

Thermodynamics

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Fundamental Concepts and Definitions

THERMODYNAMICS:

$\frac{3}{4}$ It is the science of the relations between heat,
Work and the properties of the systems.

$\frac{3}{4}$ How to adopt these interactions to our benefit?

*Thermodynamics enables us to answer this
question.*

Analogy

All currencies are not equal

Eg: US\$ or A\$ or UK£ etc. Have a better purchasing power than Indian Rupee or Thai Baht or Bangladesh Taka similarly, all forms of energy are not the same.

Human civilization has always endeavoured to obtain

$\frac{3}{4}$ Shaft work

$\frac{3}{4}$ Electrical energy

$\frac{3}{4}$ Potential energy to make life easier

Examples

If we like to

$\frac{3}{4}$ Rise the temperature of water in kettle

$\frac{3}{4}$ Burn some fuel in the combustion chamber of an aero engine to propel an aircraft.

$\frac{3}{4}$ Cool our room on a hot humid day.

$\frac{3}{4}$ Heat up our room on a cold winter night.

$\frac{3}{4}$ Have our beer cool.

What is the smallest amount of electricity/fuel we can get away with?

Examples (Contd...)

On the other hand we burn,

$\frac{3}{4}$ Some coal/gas in a power plant to generate electricity.

$\frac{3}{4}$ Petrol in a car engine.

What is the largest energy we can get out of these efforts?

Thermodynamics allows us to answer some of these questions

Definitions

$\frac{3}{4}$ In our study of thermodynamics, we will choose *a small part of the universe* to which we will apply the laws of thermodynamics.

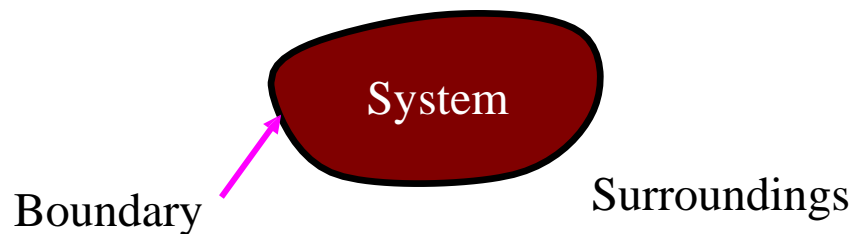
We call this subset a **SYSTEM**.

$\frac{3}{4}$ The thermodynamic system is analogous to the free body diagram to which we apply the laws of mechanics, (i.e. Newton's Laws of Motion).

$\frac{3}{4}$ **The system is a macroscopically identifiable collection of matter on which we focus our attention** (eg: the water kettle or the aircraft engine).

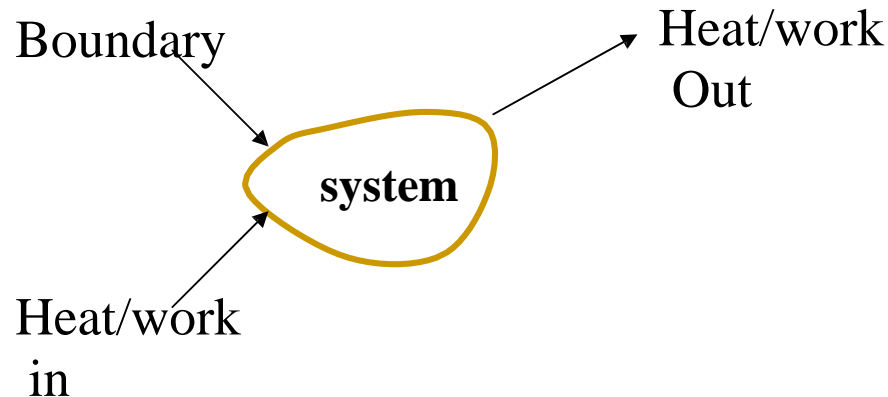
$\frac{3}{4}$ The rest of the universe outside the system close enough to the system to have some perceptible effect on the system is called the **surroundings**.

$\frac{3}{4}$ The surfaces which separates the system from the surroundings are called the **boundaries** as shown in fig below_(eg: walls of the kettle, the housing of the engine).



Types of System

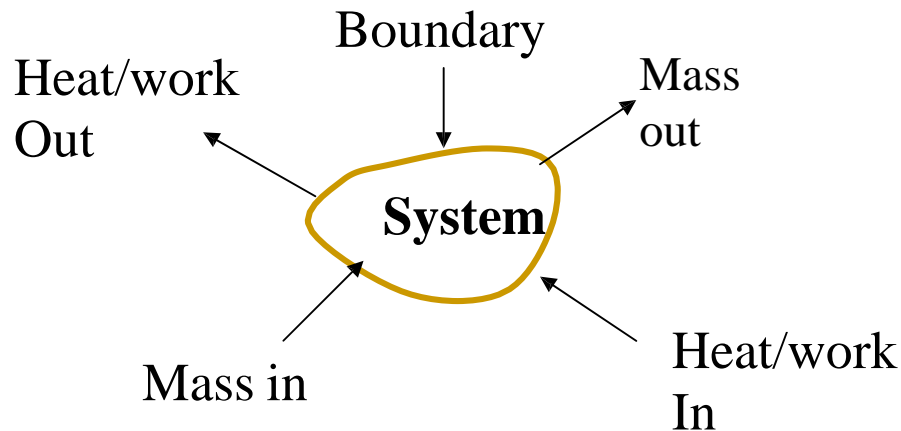
$\frac{3}{4}$ **Closed system** - in which no mass is permitted to cross the system boundary i.e. we would always consider a system of constant mass. We do permit heat and work to enter or leave but not mass.



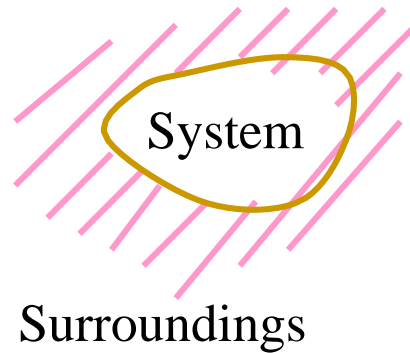
No mass entry or exit

$\frac{3}{4}$ **Open system**- in which we permit mass to cross the system boundary in either direction (from the system to surroundings or *vice versa*). In analysing open systems, we typically look at a specified region of space, and observe what happens at the boundaries of that region.

Most of the engineering devices are open system.



$\frac{3}{4}$ Isolated System - in which there is no interaction between system and the surroundings. It is of fixed mass and energy, and hence there is no mass and energy transfer across the system boundary.



Choice of the System and Boundaries Are at Our Convenience

- $\frac{3}{4}$ We must choose the system for each and every problem we work on, so as to obtain best possible information on how it behaves.
- $\frac{3}{4}$ In some cases the choice of the system will be obvious and in some cases not so obvious.
- $\frac{3}{4}$ Important: you must be clear in defining what constitutes your system and make that choice explicit to anyone else who may be reviewing your work. (eg: *In the exam paper or to your supervisor in the work place later*)

Choice of the System and Boundaries Are at Our Convenience (contd...)

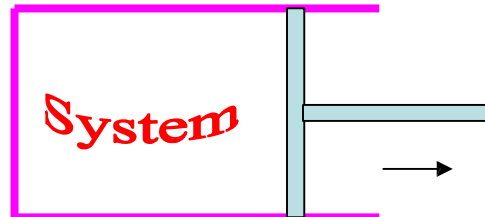
$\frac{3}{4}$ The boundaries may be real physical surfaces or they may be imaginary for the convenience of analysis.

eg: If the air in this room is the system, the floor, ceiling and walls constitute real boundaries. The plane at the open doorway constitutes an imaginary boundary.

Choice of the System and Boundaries Are at Our Convenience (contd...)

$\frac{3}{4}$ The boundaries may be at rest or in motion.

eg: If we choose a *system* that has a certain defined quantity of mass (such as gas contained in a piston cylinder device) the *boundaries* must move in such way that they always enclose that particular quantity of mass if it changes shape or moves from one place to another.



Macroscopic and Microscopic Approaches

Behavior of matter can be studied by these two approaches.

$\frac{3}{4}$ In macroscopic approach, certain quantity of matter is considered, without a concern on the events occurring at the molecular level. These effects can be perceived by human senses or measured by instruments.

$\frac{3}{4}$ eg: pressure, temperature

Microscopic Approach

$\frac{3}{4}$ In microscopic approach, the effect of molecular motion is Considered.

eg: At microscopic level the pressure of a gas is not constant, the temperature of a gas is a function of the velocity of molecules.

Most microscopic properties cannot be measured with common instruments nor can be perceived by human senses

Property

- $\frac{3}{4}$ It is some characteristic of the system to which some physically meaningful numbers can be assigned without knowing the history behind it.
- $\frac{3}{4}$ These are macroscopic in nature.
- $\frac{3}{4}$ Invariably the properties must enable us to identify the system.
- $\frac{3}{4}$ eg: Anand weighs 72 kg and is 1.75 m tall. We are not concerned how he got to that stage. We are not interested what he ate!!.

Examples (contd...)

We must choose the most appropriate set of properties.

- $\frac{3}{4}$ For example: Anand weighing 72 kg and being 1.75 m tall may be a useful way of identification for police purposes.
- $\frac{3}{4}$ If he has to work in a company you would say Anand graduated from IIT, Chennai in 1985 in mechanical engineering.
- $\frac{3}{4}$ Anand hails from Mangalore. He has a sister and his father is a poet. He is singer.---If you are looking at him as a bridegroom!!

Examples (contd...)

$\frac{3}{4}$ All of them are properties of Anand. But you pick and choose a set of his traits which describe him best for a given situation.

$\frac{3}{4}$ Similarly, among various properties by which a definition of a thermodynamic system is possible, a situation might warrant giving the smallest number of properties which describe the system best.

Categories of Properties

$\frac{3}{4}$ Extensive property:

whose value depends on the size or extent of the system
(upper case letters as the symbols).

eg: Volume, Mass (V,M).

If mass is increased, the value of extensive property also increases.

$\frac{3}{4}$ Intensive property:

whose value is independent of the size or extent of the system.

eg: pressure, temperature (p, T).

Property (contd..)

Specific property:

¾ It is the value of an extensive property per unit mass of system. (lower case letters as symbols) eg: specific volume, density (v , ρ).

¾ It is a special case of an intensive property.

¾ Most widely referred properties in thermodynamics:

¾ Pressure; Volume; Temperature; *Entropy*; *Enthalpy*; *Internal energy*

(Italicised ones to be defined later)

$\frac{3}{4}$ State:

It is the condition of a system as defined by the values of all its properties.

It gives a complete description of the system.

Any operation in which one or more properties of a system change is called a change of state.

$\frac{3}{4}$ Phase:

It is a quantity of mass that is homogeneous throughout in chemical composition and physical structure.

e.g. solid, liquid, vapour, gas.

Phase consisting of more than one phase is known as heterogenous system .

Path And Process

The succession of states passed through during a change of state is called the *path of the system*. A system is said to go through a process if it goes through a series of changes in state. Consequently:

$\frac{3}{4}$ A system may undergo changes in some or all of its properties.

$\frac{3}{4}$ A process can be construed to be the locus of changes of state

Processes in thermodynamics are like streets in a city

eg: we have north to south; east to west; roundabouts; crescents

Types of Processes

¾ As a matter of rule we allow one of the properties to remain a constant during a process.

¾ Construe as many processes as we can (with a different property kept constant during each of them)

¾ Complete the cycle by regaining the initial state

- Isothermal (T)
- Isobaric (p)
- Isochoric (v)
- Isentropic (s)
- Isenthalpic (h)
- Isosteric (concentration)
- Adiabatic (no heat addition or removal)

Quasi-static Processes

The processes can be restrained or unrestrained

We need restrained processes in practice.

A quasi-static process is one in which

- $\frac{3}{4}$ The deviation from thermodynamic equilibrium is infinitesimal.
- $\frac{3}{4}$ All states of the system passes through are equilibrium states.



Quasi-static Processes (contd...)

$\frac{3}{4}$ If we remove the weights slowly one by one the pressure of the gas will displace the piston gradually. It is quasistatic.

$\frac{3}{4}$ On the other hand if we remove all the weights at once the piston will be kicked up by the gas pressure. (This is unrestrained expansion) but we don't consider that the work is done - because it is not in a

~~$\frac{3}{4}$ In both cases the systems have undergone a change of state.~~

$\frac{3}{4}$ Another eg: if a person climbs down a ladder from roof to ground, it is a quasistatic process. On the other hand if he jumps then it is not a quasistatic process.

Equilibrium State

$\frac{3}{4}$ A system is said to be in an equilibrium state if its properties will not change without some perceivable effect in the surroundings.

$\frac{3}{4}$ Equilibrium generally requires all properties to be uniform throughout the system.

$\frac{3}{4}$ There are mechanical, thermal, phase, and chemical equilibria

Equilibrium State (contd)

Nature has a preferred way of directing changes.

eg:

¾ water flows from a higher to a lower level

¾ Electricity flows from a higher potential to a lower one

¾ Heat flows from a body at higher temperature to the one at a lower temperature

¾ Momentum transfer occurs from a point of higher pressure to a lower one.

¾ Mass transfer occurs from higher concentration to a lower one

Types of Equilibrium

Between the system and surroundings, if there is no difference in

Pressure	→	Mechanical equilibrium
Potential	→	Electrical equilibrium
Concentration of species	→	Species equilibrium
Temperature	→	Thermal equilibrium

No interactions between them occur.

They are said to be in equilibrium.

Thermodynamic equilibrium implies all those together.

A system in thermodynamic equilibrium does not deliver anything.

Definition Of Temperature and Zeroth Law Of Thermodynamics

$\frac{3}{4}$ Temperature is a property of a system which determines the degree of hotness.

$\frac{3}{4}$ Obviously, it is a relative term.

eg: A hot cup of coffee is at a higher temperature than a block of ice. On the other hand, *ice is hotter than liquid hydrogen.*

Thermodynamic temperature scale is under evolution. What we have now is empirical scale.

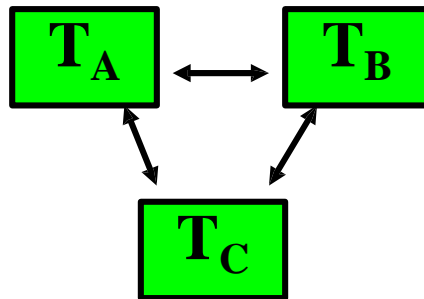
Zeroth Law Of Thermodynamics (Contd...)

$\frac{3}{4}$ Two systems are said to be equal in temperature, when there is no change in their respective observable properties when they are brought together. In other words, “when two systems are at the same temperature they are in thermal equilibrium” (They will not exchange heat).

Note: They need not be in thermodynamic equilibrium.

Zeroth Law

$\frac{3}{4}$ If two systems (say A and B) are in thermal equilibrium with a third system (say C) separately (that is A and C are in thermal equilibrium; B and C are in thermal equilibrium) then they are in thermal equilibrium themselves (that is A and B will be in thermal equilibrium)



Explanation of Zeroth Law

¾ Let us say T_A, T_B and T_C are the temperatures of A, B and C respectively.

¾ A and c are in thermal equilibrium. $T_a = t_c$

¾ B and C are in thermal equilibrium. $T_b = t_c$

Consequence of of '0'th law

¾ A and B will also be in thermal equilibrium $T_A = T_B$

¾ Looks very logical

¾ All temperature measurements are based on this LAW.

Work and Heat

We Concentrate On Two Categories Of Heat And Work

$\frac{3}{4}$ Thermodynamic definition of work:

Positive work is done by a system when the **sole effect external** to the system **could be** reduced to the rise of a weight.

$\frac{3}{4}$ Thermodynamic definition of heat:

It is the **energy in transition** between the system and the surroundings by virtue of the difference in temperature.

Traits of Engineers

$\frac{3}{4}$ All our efforts are oriented towards how to convert heat to work or vice versa:

Heat to work  Thermal power plant

Work to heat  Refrigeration

$\frac{3}{4}$ Next, we have to do it in a sustained manner (we can't use fly by night techniques!!)

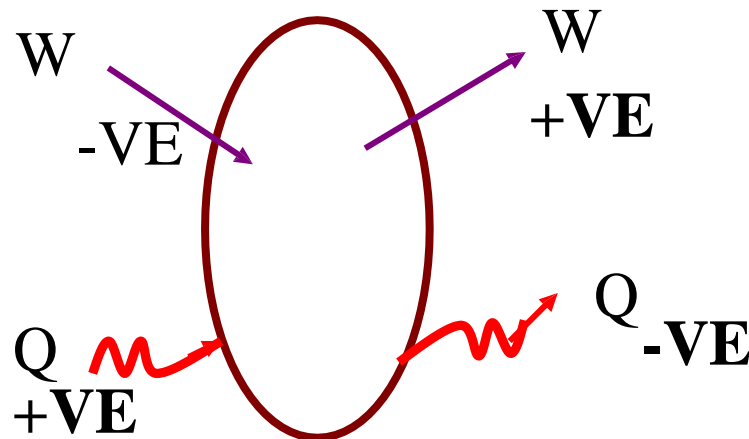
$\frac{3}{4}$ We require a combination of processes.

