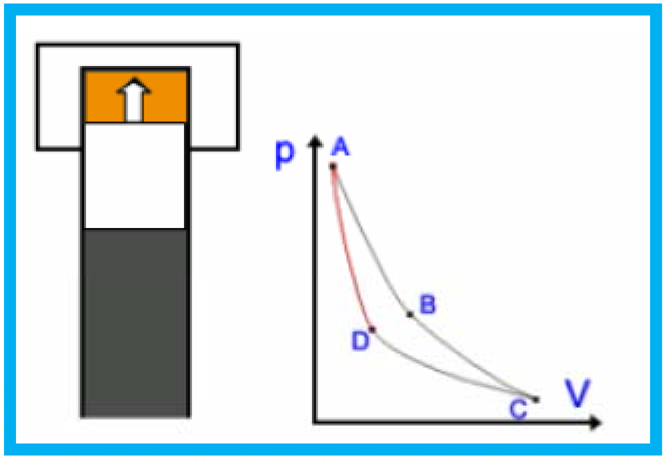
4. **Reversible adiabatic compression of the gas.** work done on the gas, compressing, causing the temperature to rise to T_H, at same point as step 1.


A
Adiabat
Isotherm
p
B
D
Adiabat
Isotherm
C


Q
p
A
B
D
C
V


p
A
B
D
C
V


Q
p
A
B
D
C
V


p
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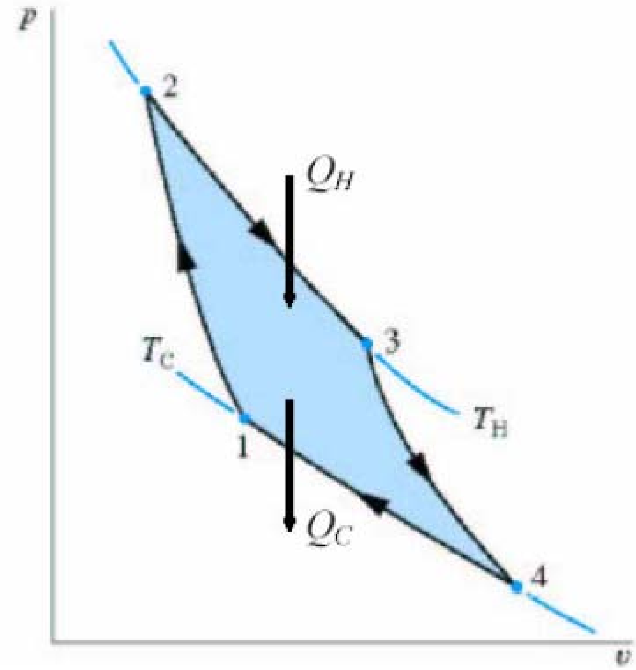
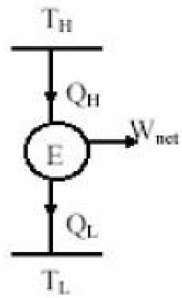




Net work per cycle per unit mass = ∫ PdV

$$W_{cycle} = \int_1^2 PdV + \int_2^3 PdV + \int_3^4 PdV + \int_4^1 PdV$$

= shaded area (net work out)

Net heat transfer per cycle = Q_H - Q_C

(Note: $Q_C = Q_L$)

At the Hot Reservoir:

The hot reservoir loses entropy: $\Delta S_h = - Q_h/T_h$ the engine gains this entropy.