$\frac{3}{4}$ Sustainability is ensured from a cycle

$\frac{3}{4}$ A system is said to have gone through a cycle if the initial state has been regained after a series of processes

Sign Conventions

- $\frac{3}{4}$ Work done BY the system is +ve
- $\frac{3}{4}$ Obviously work done ON the system is -ve
- $\frac{3}{4}$ Heat given TO the system is +ve
- $\frac{3}{4}$ Obviously Heat rejected by the system is -ve



Types of Work Interaction

Types of work interaction

- $\frac{3}{4}$ Expansion and compression work
(displacement work)
- $\frac{3}{4}$ Work of a reversible chemical cell
- $\frac{3}{4}$ Work in stretching of a liquid surface
- $\frac{3}{4}$ Work done on elastic solids
- $\frac{3}{4}$ Work of polarization and magnetization

Notes on Heat

$\frac{3}{4}$ All temperature changes need not be due to heat alone

eg: Friction

$\frac{3}{4}$ All heat interaction need not result in changes in temperature

eg: condensation or evaporation

Various Types of Work

¾ Displacement work (pdV work)

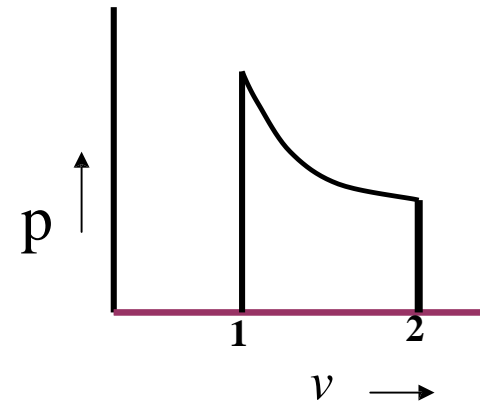
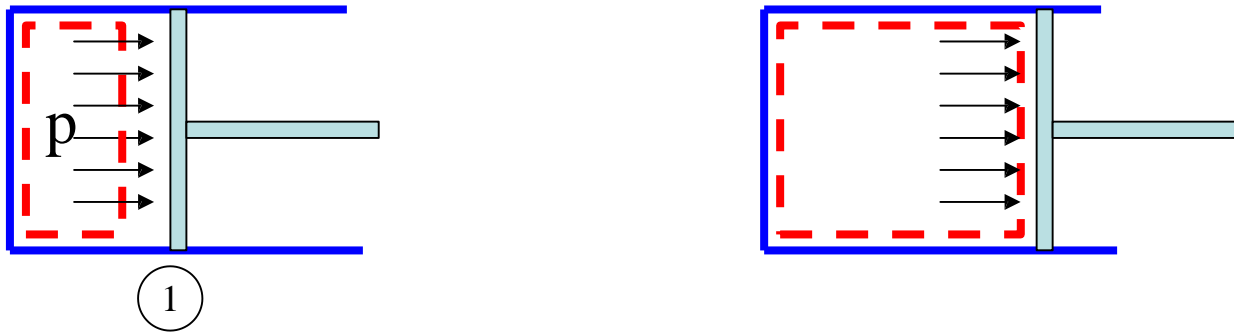
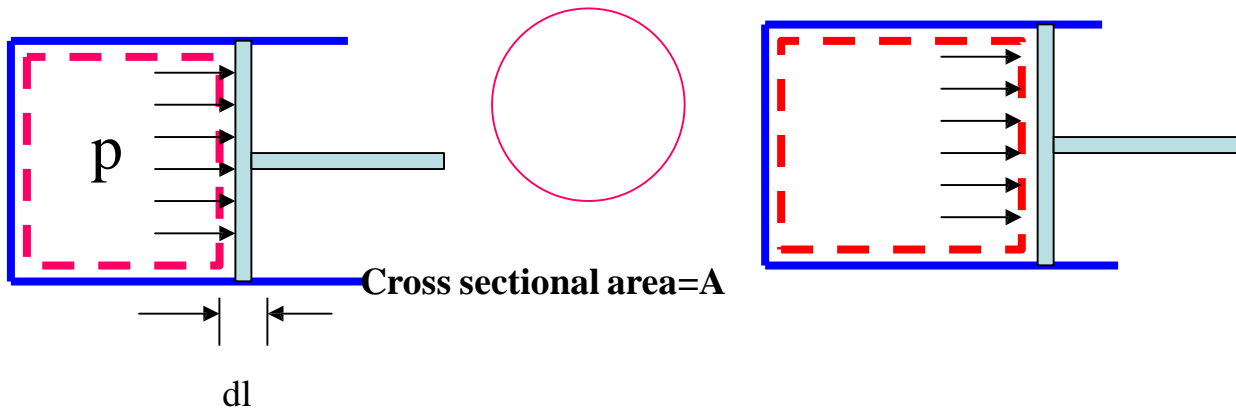
¾ Force exerted, $F = p \cdot A$

¾ Work done

$$dW = F \cdot dL = p \cdot A \cdot dL = p \cdot dV$$

¾ If the piston moves through a finite distance say 1-2, Then work done has to be evaluated by integrating $\delta W = \int p dV$

Work (Contd...)



Discussion on Work Calculation

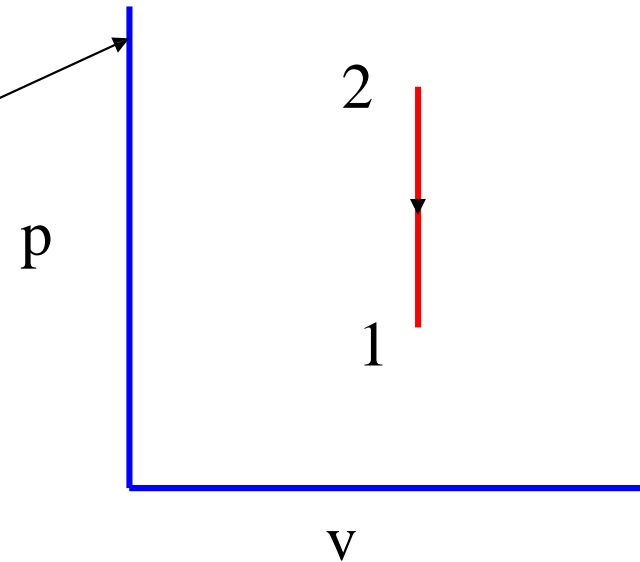
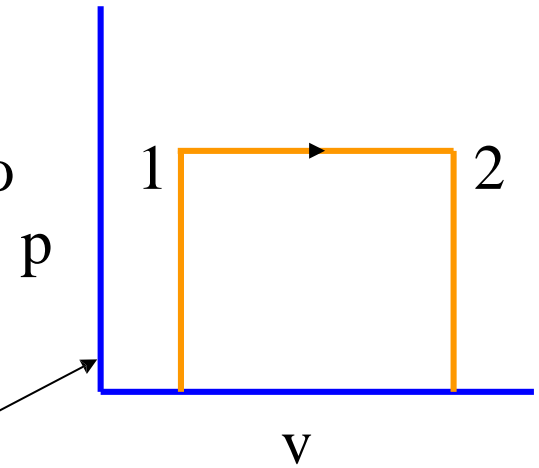
The system (shown by the dotted line) has gone through a change of state from 1 to 2. We need to know how the pressure and volume change.

Possibilities:

$\frac{3}{4}$ Pressure might have remained constant
or

$\frac{3}{4}$ It might have undergone a
change as per a relation $p(V)$
or

$\frac{3}{4}$ The volume might have remained constant
In general the area under the process on p - V
plane gives the work

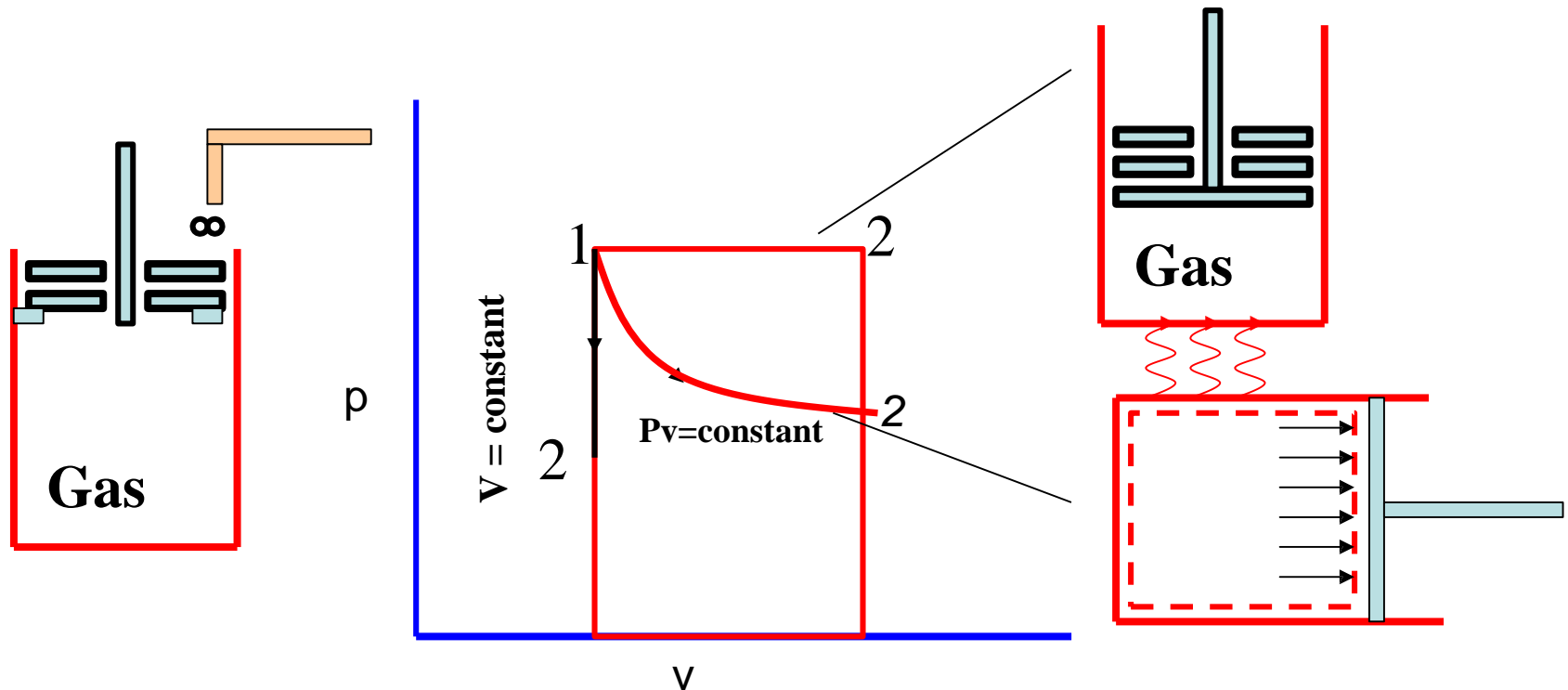


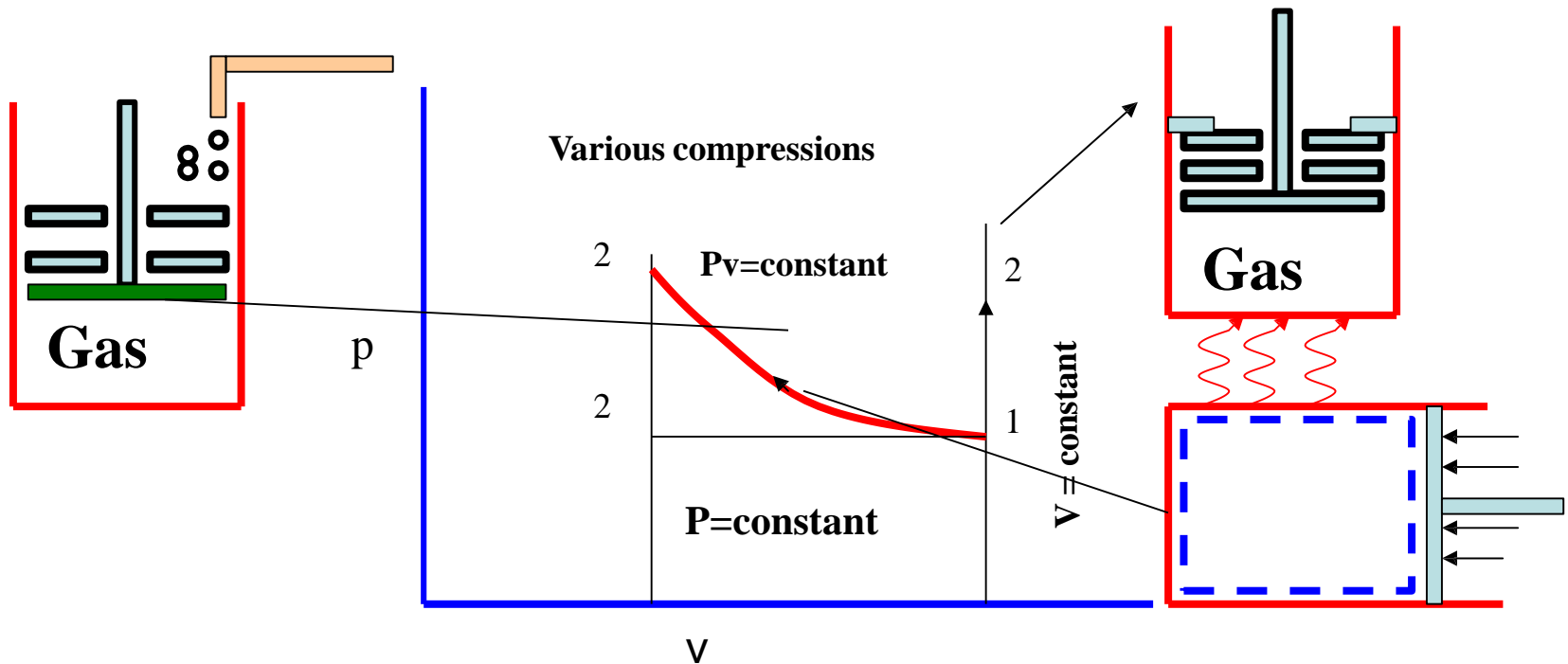
Other Possible Process

$\frac{3}{4}$ $pV = \text{constant}$ (it will be a rectangular hyperbola)

$\frac{3}{4}$ In general $pV^n = \text{constant}$

IMPORTANT: always show the states by numbers/alphabet and indicate the direction.





$\frac{3}{4}n = 0$ Constant pressure

($V_2 > V_1$ - **expansion**)

$\frac{3}{4}n = 1$ $p v = \text{constant}$

($p_2 < p_1$; $V_2 > V_1$ - **expansion**)

$\frac{3}{4}n = \infty$ Constant volume

($p_2 < p_1$ - **cooling**)

Others Forms Of Work

Stretching of a wire:

Let a wire be stretched by dL due to an application of a force F

Work is done on the system. Therefore $dW = -FdL$

Electrical Energy:

Flowing in or out is always deemed to be work

$$dW = -EdC = -EIdt$$

Work due to stretching of a liquid film due to surface tension:

Let us say a soap film is stretched through an area dA

$$dW = -\sigma dA$$

where σ is the surface tension.

IRREVERSIBILITY

The entropy of a system plus its surroundings (i.e. an isolated system) can never decrease (2nd law).

The second law states:

$$(\Delta S)_{system} + (\Delta S)_{surr} = 0 \text{ where } \Delta = \textit{final - initial}$$

> 0 irreversible (real world)
 $= 0$ reversible (frictionless, ideal)

In an ideal case if Q is the heat supplied from a source at T , its availability or the maximum work it can deliver is $Q(1-T_0/T)$ where T_0 is the temperature of the surroundings. Invariably it will be less than this value. The difference is termed as irreversibility.

Availability = Maximum possible work-Irreversibility

$$W_{\text{useful}} = W_{\text{rev}} - I$$

Irreversibility can also be construed as the amount of work to be done to restore the system to the original state.

Eg: If air at 10 bar is throttled to 1 bar, the irreversibility will be $p v \ln(10)$ which is the work required to get 10 bar back. Here p is 1 bar and v is the specific volume at this condition.

Note that the system has been restored to the original state but not the surroundings Therefore increase in entropy will be

$R \ln 10$.