At the Cold Reservoir:

The cold reservoir gains entropy: $\Delta S_c = + Q_c/T_c$ The engine loses entropy

Carnot cycle ---- reversible cycle

Hence: $\Delta S_{cycle} = 0$

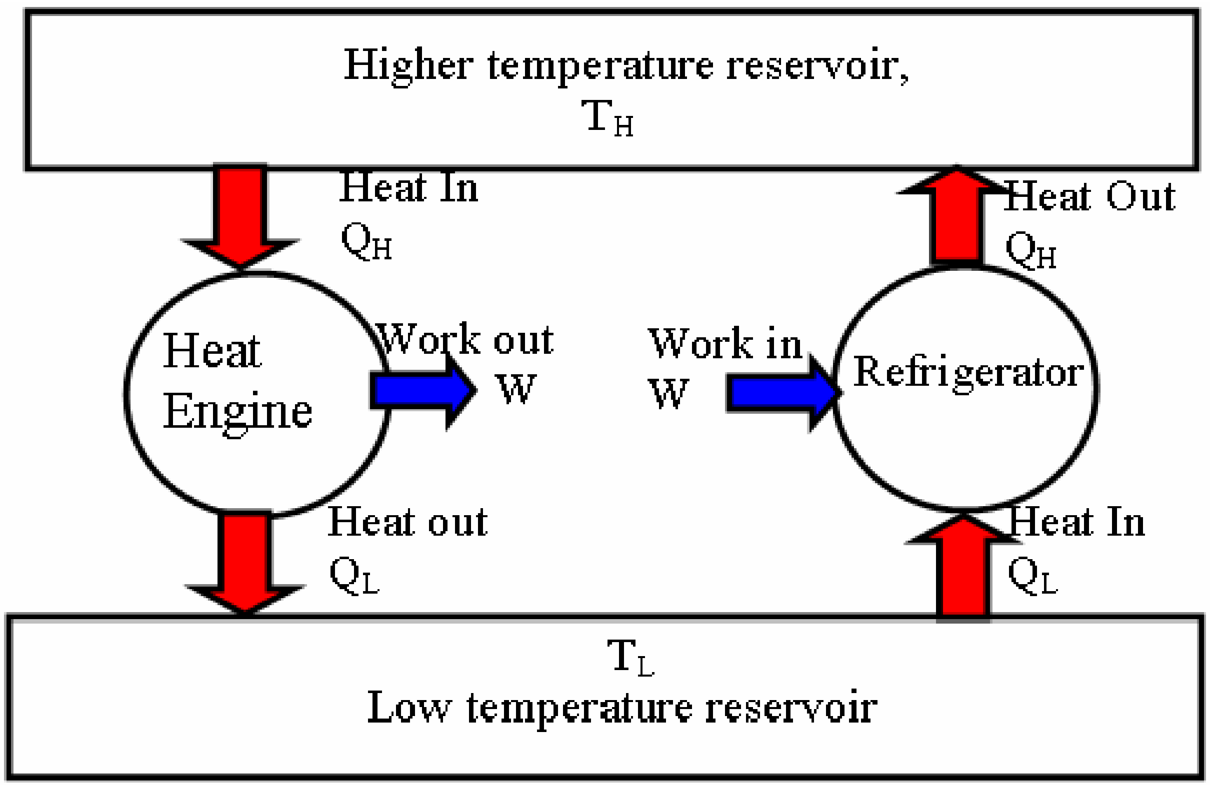
$\Delta S_h + \Delta S_c = + Q_c/T_c - Q_h/T_h$ or $Q_c/T_c = Q_h/T_h$

Carnot efficiency;