Combining I & II laws

$$T dS \geq \Delta u + \delta W$$

equality sign being for the reversible process. It implies that the amount of heat energy to be supplied in a real process is larger than the thermodynamic limit.

Second Law of Thermodynamics

- Irreversible Processes increase the entropy of the universe
- Reversible Processes do not effect the entropy of the universe
- Impossible Processes decrease the entropy of the universe

$$\Delta S_{universe} = 0$$

Entropy Generation in the universe is a measure of lost work

$$\Delta S_{Universe} = \Delta S_{System} + \Delta S_{Surroundings}$$

The losses will keep increasing

The sin keeps accumulating

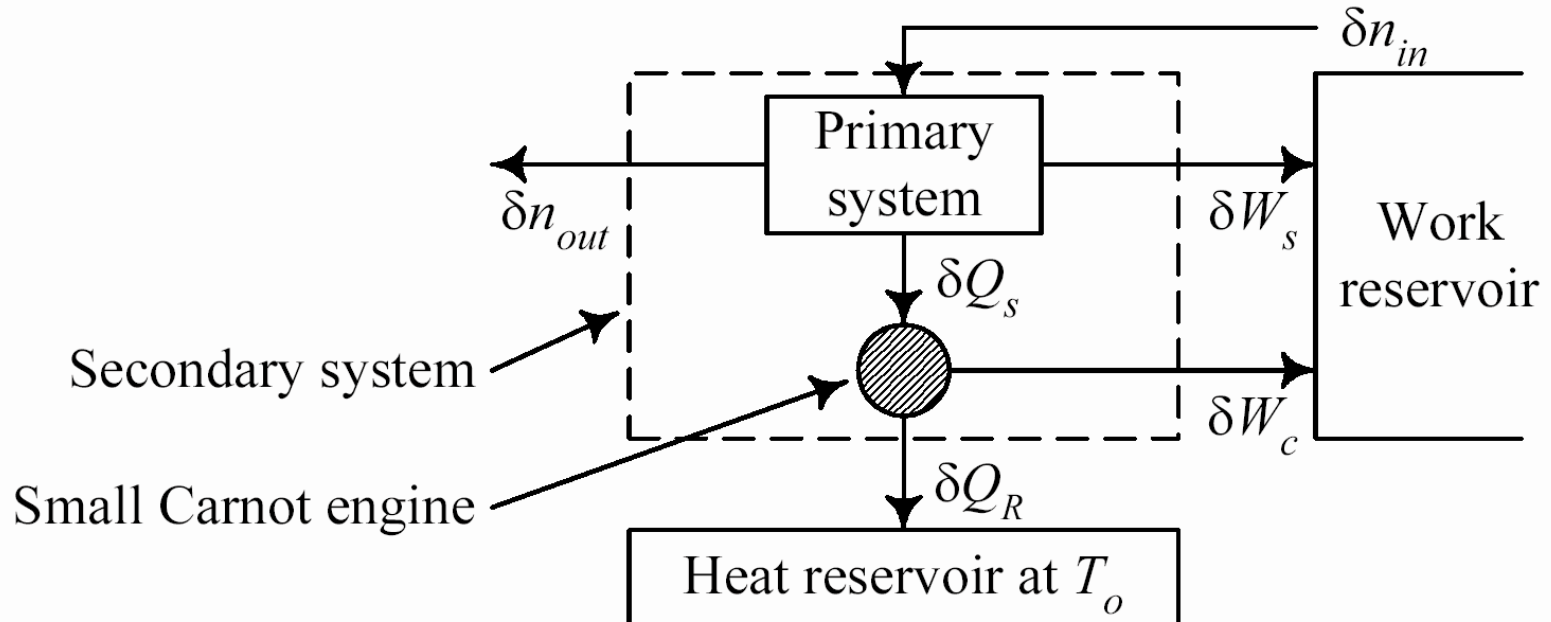
Damage to environment keeps increasing

When the entropy of the universe goes so high, then some one has to come and set it right. **HE SAYS HE WILL COME**. Every religion confirms this.

Let us all wait.

Cheer up, things are not that bad yet!!

Ideal maximum work – Availability or Exergy



Consider a fully reversible process with no dissipative effects – that is all work is transferred without loss and all heat is transferred using an ideal Carnot process to generate additional work.

Availability or Exergy (cont...)

The resulting maximum work in Secondary system given by

$$\Delta B = H_{out} - H_{in} - T_o (S_{out} - S_{in}) = \Delta H - T_o \Delta S$$

ΔB = change in availability or exergy

= maximum work output or minimum work input

$$\Delta B = \Delta H - T_o \left[S_{out} - S_{in} \right]$$

Normally, $T_{out}, P_{out} = T_o, P_o$ = ambient or dead state condition

Availability or Exergy (cont...)

Clearly, the availability B is a state function in the strictest mathematical sense so the maximum (or minimum) work associated with any steady state process is also independent of the path.

Availability:

- *Yields the maximum work producing potential or the minimum work requirement of a process*
- *Allows evaluation and quantitative comparison of options in a sustainability context*

Exergy analysis

Exergy analysis is a formalised way of applying availability theory to engineering installations such as power generating plants. Energy (First Law) analysis keeps track of the heat and work transfers but does not indicate the source and magnitude of the irreversible entropy creation. Exergy (Second Law) analysis provides this information. It is useful in indicating where research resources can be directed to best advantage.

Steady-flow exergy equation

The specific *steady-flow availability function* is defined by,

$$b = h - T_0 s$$

- T_0 is the temperature of a heat reservoir (usually the environment).
- The datum level for b (the state at which $b = 0$) depends on the datum levels for h and s . These can be chosen arbitrarily because it is only differences in h , s and b which are meaningful.

Steady-flow exergy equation....(cont.)

- When a fluid is at equilibrium with the environment, it has zero potential for doing work
- It would therefore be physically meaningful if b were zero at this condition.
- This will not be so unless h and s also happen to be zero. Rather than change the h and s datum levels in all the different thermodynamic tables, we choose instead to replace the *availability function* with a new quantity called the *exergy*.
- When the fluid is at equilibrium with the environment it is said to be in its *dead state* (p_D, T_D).
- The dead state is usually taken as $p_D = 1$ bar and $T_D = 25$ °C (which coincides with what is known as the ‘standard state’).
- The *specific steady-flow exergy* e is then defined as the difference between the actual value of b and its value b_D at the dead state,

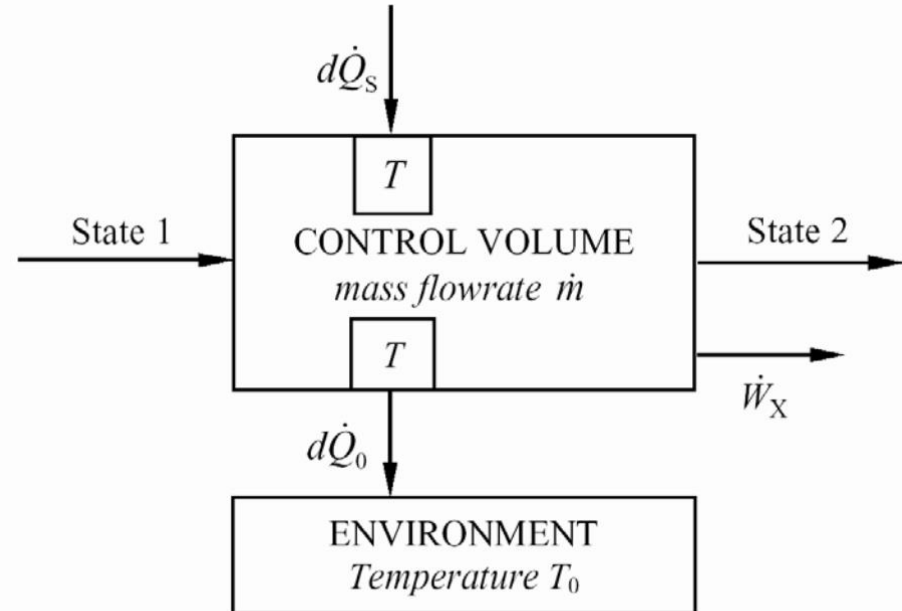
$$e = b - b_D = (h - T_0 s) - (h_D - T_0 s_D)$$

where h_D and s_D are the fluid specific enthalpy and entropy at (p_D, T_D). Hence, $e_D = 0$.

Steady-flow exergy equation....(cont.)

- The *steady-flow exergy* of a fluid at a given state is therefore the maximum power which could be obtained by taking the fluid, in steady-flow, from the given state to the dead state (allowing heat transfer only with the environment at T_0).
- Although this confers a certain absolute status on e , it is important to appreciate that the only truly meaningful quantities are changes in e and b and that these are equal, $(e_2 - e_1) = (b_2 - b_1)$.

The figure shows a device such as a turbine, boiler, condenser, etc. The device may produce shaft power \dot{W}_x and there may be a heat transfer $d\dot{Q}_0$ between the control volume at local temperature T and the environment at T_0 . Also indicated is a possible heat transfer $d\dot{Q}_s$ between an unspecified heat source and the control volume. The work and heat transfers are positive in the direction of the arrows.



Steady-flow exergy equation....(cont.)

Neglecting changes in KE and PE between inlet and outlet states, the steady-flow energy and entropy equations applied to the control volume are :

$$\dot{m}(h_2 - h_1) = \int_1^2 \dot{Q}_s - \dot{W}_x \quad (1)$$

$$\dot{m}(s_2 - s_1) = \int_1^2 \frac{\dot{Q}_s}{T} + \Delta \dot{S}_{irrev} \quad (2)$$

where $\Delta \dot{S}_{irrev}$ is the rate of entropy creation in the control volume due to irreversibilities. Multiplying eq. (2) by T_0 and subtracting from eq. (1), we obtain,

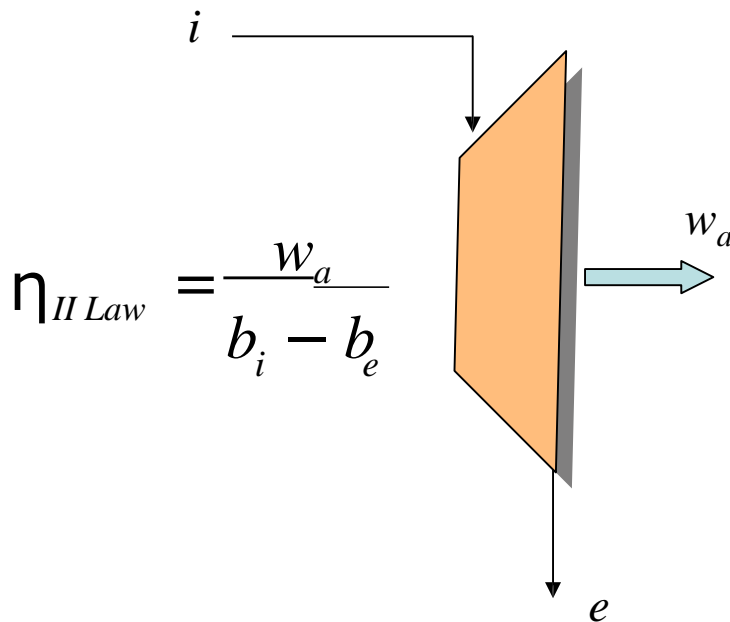
$$\dot{m} \left[h_2 - T_0 s_2 - (h_1 - T_0 s_1) \right] = \int_1^2 \left(\frac{T_0}{T} \right) \dot{Q}_s - \dot{W}_x - T_0 \Delta \dot{S}_{irrev} = \int_1^2 \left(\frac{T_0}{T} \right) \dot{Q}_s - \dot{W}_x$$

Second Law Efficiency

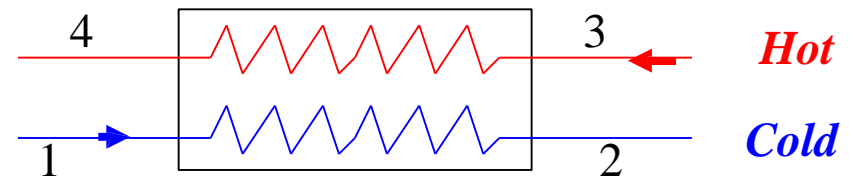
The general definition of second law efficiency of a process can be obtained in terms of change in availability during the process:

$$\text{Second Law Efficiency} = \eta_{II \text{ Law}} = \frac{\text{Production of availability}}{\text{Destruction of availability}}$$

Steam Turbine



Heat Exchanger

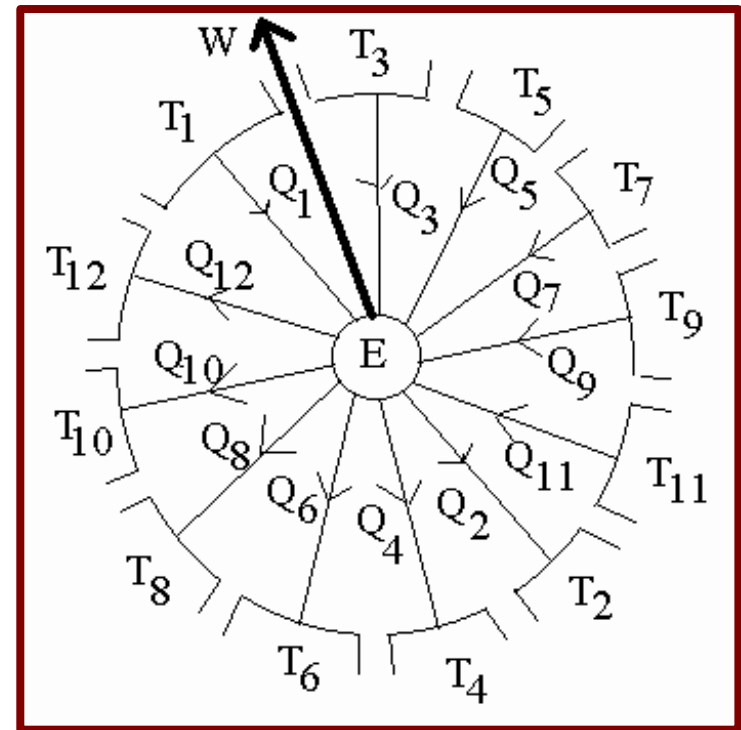


$$\eta_{II \text{ Law}} = \frac{\dot{m}_1 (b_2 - b_1)}{\dot{m}_3 (b_3 - b_4)}$$

Entropy

Clausius Inequality

Suppose we have an engine that receives from several heat reservoirs and rejects heat to several reservoirs, we still have the equation valid.



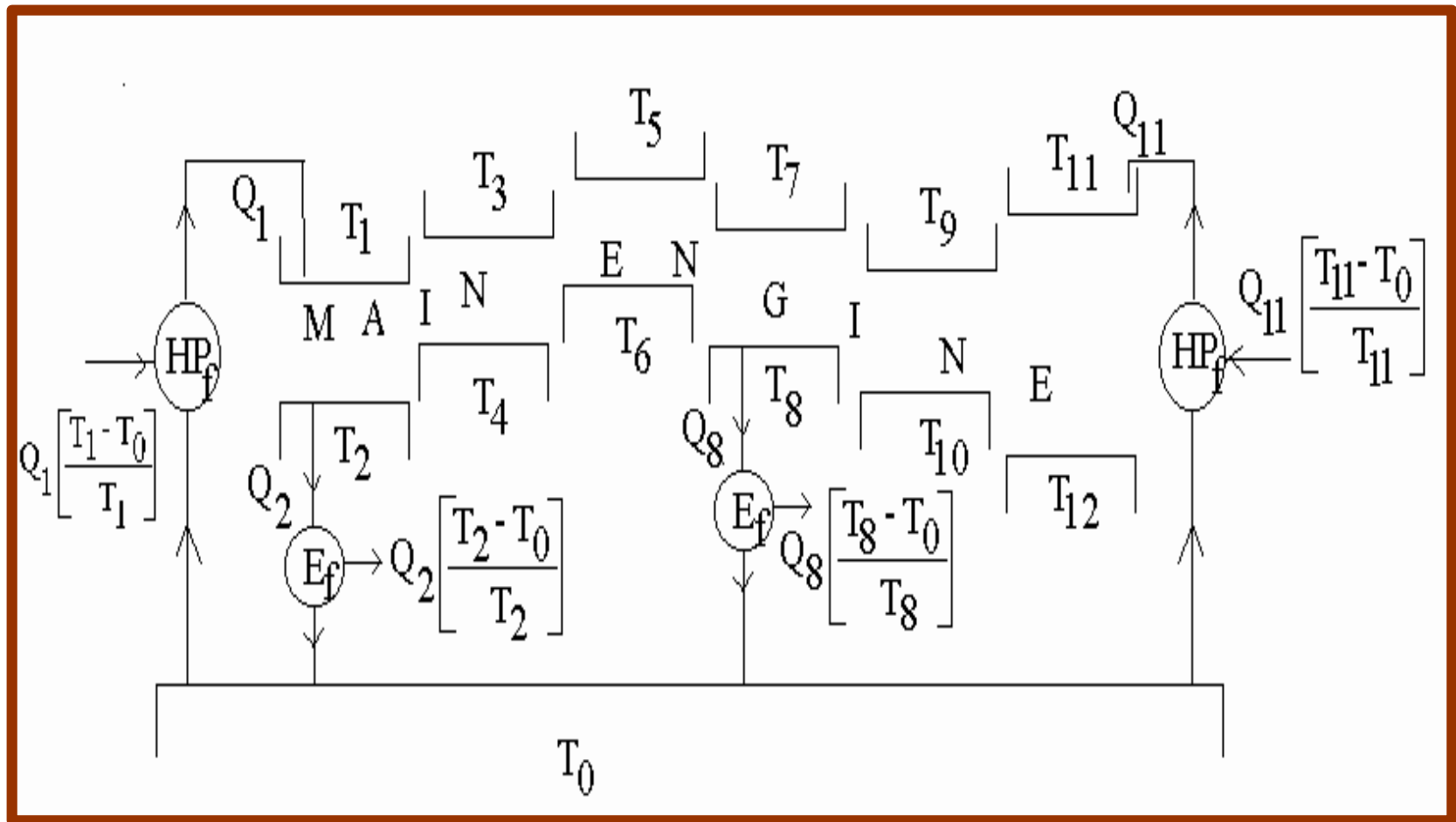
Clausius Inequality (contd...)