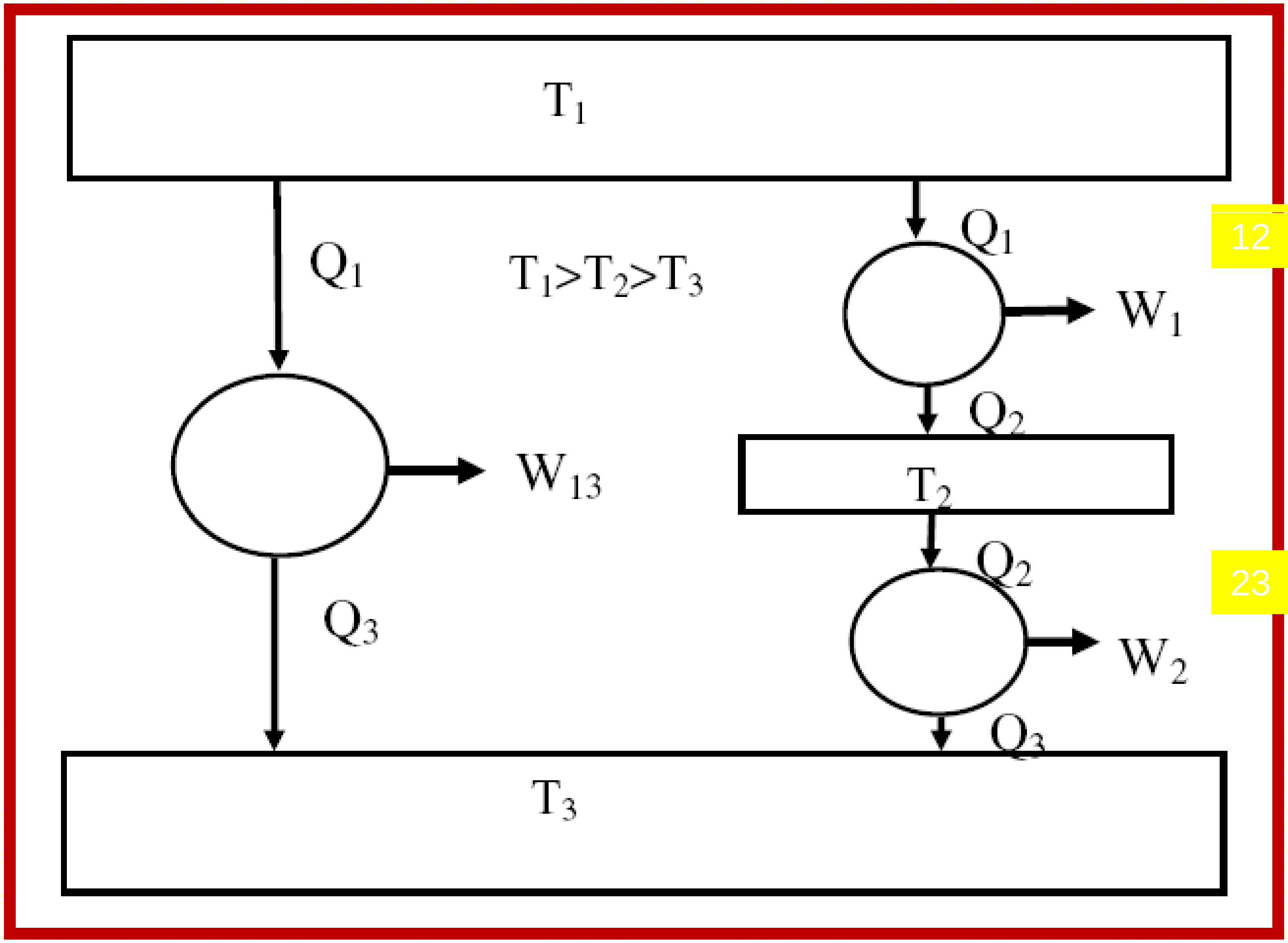
$$\eta_C = 1 - \frac{T_C}{T_H}$$

Schematic diagram of a reversible heat engine operating in forward and reversed modes.

No HE can have efficiency greater than a RHE.



Schematic diagram of RHE operating between three different temperature heat reservoirs



The first and second engine takes the same heat Q_1 from the hotest reservoir

$W_{13} = W_{12} + W_{23}$

Reject the same heat Q_3 to the lowest temperature (T_3) heat reservoir.