^{TW}With reference to previous fig,

- ³/₄ Assume that reservoir at T_1 gets its Q_1 with the help of a fictitious heat pump operating between a source T_0 and T_1 .
The same for 3,5,7....
- ³/₄ Similarly, assume that reservoir at T_2 rejects the heat Q_2 through a fictitious heat engine to the sink at T_0 . The same for 4,6,8....



Clausius Inequality (contd...)



Clausius Inequality (contd...)

$\frac{3}{4}$ Sum of work inputs for = $-Q_1 - Q_3 \dots + Q_1 \frac{T_0}{T_1} + Q_3 \frac{T_0}{T_3} \dots$

All fictitious heat pumps

$\frac{3}{4}$ Sum of work outputs of = $Q_2 + Q_4 \dots - Q_2 \frac{T_0}{T_2} - Q_4 \frac{T_0}{T_4} \dots$

All fictitious heat engines

[Note that the sign convention for work is already taken into account]



Clausius inequality (contd...)



The net of work inputs + work outputs of all the fictitious units

$$= -Q_1 - Q_3 \dots + Q_2 + Q_4 \dots + T_0 [Q_1 / T_1 + Q_3 / T_3 \dots - Q_2 / T_2 - Q_4 / T_4 \dots]$$

But we know that for the main engine at the centre

$$W = Q_1 + Q_3 \dots - Q_2 - Q_4 \dots \quad [\text{after taking the sign into account}]$$

Clausius Inequality (Contd...)

$\frac{3}{4}$ If we consider the entire system consisting of all the reservoirs 1-12 and the fictitious source at T_0 , the work output of our main engine must be compensated by the works of fictitious engines (Otherwise the overall system will be delivering work by interaction with a single source at T_0).



Clausius Inequality (Contd...)



This is possible only when

$$\frac{3}{4} \quad T_o [Q_1 / T_1 + Q_3 / T_3 \dots - Q_2 / T_2 - Q_4 / T_4 \dots] = 0$$

$$\frac{3}{4} \quad \text{which implies that } Q_1 / T_1 + Q_3 / T_3 \dots - Q_2 / T_2 - Q_4 / T_4 \dots = 0$$

$\frac{3}{4}$ In general, $S(Q/T) = 0$ provided the engine is perfectly reversible.

If it is not $S(Q/T) < 0$

Therefore in general $S(Q/T) \leq 0$

Since, summation can be replaced by an integral $(\delta Q / T) \leq 0$.

Clausius Inequality (contd...)

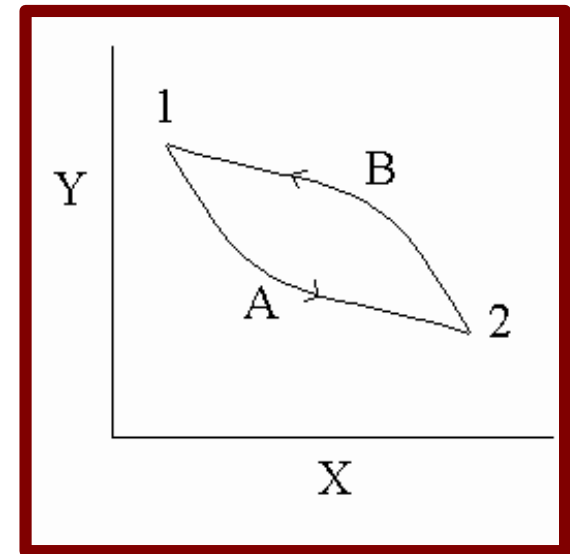
- ¾ The cyclic integral is to remind us that II Law holds only for a cycle.
- ¾ Note: Equality holds when the cycle is reversible.
< sign will be the most probable one for real cycles.
- ¾ Just as we had $dW = p dV$
- ¾ Can we guess that there is something emerging to define Q ?

Clausius Inequality (contd...)

- 9 Is there (something) which is $= dQ/T$? Or $dQ = T \cdot$ (something) ???
- 9 In W, p, V relation on the right hand side p and V are properties.
- 9 Is this (something) also a property?
- 9 For an adiabatic process we said $dQ = 0$. Does that (something) remain invariant during an adiabatic process?

The Concept Of Entropy

Consider a reversible cycle constructed as shown. Since we will be integrating $\int \delta Q / T$ over the entire process say 1-2 along A or B, processes A and B need not be isothermal.



The Concept of Entropy (contd...)

$$\frac{3}{4} \quad (\delta Q / T) = \int \delta Q / T \angle_{\text{along } 1A2} + \int \delta Q / T \angle_{\text{along } 2B1} = 0$$

$\frac{3}{4}$ If A and B are reversible and <0 if they are not.

$$\frac{3}{4} \quad \int \delta Q / T \angle_{\text{along } 1A2} = - \int \delta Q / T \angle_{\text{along } 2B1}$$

$$\frac{3}{4} \quad \int \delta Q / T \angle_{\text{along } 1A2} = \int \delta Q / T \angle_{\text{along } 1B2}$$

The Concept of Entropy (contd...)

^T~~M~~In other words the integral remains the same no matter what the path is. It can be simply written as $S_2 - S_1$. The value depends only on the end states and not on the path followed. So it is a state function or a property.

^T~~M~~Like energy entropy (s) is also an extensive property. It will have the units of J/K. Similar to energy where we converted it into specific property, specific entropy (lower case s) will have units of J/kg K (same as specific heat)

The Concept of Entropy (contd...)

$${}^1\int_2 \delta Q / T = S_2 - S_1 \quad \text{or} \quad {}^1\int_2 \delta q / T = s_2 - s_1 \quad \angle \delta q / T = \delta s \quad \text{or} \quad \delta q = T \delta s$$

Lesson learnt:

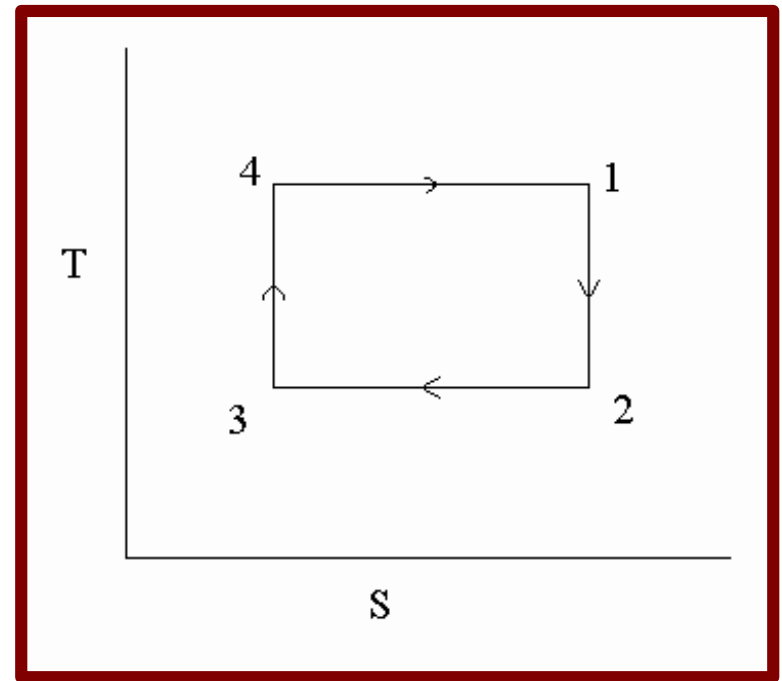
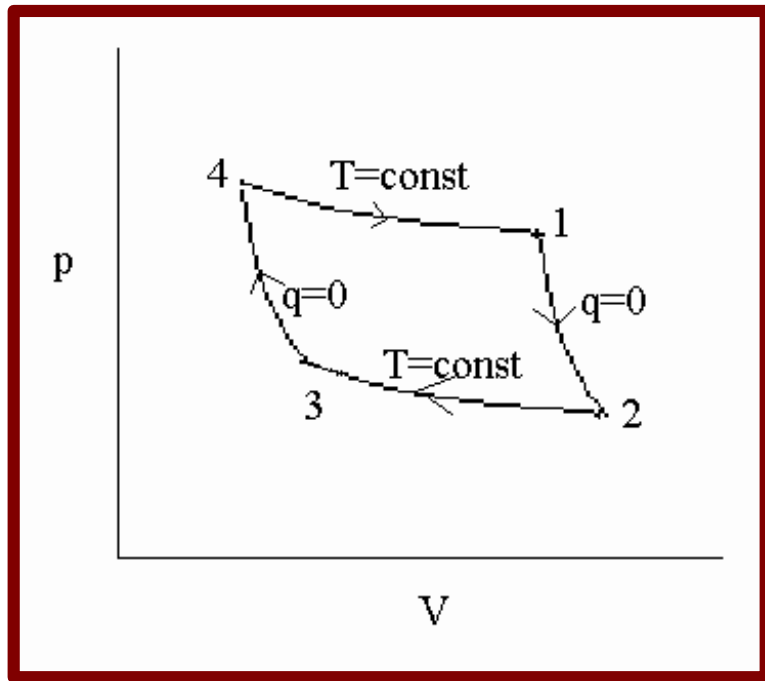
$\frac{3}{4}$ Just as we can represent work interactions on P-V plane

$\frac{3}{4}$ we can represent heat interactions on T-S plane.

$\frac{3}{4}$ Naturally, T will be the ordinate and S will be the abscissa.

$\frac{3}{4}$ All constant temperature lines will be horizontal and constant entropy lines vertical. So Carnot cycle will be just a rectangle.

The Concept of Entropy (contd...)



Integrals under P-V plane give work interaction

Integrals under T-S plane give heat interactions

Calculations

¾ Let us invoke the I law for a process namely $\delta q = \delta w + du$

¾ Substitute for $\delta q = Tds$ and $\delta w = p dv$ $Tds = pdv + du$

¾ For a constant volume process we have $Tds = du \dots (1)$

¾ We have by definition

$$h = u + pv$$

¾ Differentiating

$$dh = du + pdv + vdp$$

$$dh = Tds + vdp$$

¾ For a constant pressure process

$$Tds = dh \dots (2)$$

Calculations (contd...)

~~T~~For a perfect gas $du = c_v dT$ and $dh = c_p dT$

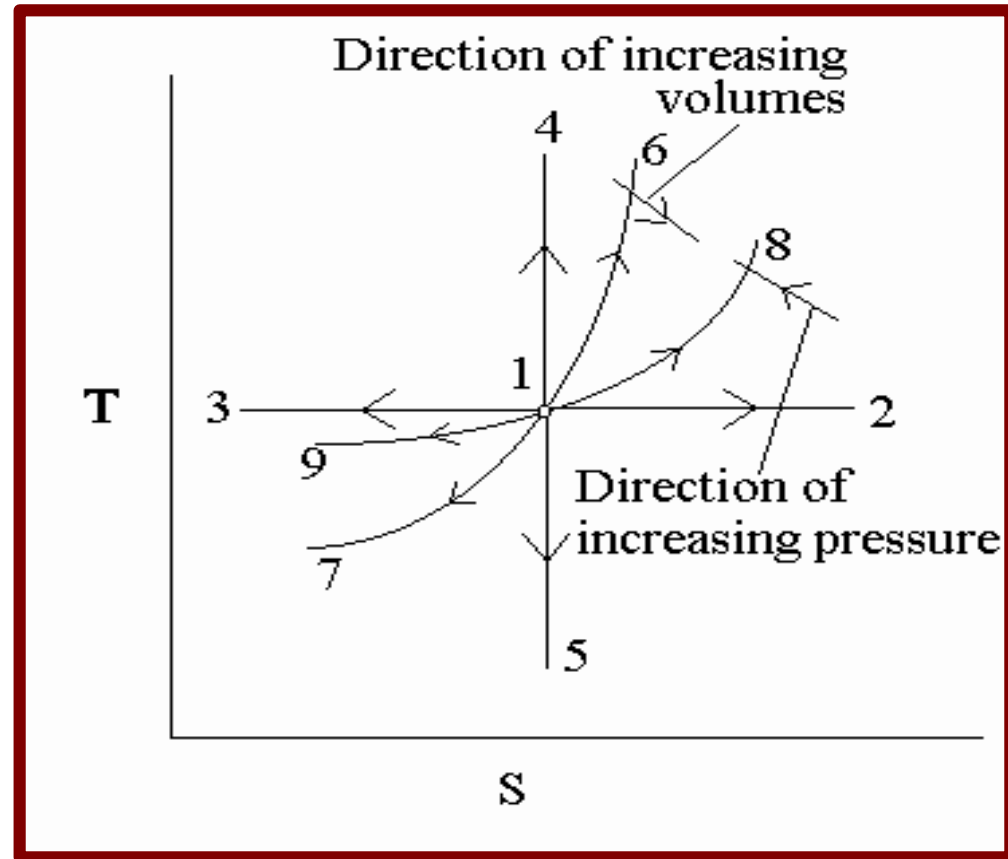
Substitute for du in (1) and dh in (2)

for $v = \text{const}$ $T ds = c_v dT$ or $dT/ds|_{v=\text{const}} = T / c_v$

for $p = \text{const}$ $T ds = c_p dT$ or $dT/ds|_{p=\text{const}} = T / c_p$

1. Since $c_p > c_v$ a constant pressure line on T-s plane will be flatter than a constant volume line.
2. The both (isobars and isochores) will have +ve slopes and curve upwards because the slope will be larger as the temperature increases

Calculations (contd...)



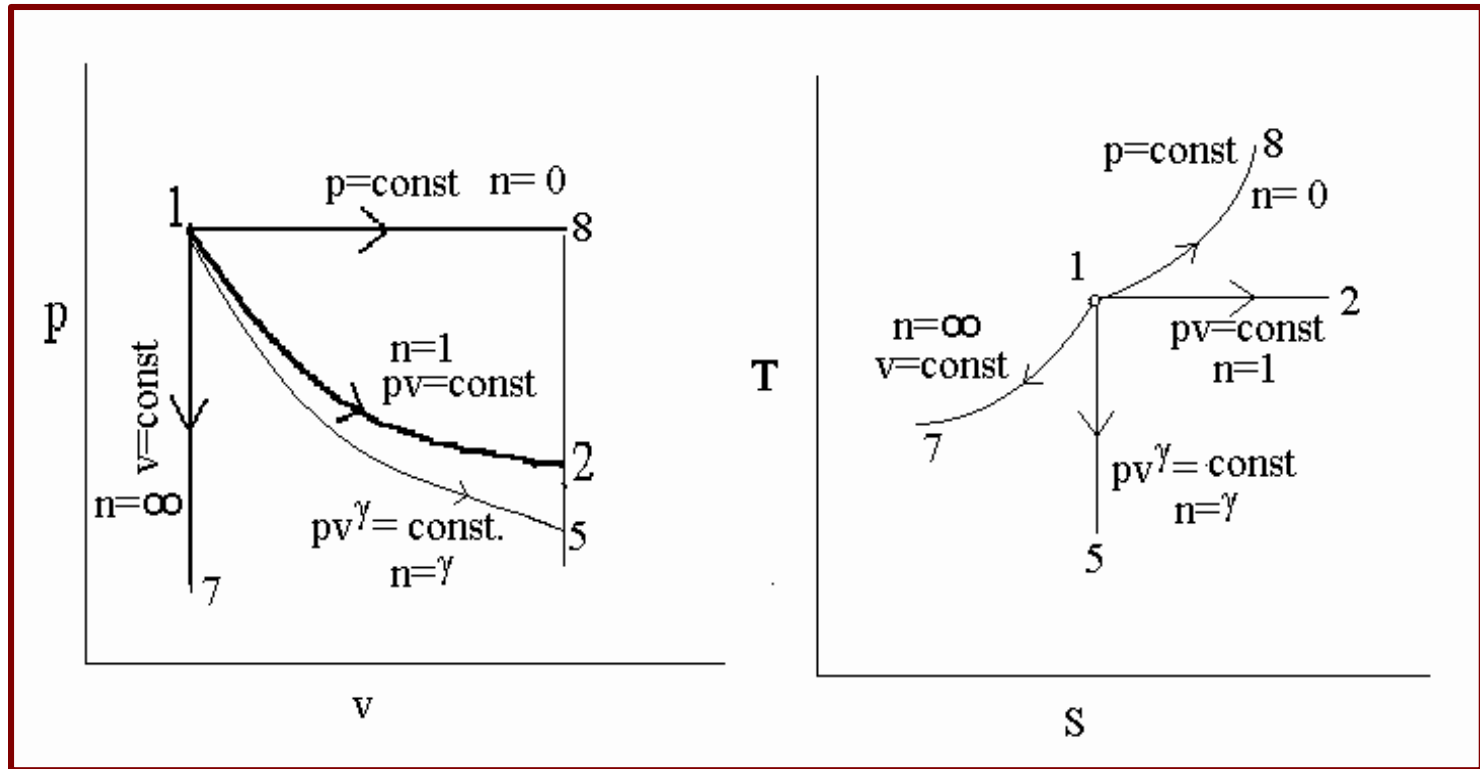
7-1-6 Const V line

9-1-8 Const. p line

Calculations (contd...)

	s	T	p	v
1-2 Isothermal expansion	↑	↓	↓	↑
1-3 Isothermal compression	↓	↓	↑	↓
1-4 Isentropic compression	↓	↑	↑	↓
1-5 Isentropic expansion	↓	↓	↓	↑
1-6 Isochoric heating	↑	↑	↑	↓
1-7 Isochoric cooling	↓	↓	↓	↓
1-8 Isobaric heating/expansion	↑	↑	↓	↑
1-9 Isobaric cooling/compression	↓	↓	↓	↓

Comparison Between p-v and T-s Planes



Comparison Between p-v and T-s Planes (contd...)

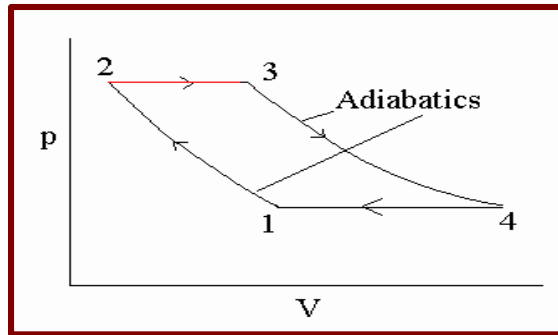
- ¾ A similar comparison can be made for processes going in the other direction as well.
- ¾ Note that n refers to general index in $p v^n = \text{const.}$

Note:

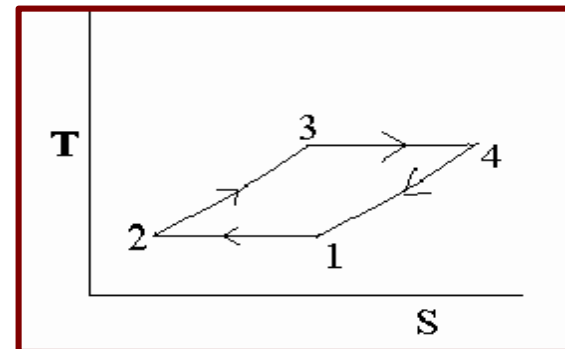
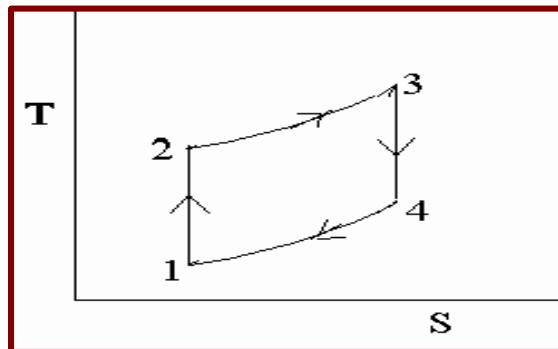
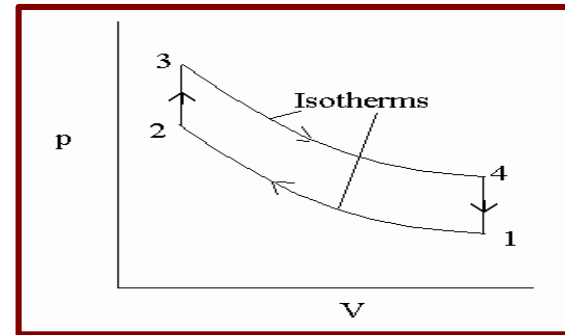
- ¾ For $1 < n < \gamma$ the end point will lie between 2 and 5
- ¾ For $n > \gamma$ the end point will lie between 5 and 7

Comparison Between P-v and T-s Planes (contd...)

Brayton cycle



Stirling cycle

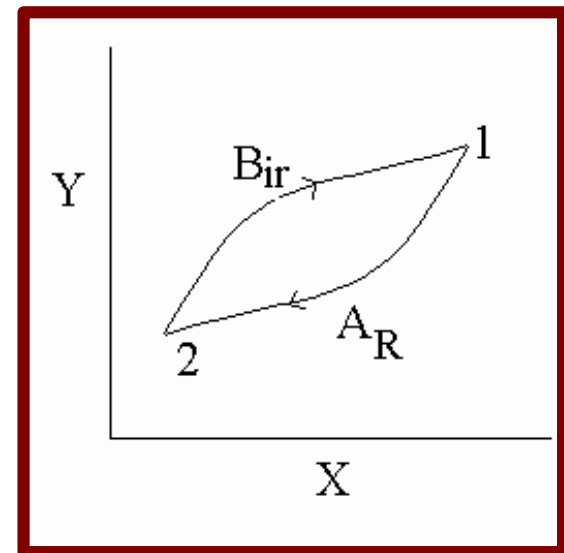


Note: All work producing cycles will have a clockwise direction even on the T-s plane

Consider the Clausius inequality

$$\oint \delta Q / T \leq 0$$

In the cycle shown let A be a reversible process (R) and B an irreversible one (ir), such that 1A2B1 is an irreversible cycle.



Applying Clausius inequality

$$\int \delta Q / T_{\text{along } 1A2} + \int \delta Q / T_{\text{along } 2B1} < 0$$

(because the cycle is irreversible < sign applies)

Since A is reversible $\int \delta Q / T_{\text{along } 1A2} = S_2 - S_1$

$$S_2 - S_1 + \int \delta Q / T_{\text{along } 2B1} < 0$$

- Implying that $\int \delta Q / T \text{ along } 2B1 < S_1 - S_2$
- Or $S_1 - S_2 > \int \delta Q / T \text{ along } 2B1$
- Had B also been reversible $\int \delta Q / T \text{ along } 2B1$ would have been equal to $S_1 - S_2$

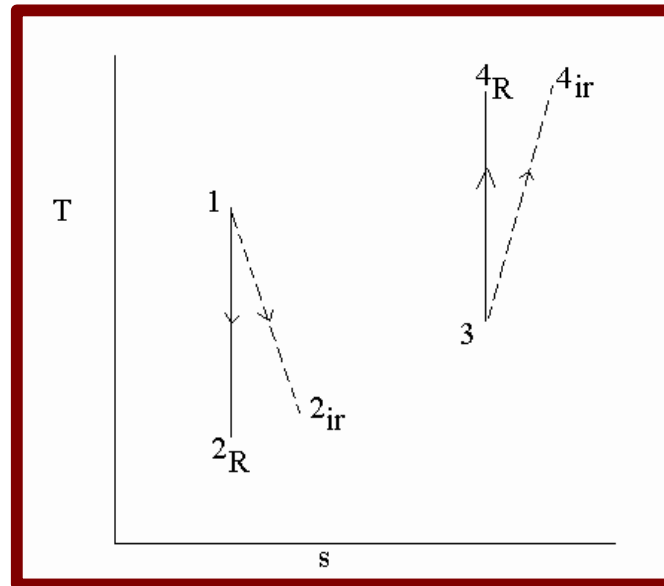
Moral 1

$$(S_1 - S_2)_{\text{irreversible}} > (S_1 - S_2)_{\text{reversible}}$$

An irreversible process generates more entropy than a reversible process.

Moral 2:

If process B is adiabatic but irreversible $S_1 - S_2 > 0$ or $S_1 > S_2$



In general we can say $ds \geq \delta Q / T$ or $\delta Q \leq T ds$
(equality holding good for reversible process)

1-2_R Isentropic expansion (reversible)

1-2_{ir} Non-isentropic expansion (irreversible)

3-4_R Isentropic compression (reversible)

3-4_{ir} Non-isentropic compression (irreversible)

An irreversible engine can't produce more work than a reversible one.

TM*An irreversible heat pump will always need more work than a reversible heat pump.*

- An irreversible expansion will produce less work than a reversible expansion

TM*An irreversible compression will need more work than a reversible compression*

Calculation of change in entropy during various reversible processes for perfect gases

Starting point of equation

$$\delta q - \delta w = du$$

Rewritten as

$$Tds = pdv + c_v dT$$

1. Constant volume process $dv=0$

$$ds = c_v dT/T$$

which on integration yields

$$s_2 - s_1 = c_v \ln(T_2/T_1)$$

2. For constant pressure process

$$ds = c_p dT/T$$

which on integration yields

$$s_2 - s_1 = c_p \ln(T_2/T_1)$$

3. Constant temperature process ($dT=0$)

$$Tds = pdv$$

But $p = RT/v$

$$ds = R dv/v$$

Which on integration yields $s_2 - s_1 = R \ln(v_2/v_1) = R \ln(p_1/p_2)$

Calculation Of Change In Entropy During Various Reversible Processes For Perfect Gases

Starting point of equation

$$\delta q - \delta w = du$$

Rewritten as

$$Tds = pdv + cvdT$$

1. Constant volume process $dv=0$

$$ds = c_v dT/T$$

which on integration yields

$$s_2 - s_1 = c_v \ln(T_2/T_1)$$

2. For constant pressure process

$$ds = c_p dT/T$$

which on integration yields

$$s_2 - s_1 = c_p \ln(T_2/T_1)$$

Calculation Of Change In Entropy During Various Reversible Processes For Perfect Gases (contd...)

4. General equation $ds = p dv/T + c_v dT/T = R dv/v + c_v dT/T$

Which on integration yields $s_2 - s_1 = R \ln(v_2/v_1) + c_v \ln(T_2/T_1)$

Using $Tds = c_p dT - v dp$ (see slide 130) $s_2 - s_1 = c_p \ln(T_2/T_1) - R \ln(p_2/p_1)$

5. Throttling $dT=0$ $p=RT/v$ from which $s_2 - s_1 = R \ln(p_1/p_2)$

Since $p_2 < p_1$, throttling is always irreversible



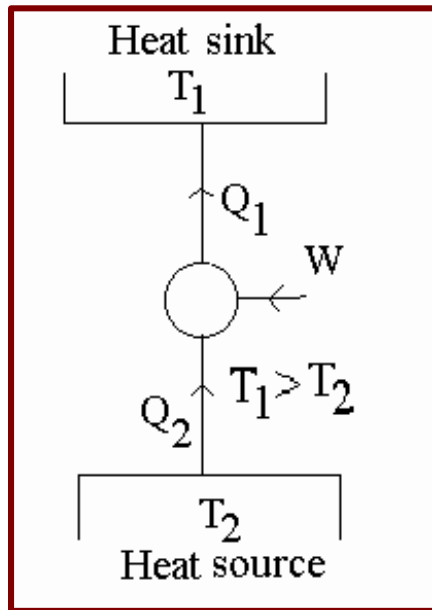
Refrigeration Processes



- As per II law we need to put in work to transfer heat from a colder system to a warmer one.
- We need to put in work to remove moisture from air (unmixing is an energy intensive process).
- Therefore, refrigeration and air conditioning are energy intensive processes

Refrigeration Processes (contd...)

To take Q_2 out of source at T_2 we need a medium. This is the refrigerant



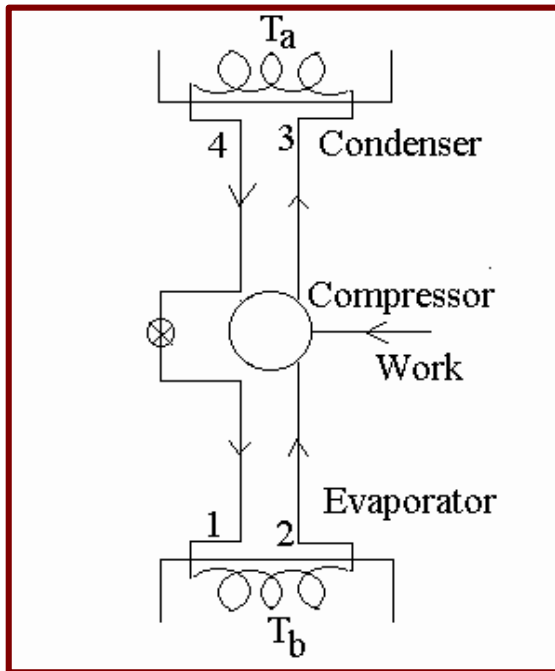
The same medium (refrigerant) will reject Q_1 to sink at T_1 .

In other words, there is a need for an “agent” to collect heat from one source to transfer it over to the other source.

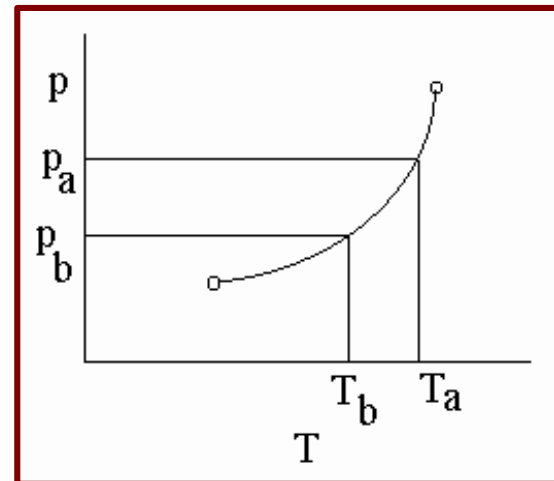
One of the easiest ways of transferring heat at constant temperature is by evaporation and condensation.

Refrigeration Processes (contd...)

Technically we should have refrigerant evaporating at T_2 and condensing at T_1 . The only way to do this is to raise the pressure.



Vapour pressure curve



Refrigeration Processes

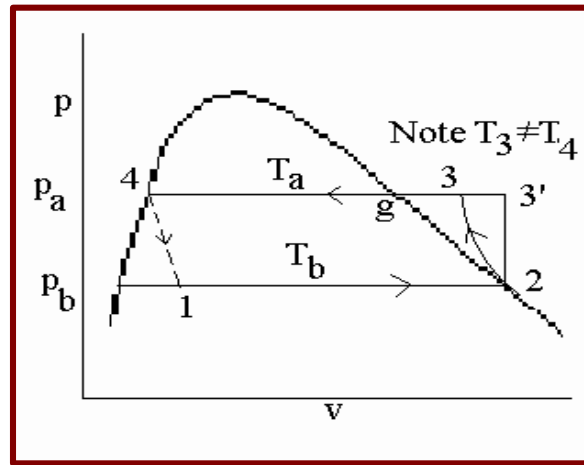
(contd...)

Raising of the pressure occurs in the compressor which receives work.

What options are available?

- i) Constant volume heating
- ii) polytropic compression $pv^n = \text{const}$

Refrigeration Processes (contd...)



Option 1: $T_3 > T_a$

We like to get the state 3 as close as possible to the saturated vapour (g) state at p_a .

Ideally the process should follow the path 2-g.

We are left with no choice but to use polytropic compression. Ideally we like to have $n=\gamma$.

Refrigeration Processes

(contd...)