$W_{13} - W_{23} = (Q_1 - Q_3) - (Q_2 - Q_3) = Q_1 - Q_2 = W_{12}$

If one RHE absorbs heat Q_1 at temperature T_1 and delivers the heat Q_3 at temperature T_3, then a RHE that absorbs heat Q_2 at temperature T_2 will deliver the same heat Q_3 to temperature T_3.

Heat Q_i absorbed at temperature T_i will deliver the same heat Q_3 at temperature T_3.

Need to define one temperature as the standard temperature

can relate the heat extracted by a reversible heat engine at any other temperature.

Let RHE: absorbs Q at temperature T then rejects Qs at standard temperature Ts.

$$\eta = 1 - (\text{Heat Out}) / (\text{Heat In}) = 1 - Q_S / Q$$

$$Q_S = (1 - \eta)\, Q \quad \text{or} \quad Q = Q_S / (1 - \eta)$$

The efficiency can only depend upon the temperature T.

$$Q = Q_S / (1 - \eta) = Q_S F(T)$$

Lord Kelvin (William Thomson 1824-1907) suggested:

$$F(T) = T / T_S$$

$$Q = Q_S T / T \quad \text{or} \quad Q/T = Q_S/T_S$$

$$\eta = 1 - T_C/T_H$$

and $\quad Q_1/T_1 = Q_2/T_2 = Q_3/T_3 = \text{constant} = S.$

$Q = S\,T$ Constant S is given the name entropy.

The entropy is constant ($\Delta S = 0$) for a reversible process

The entropy tends to increase ($\Delta S > 0$) in irreversible processes.

Thermodynamic definition of entropy

There is no device that can transform heat withdrawn from a reservoir completely into work with no other effect.

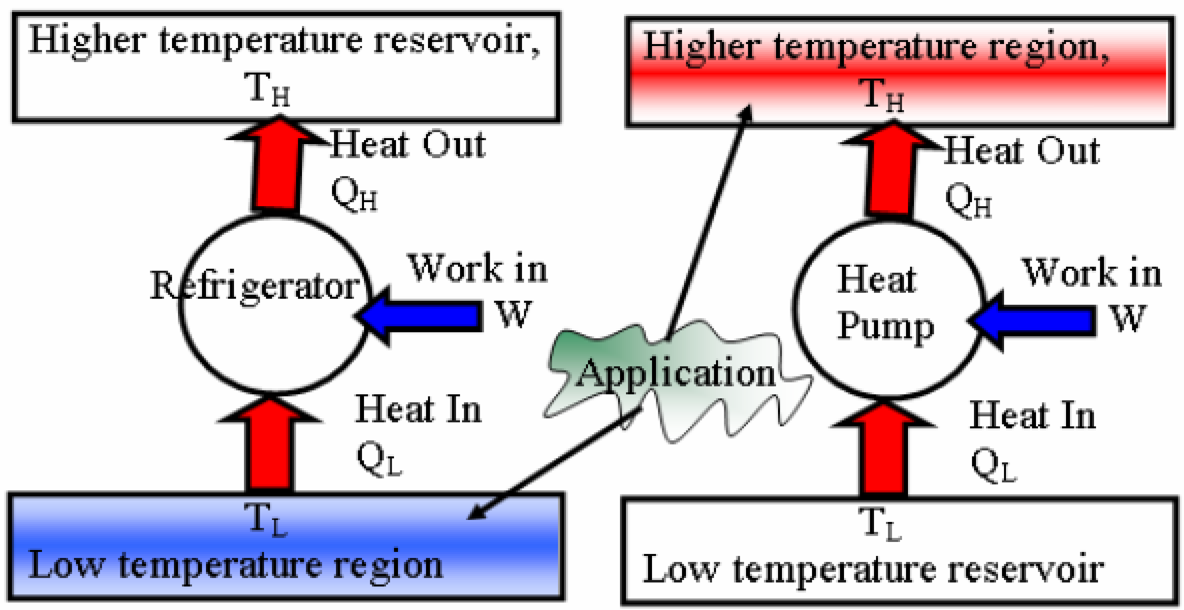
There is no device that can transfer heat from a colder to a warmer reservoir without requiring an input of work.