- $\frac{3}{4}$ The process 4-1 is a pressure reduction process. Possibilities are polytropic or isentropic expansion. State 4 is saturated liquid.
- $\frac{3}{4}$ In practice, it is extremely difficult to compress or expand liquids.
- $\frac{3}{4}$ What happens in an actual refrigeration cycle is the liquid at 4 is throttled from pressure p_4 to p_1 . But throttling is an irreversible process. Consequently, the cycle is irreversible.
- $\frac{3}{4}$ As a convention we depict irreversible processes by dashed lines.
- $\frac{3}{4}$ The above cycle is called vapour compression refrigeration cycle.

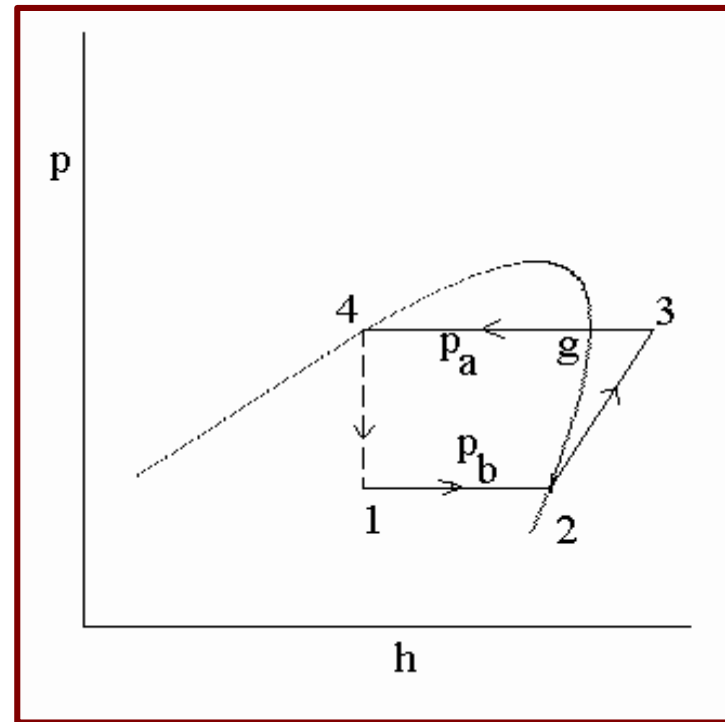
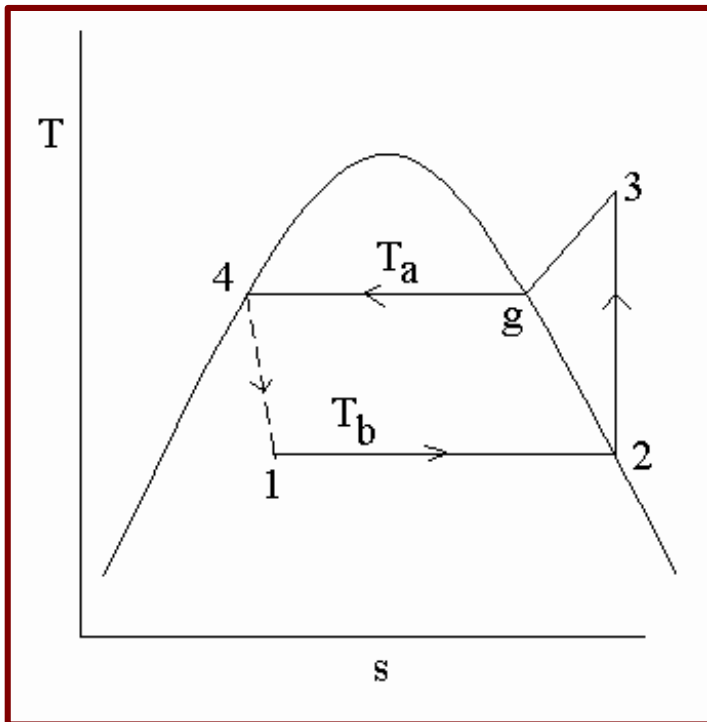
Refrigeration Processes

(contd...)

- $\frac{3}{4}$ The working fluid that goes through those cycle changes is called a refrigerant.
- $\frac{3}{4}$ Ammonia (NH_3), CO_2 , SO_2 , methyl chloride were some of the early refrigerants.
- $\frac{3}{4}$ Chlorofluorocarbons (commonly called as freons) revolutionalised the refrigeration industry from about late 30's.
- $\frac{3}{4}$ There is a rethinking on them because of their ozone depletion potential.
- $\frac{3}{4}$ General trend is to use naturally occurring substances eg: NH_3 , CO_2

Refrigeration Processes (contd...)

The vapour compression refrigeration cycle is seldom analyzed on the p-V plane. T-s is slightly better. p-h is the best.



Refrigeration Processes

(contd...)

Selection criteria for refrigerants:

- 9 $p_b > \text{atm. pr.}$ or else if there is a leak atmospheric air will enter the system.
- 9 Heat of vaporization at T_b (or p_b) should be large - so that we can circulate only the minimal amount of refrigerant
- 9 p_a/p_b should be small so that the work of compression is the least.

Refrigeration Processes

(contd...)

¢ Components of a refrigeration system

- $\frac{3}{4}$ The **compressor** is the heart - Process 2-3 occurs in this. It is here that we meet the II law requirement of giving the work input. This is the “black box” at the rear bottom of your domestic refrigerator. This is the one which makes noise while running
- $\frac{3}{4}$ The **evaporator** - or the freezer is where process 1-2 occurs. This is where we get the cooling. This is the unit inside your refrigerator and on which a lot of frost forms. This serves the role of the low temperature heat source.

Refrigeration Processes

(contd...)

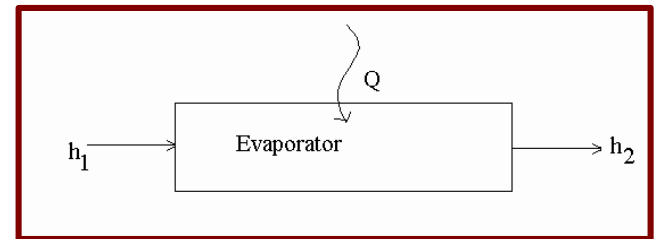
- The **condenser** - where the process 3-4 occurs. It is the black painted serpentine tube with grill on it at the rear of the refrigerator. Usually it feels warm. This serves the purpose of high temperature sink. (In the modern refrigerator it is embedded beneath outer surface of the refrigerator - so don't be surprised if you don't physically see one!!)
- The **expansion device** - where process 4-1 occurs. It takes the form of a capillary tube (a small diameter tube) in domestic refrigerators. In large cold rooms it takes the form of a valve (on which you may see a lot of frost). The capillary is usually attached to the end of the condenser tube at the rear of the refrigerator. (In many units you may not see it as it passes through the body)

Application of SFEE to the evaporator yields

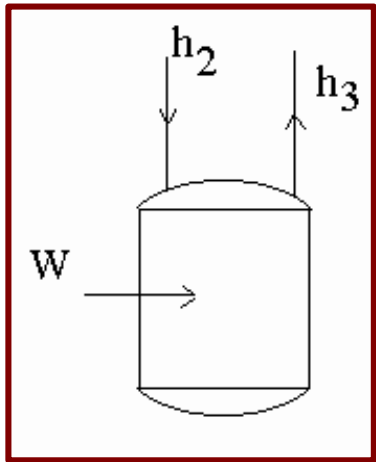
Heat taken out of the source at T_b

$$Q_b = m (h_2 - h_1)$$

This is the area under the line 1-2 in the T-s diagram $m T_b (s_2 - s_1)$



Application of SFEE to the evaporator yields (contd...)



Application of SFEE to the compressor (assuming it to be insulated) yields

$$-W = m(h_3 - h_2)$$

$$\text{COP}_R = \frac{Q}{W} = \frac{h_2 - h_1}{h_3 - h_2}$$

Application of SFEE to the condenser yields

$$Q_a = m(h_4 - h_3)$$

(which will be negative because $h_4 < h_3$ or condenser rejects heat)

Application of SFEE to the evaporator yields (contd...)

The above aspects are easy to determine from the p-h plane. It is not difficult to see that $(h_2 - h_1) + (h_3 - h_2) = h_3 - h_1$ (mathematically and on the p-h diagram)

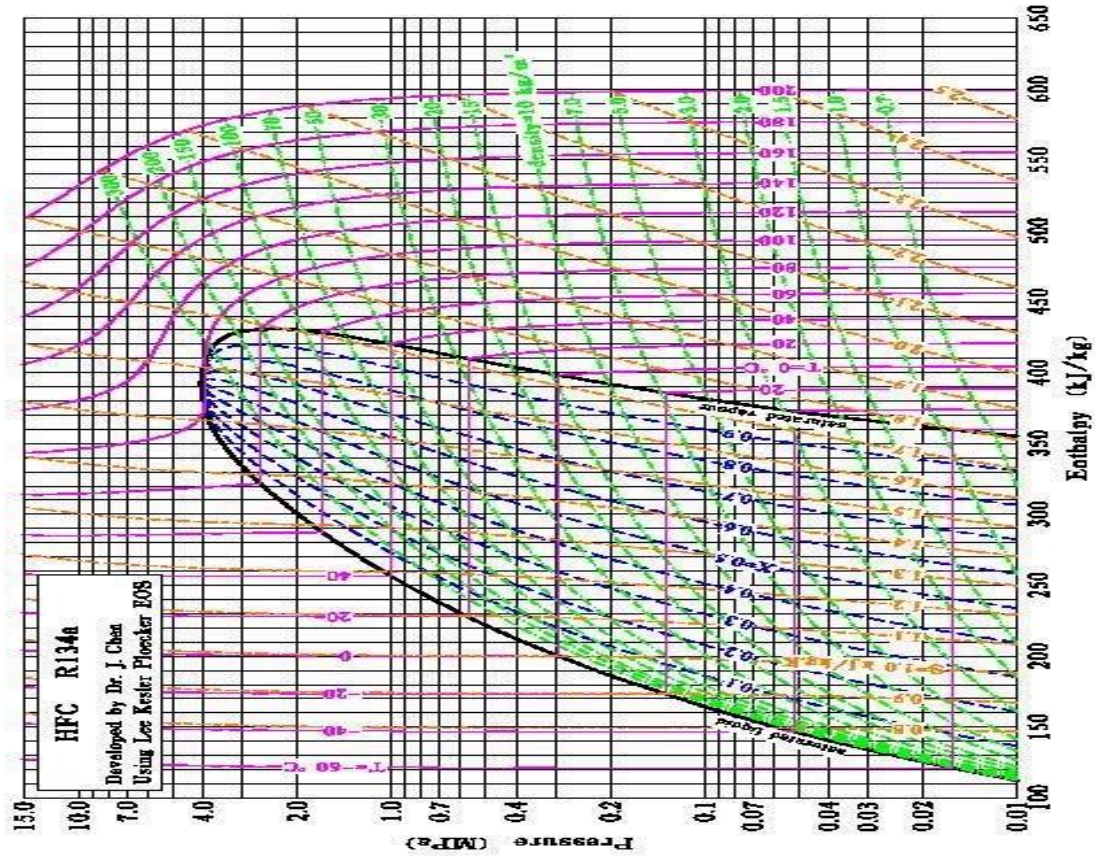
Further, since $h_4 = h_1$ (for the throttling process)

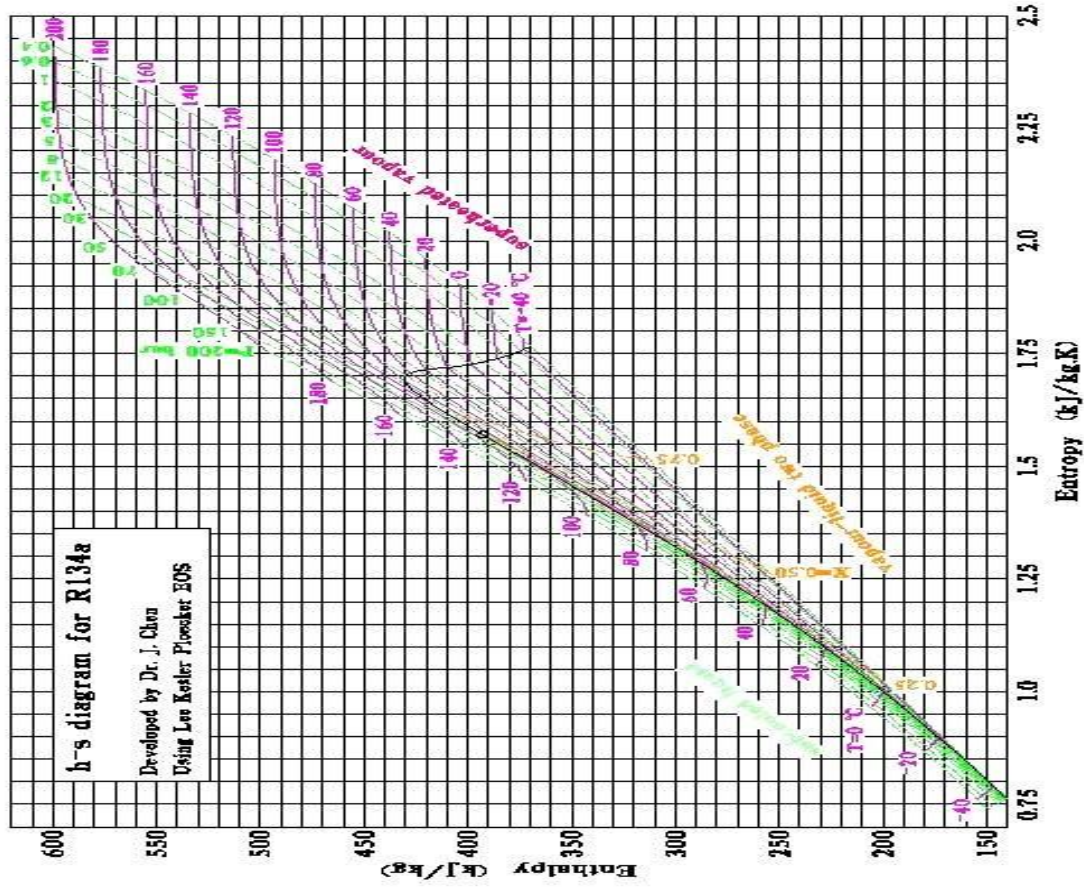
$h_3 - h_1 = h_3 - h_4$ (which is exactly the heat rejected in the condenser)

Moral: The condenser has to reject the heat taken in from the evaporator and the work put in at the compressor

What the thermal engineer should be able to do

1. *Identify any process or series of processes including components of cyclic processes*
2. *Select control masses or volumes as appropriate*
3. *Identify interactions between subsystems*
4. *Sketch a diagram showing control surfaces and interactions and a process diagram showing state changes*
5. *Obtain all necessary properties at each state given independent properties - u , v , h , s , T , P , composition*
6. *Calculate interactions directly where possible*
7. *Apply the 1st Law to any process or set of processes*
8. *Calculate the behavior of an isentropic process or a non-isentropic process given the isentropic efficiency (s_i and s_e related)*
9. *Put it all together and solve the system of algebraic equations*
10. *Estimate the system performance*





Irreversibility

%The entropy of a system plus its surroundings (i.e. an isolated system) can never decrease (2nd law).

The second law states:

$(\Delta S)_{system} + (\Delta S)_{surr}$ where $\Delta = final - initial$

> 0 *irreversible (real world)*

$= 0$ *reversible (frictionless, ideal)*

Irreversibility (contd...)

In an ideal case if Q is the heat supplied from a source at T , its availability or the maximum work it can deliver is $Q(1 - T_0/T)$ where T_0 is the temperature of the surroundings. Invariably it will be less than this value. The difference is termed as irreversibility

Availability = Maximum possible work - Irreversibility

$$W_{\text{useful}} = W_{\text{rev}} - I$$

Irreversibility (contd...)

- ¾ Irreversibility can also be construed as the amount of work to be done to restore the system to the original state.
- ¾ Eg: If air at 10 bar is throttled to 1 bar, the irreversibility will be
- ¾ $p v \ln(10)$ which is the work required to get 10 bar back. Here p is 1 bar and v is the specific volume at this condition.

Irreversibility (contd...)

Note that the system has been restored to the original state but not the surroundings Therefore increase in entropy will be

$R \ln 10$.

Combining I & II laws

$$TdS \geq du + \delta W$$

equality sign being for the reversible process. It implies that the amount of heat energy to be supplied in a real process is larger than the thermodynamic limit.

Second Law of Thermodynamics

- 9 Irreversible Processes increase the entropy of the universe
- 9 Reversible Processes do not effect the entropy of the universe
- 9 Impossible Processes decrease the entropy of the universe

$$\Delta S_{universe} = 0$$

Entropy Generation in the universe is a measure of lost work

$$\Delta S_{Universe} = \Delta S_{System} + \Delta S_{Surroundings}$$

The losses will keep increasing

The sin keeps accumulating

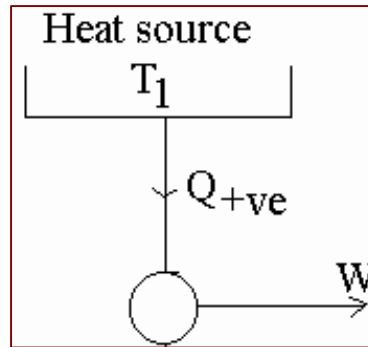
Damage to environment keeps increasing

%oWhen the entropy of the universe goes so high, then some one has to come and set it right.

Second Law of Thermodynamics

Leads Up To Second Law Of Thermodynamics

It is now clear that we can't construct a heat engine with just one +ve heat interaction.

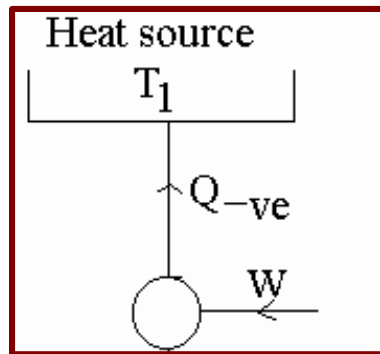


The above engine is not possible.

Second Law Of Thermodynamics (contd...)

Is it possible to construct a heat engine with only one -ve heat interaction?

Is the following engine possible?

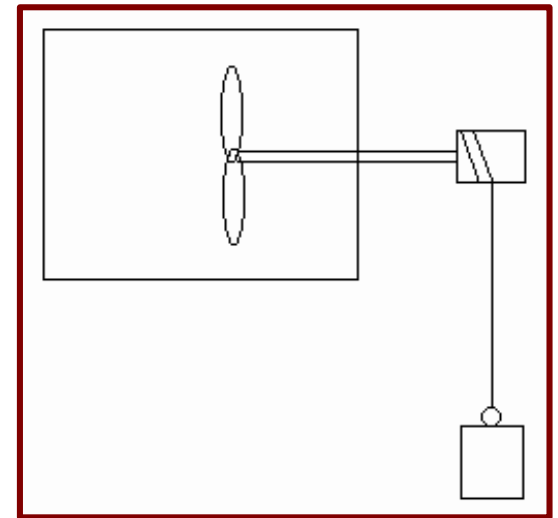
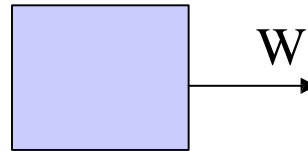


The answer is yes, because
This is what happens in a
stirrer

Second Law Of Thermodynamics (contd...)

Perpetual motion machine of the second kind is not possible.

Perpetual motion machine of
the first kind violates I LAW
(It produces work without
receiving heat)



Enunciation of II Law of Thermodynamics

Statement 1: It is impossible to construct a device which operating in a cycle will produce no effect other than raising of a weight and exchange of heat with a single reservoir.

Note the two underlined words.

II Law applies only for a cycle - not for a process!! (We already know that during an isothermal process the system can exchange heat with a single reservoir and yet deliver work)

!!There is nothing like a 100% efficient heat engine!!

Enunciation of II Law of Thermodynamics

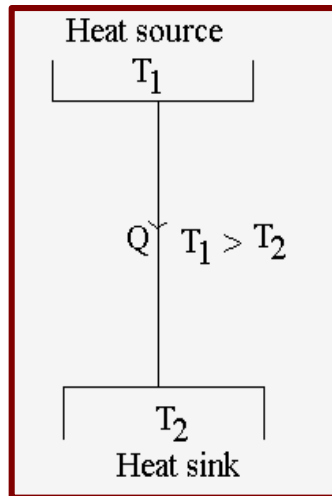
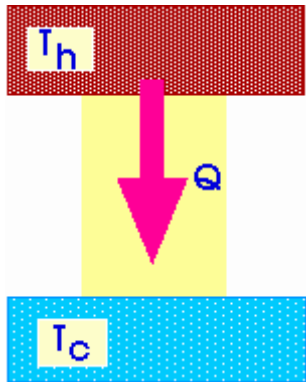
To enunciate the II law in a different form

$\frac{3}{4}$!!! We have to appreciate some ground realities !!!

$\frac{3}{4}$ All processes in nature occur unaided or spontaneously in one direction. But to make the same process go in the opposite direction one needs to spend energy.

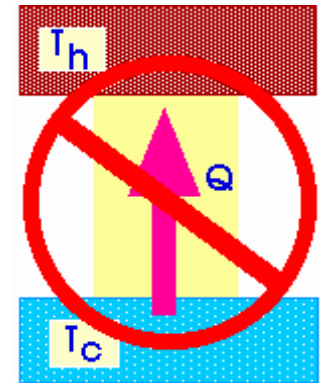
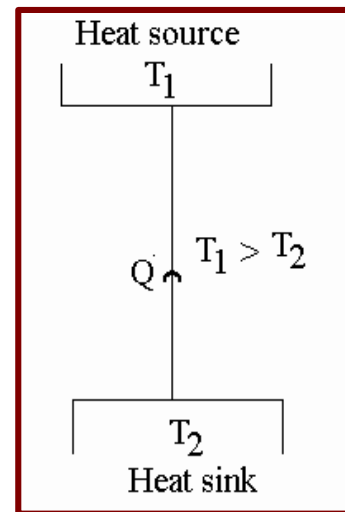
Common sense tells us that

Heat flows from a body at higher temperature to a body at lower temperature



Possible

A hot cup of coffee left in a room becomes cold. We have to expend energy to rise it back to original temperature



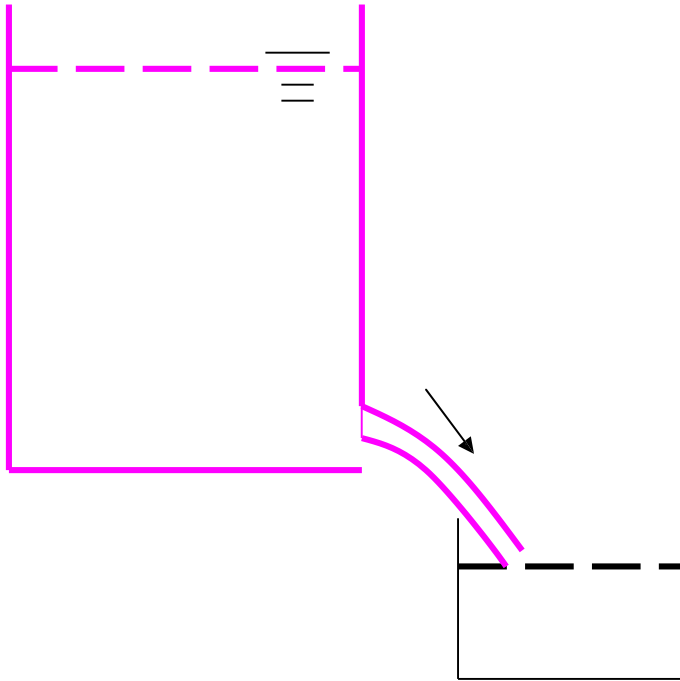
Not possible

(you can't make room heat up your coffee!!)

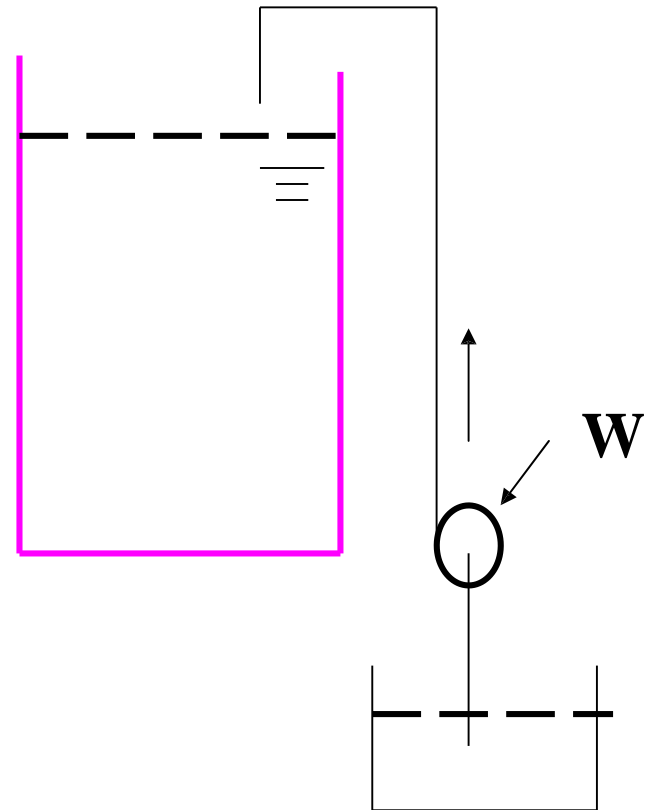
Common sense tells us that

2. Fluid flows from a point of higher pressure or potential. to a lower one

Water from a tank can flow down
To get it back to the tank you have to use a pump i.e, you spend energy



Possible



Common sense tells us that

3. Current flows from a point of higher potential to lower one Battery can discharge through a resistance, to get the charge
4. You can mix two gases or liquids. But to separate them you have to spend a lot of energy. (You mix whisky and soda without difficulty - but can't separate the two - Is it worthwhile?)
5. All that one has to say is "I do". To get out of it one has to
6. spend a lot of money
- When you go to a bank and give 1US\$ you may get Rs 49. But if you give Rs 49 to the bank they will give you only 95 US cents (*if you are lucky !!*). You spend more.

Common sense tells us that

6. When you go to a bank and give 1US\$ you may get Rs 49. But if you give Rs 49 to the bank they will give you only 95 US cents (if you are lucky !!). You spend more.
7. You can take tooth paste out of the tube but can't push it back!!

Moral:

All processes such as 1-7 occur unaided in one direction but to get them go in the other direction there is an expenditure - money, energy, time, peace of mind?

They are called irreversible processes

Definitions of Reversible Process

A process is reversible if after it, means can be found to restore the system and surroundings to their initial states.

Some reversible processes:

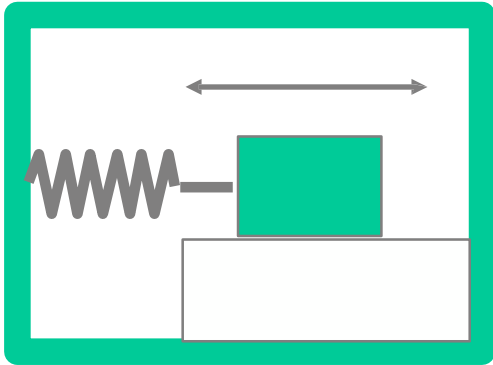
$\frac{3}{4}$ Constant volume and constant pressure heating and cooling - the heat given to change the state can be rejected back to regain the state.

Reversible Process (contd...)

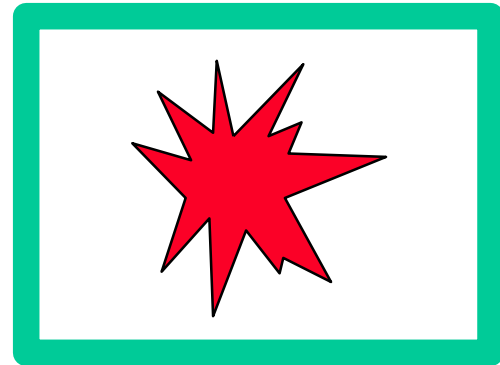
- $\frac{3}{4}$ Isothermal and adiabatic processes -the work derived can be used to compress it back to the original state
- $\frac{3}{4}$ Evaporation and condensation
- $\frac{3}{4}$ Elastic expansion/compression (springs, rubber bands)
- $\frac{3}{4}$ *Lending money to a friend (who returns it promptly)*

Some Irreversible Process

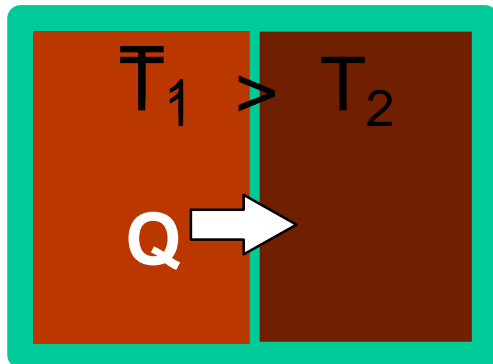
motion with friction



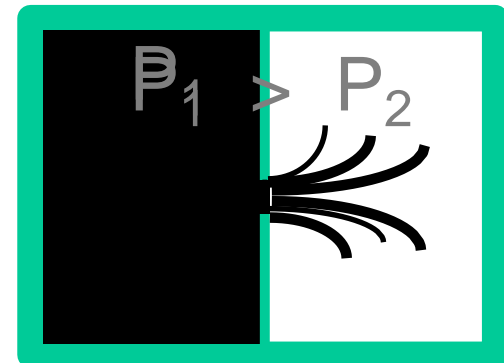
spontaneous
chemical reaction



heat transfer

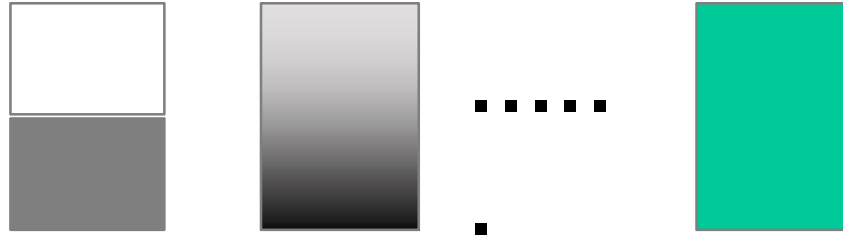


unrestrained
expansion



Irreversible Process (contd...)

mixing



Flow of current through a resistance - when a battery discharges through a resistance heat is dissipated. You can't recharge the battery by supplying heat back to the resistance element!!

Pickpocket

!!!Marriage!!!!

Reversible Cycle

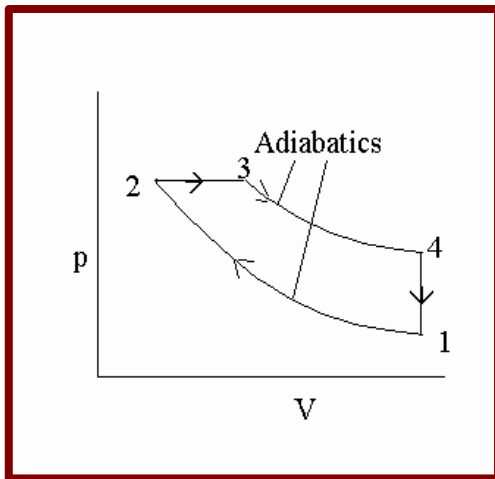
$\frac{3}{4}$ A cycle consisting of all reversible processes is a reversible cycle. Even one of the processes is irreversible, the cycle ceases to be reversible.

Otto, Carnot and Brayton cycles are all reversible.

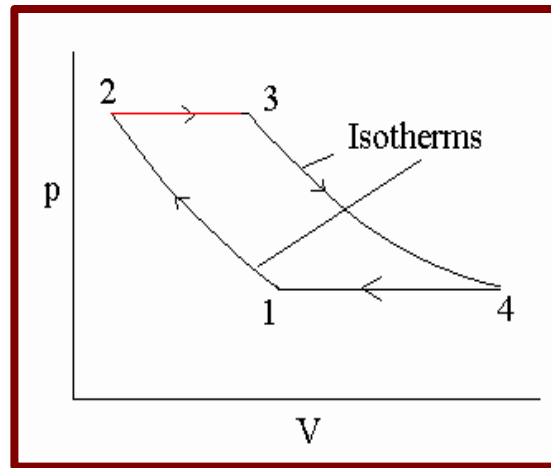
A reversible cycle with clockwise processes produces work with a given heat input. The same while operating with counter clockwise processes will reject the same heat with the same work as input.

Other reversible cycles:

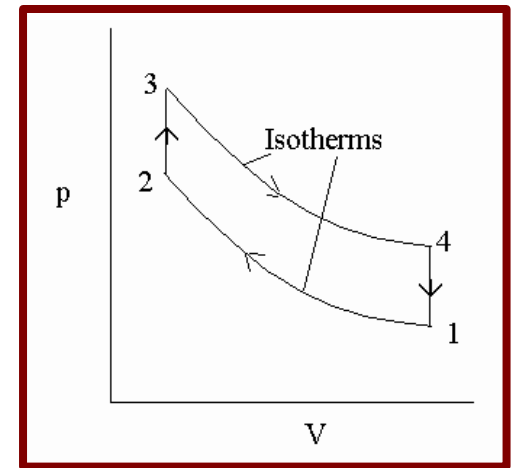
Diesel cycle



Ericsson cycle



Stirling cycle



Clausius Statement of II Law of Thermodynamics

It is impossible to construct a device which **operates in a cycle** and produces no effect other than the transfer of heat from a cooler body to a hotter body.