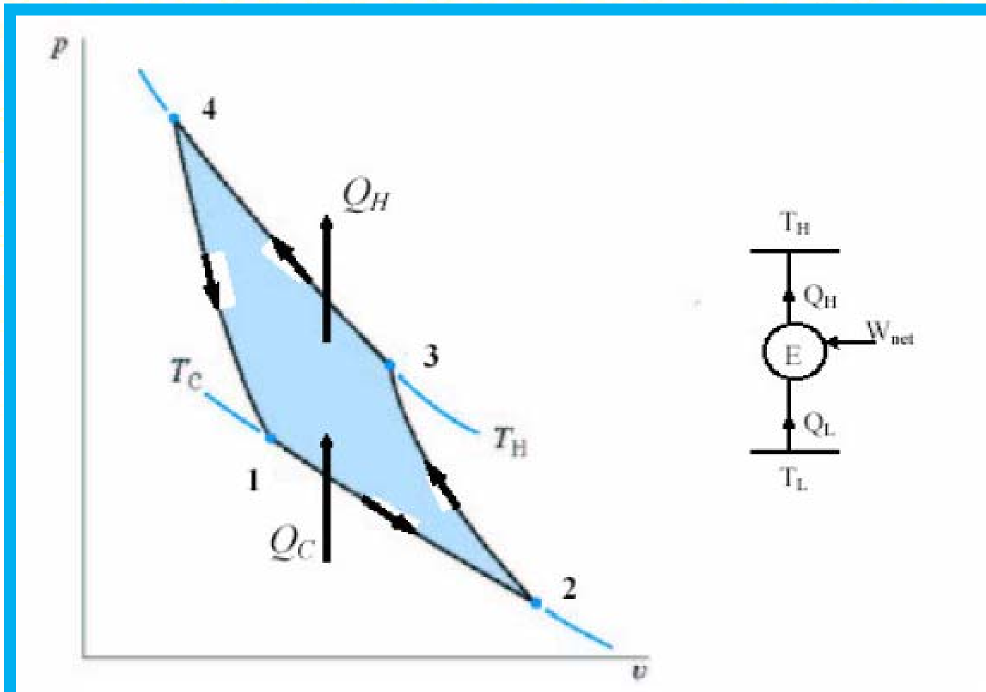
The Reversed Carnot Cycle

A reversible heat engine can be reversed in operation to work as a refrigerating machine.

A reversible refrigeration cycle has the maximum Coefficient of Performance (COP).

Diagram:





Q_C: heat is removed from cold reservoir

Q_H: heat is added to the hot reservoir

$$W_{cycle} = \int_1^2 PdV + \int_2^3 PdV + \int_3^4 PdV + \int_4^1 PdV$$

= shaded area (net work in)

Coefficient of performance (COP)

is the measure of performance of refrigerators and heat pumps.

It is expressed in terms of the desired result for each device (Q absorbed from the refrigerated space for the Rf or Q added to the hot space by the HP) divided by the work input

$$COP_R = \frac{Desired\ \ Output}{\mathrm{Re}\ quired\ \ Input} = \frac{Cooling\ \ effect}{Work\ \ Input} = \frac{Q_L}{W_{net,in}}$$

$$COP_{HP} = \frac{Desired\ \ Output}{\mathrm{Re}\ quired\ \ Input} = \frac{Heating\ \ effect}{Work\ \ Input} = \frac{Q_H}{W_{net,in}}$$

For Carnot engine

$$COP_R = \frac{1}{\frac{T_H}{T_L} - 1} = \frac{T_L}{T_H - T_L}$$

$$COP_{HP} = \frac{1}{1 - \frac{T_L}{T_H}} = \frac{T_H}{T_H - T_L}$$

The END….

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