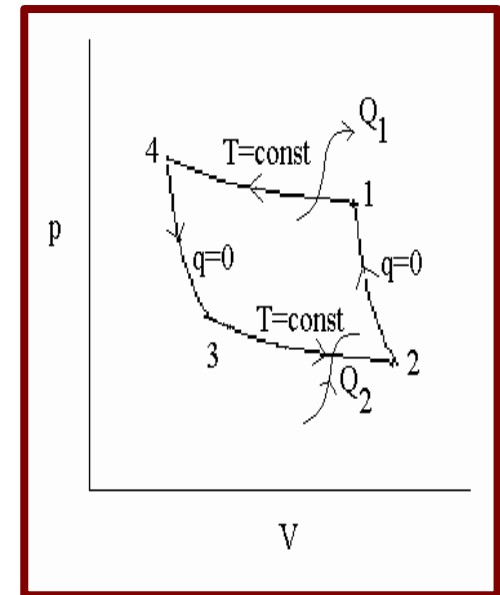
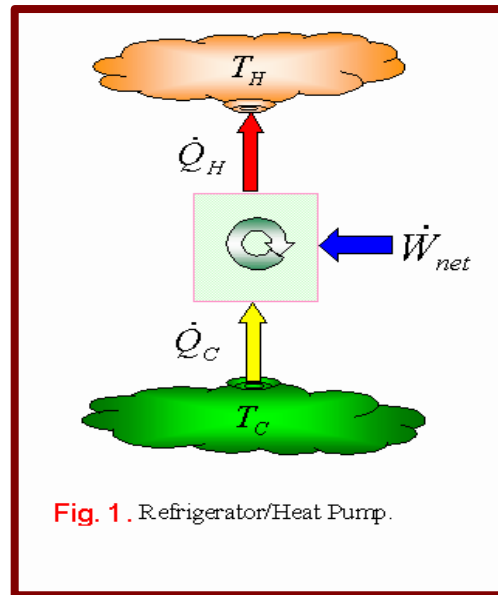
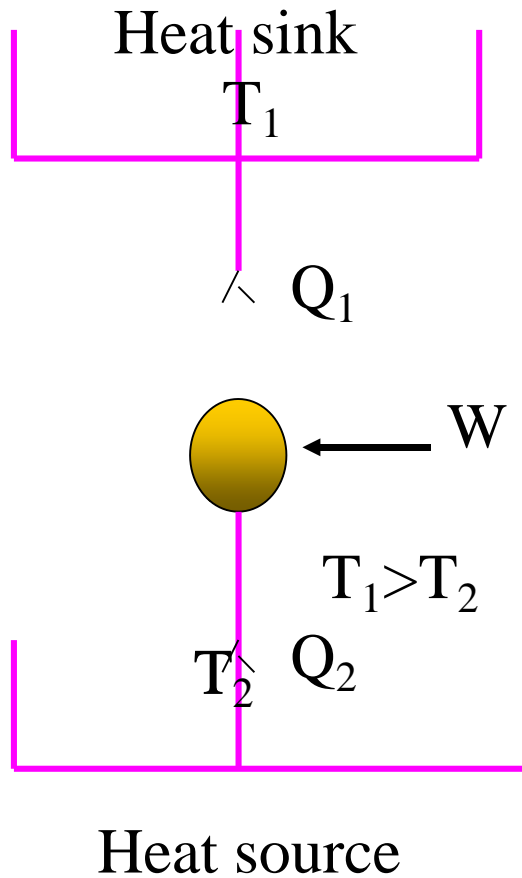
~~No~~ Yes, you can transfer heat from a cooler body to a hotter body by expending some *energy*.

Clausius Statement (contd...)

$\frac{3}{4}$ *Note : It is not obligatory to expend work, even thermal energy can achieve it.*

$\frac{3}{4}$ Just as there is **maximum +ve work** output you can derive **out of a heat engine**, there is a **minimum work** you have to **supply (-ve) to a device** achieve transfer of thermal energy from a cooler to a hotter body.

Carnot Cycle for a Refrigerator/heat Pump



$$T_H = T_1$$

$$T_C = T_2$$

Heat pump

A device which transfers heat from a cooler to a warmer body (by receiving energy) is called a heat pump. A refrigerator is a special case of heat pump.

Just as efficiency was defined for a heat engine, for a heat pump the coefficient of performance (COP) is a measure of how well it is doing the job.

Heat Pump (contd...)

TM A heat pump

- Invoke the definition: what we have achieved , what we spent for it
- $\text{COP}_{\text{HP}} = \text{heat given out} / \text{work done} = Q_1 / W$
- **Note :** The entity of interest is how much heat could be realised. Work is only a penalty.

Heat Pump (contd...)

Reverse cycle air conditioners used for winter heating do the above. Heat from the ambient is taken out on a cold day and put into the room.

The heat rejected at the sink is of interest in a heat pump , ie., Q_1 .

In a refrigerator the entity of interest is Q_2 .

In this case $\text{COP}_R = Q_2/W$

NOTE: η , COP_{HP} , COP_R are all positive numbers $\eta < 1$ but COPs can be $>$ or < 1

Heat Pump (contd...)

Relation between η and COP_{HP}

It is not difficult to see that $\eta \text{ COP}_{\text{HP}} = 1$

Apply I law to Carnot cycle as a heat pump/refrigerator:

$$-Q_1 + Q_2 = -W \quad \text{or} \quad Q_1 = Q_2 + W$$

Divide both sides with W

$$Q_1 / W = Q_2 / W + 1$$

or

$$\text{COP}_{\text{HP}} = \text{COP}_{\text{R}} + 1$$

The highest COP_{HP} obtainable therefore will be $T_1 / (T_1 - T_2)$

and highest COP_{R} obtainable therefore will be $T_2 / (T_1 - T_2)$

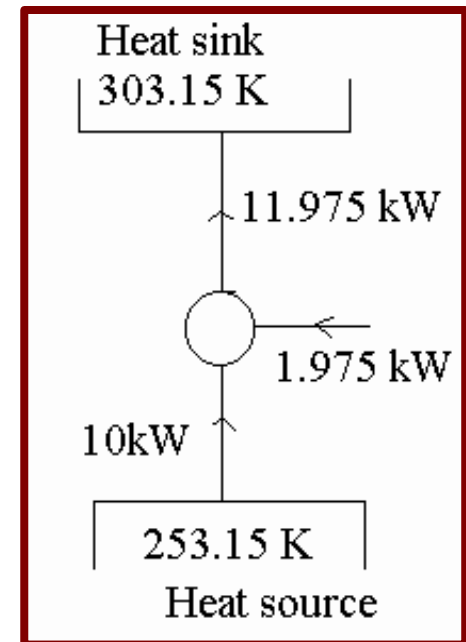
Examples

Eg: If 10 kw of heat is to be removed from a cold store at -20°C and rejected to ambient at 30°C.

$$\text{COP}_R = 253.15 / (303.15 - 253.15) = 5.063$$

$$W = Q_2 / \text{COP}_R ; Q_2 = 10 \text{ kW}$$

$$\text{Therefore } W = 10 / 5.063 = 1.975 \text{ kW}$$



Examples (contd...)

Another example: Let us say that the outside temperature on a hot summer day is 40°C. We want a comfortable 20°C inside the room. If we were to put a 2 Ton (R) air conditioner, what will be its power consumption?

Answer: 1 Ton (R) = 3.5 kw. Therefore $Q_2=7$ kW

$COP_R = 293.15/(313.15-293.15) = 14.66$ ie., $W=7/14.66 = 0.47$ kW

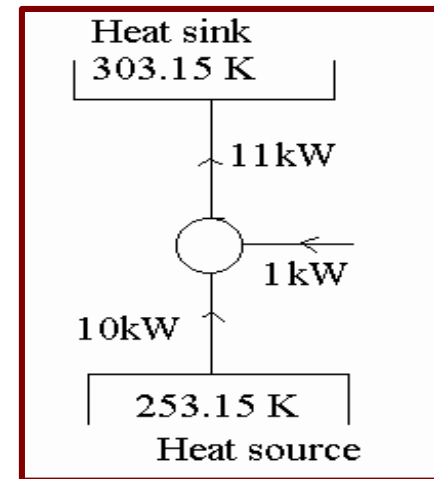
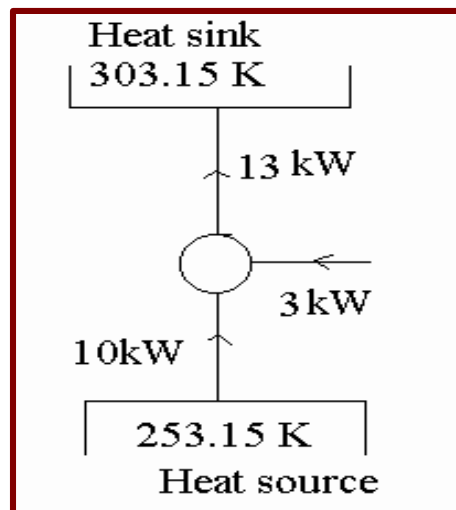
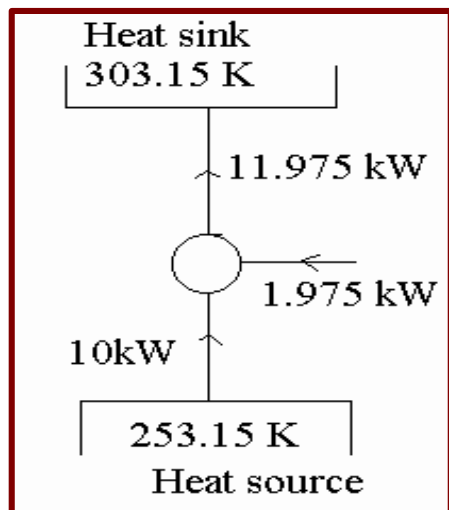
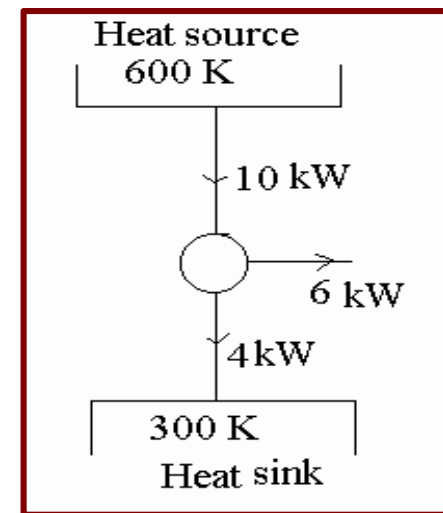
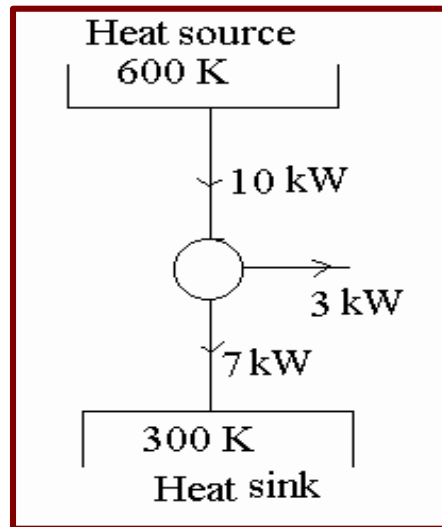
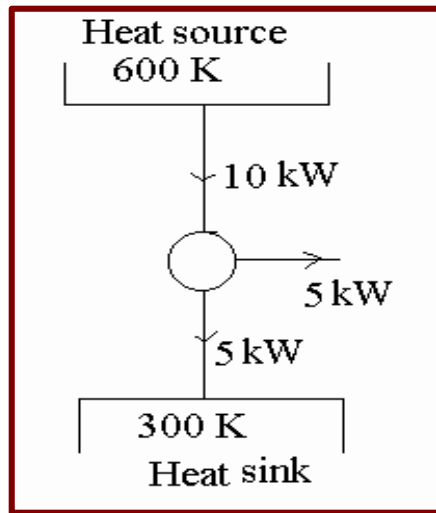
Actually a 2 Ton air-conditioner consumes nearly 2.8 kW (much more than an ideal cycle!!)

Ideal but possible

Real and possible

Not possible

HEAT ENGINE



HEAT PUMP

This is the best that can happen

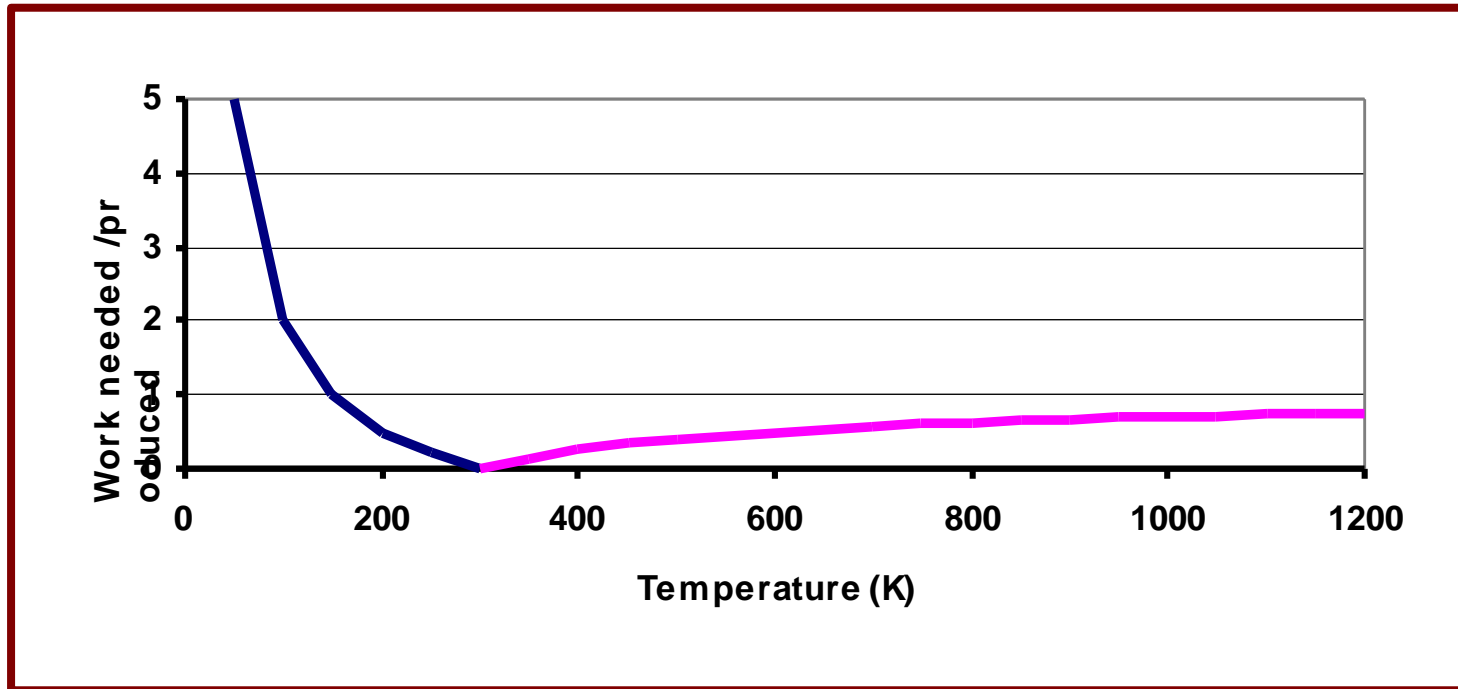
This is what happens in reality

You derive work > what is thermodynamic maximum nor can you expend work < what is thermodynamic minimum

Examples (contd...)

Suppose the ambient is at 300 K. We have heat sources available at temperatures greater than this say 400, 500, 600.....K. How much work can you extract per kW of heat ? Similarly, let us say we have to remove 1 kW of heat from temperatures 250, 200, 150 K. How much work should we put in?

Examples (contd...)



Some Interesting Deductions

$\frac{3}{4}$ Firstly, there isn't a meaningful temperature of the source from which we can get the full conversion of heat to work. Only at ∞ temp. one can dream of getting the full 1 kW work output.

Some Interesting Deductions

TMSecondly, more interestingly, there isn't enough work available to produce 0 K. In other words, 0 K is unattainable. This is precisely the III LAW.

TMBecause, we don't know what 0 K looks like, we haven't got a starting point for the temperature scale!! That is why all temperature scales are at best empirical.

Summation of 3 Laws

You can't get something for nothing

To get work output you must give some thermal energy

You can't get something for very little

To get some work output there is a minimum amount of thermal energy that needs to be given

You can't get every thing

However much work you are willing to give 0 K can't be reached.

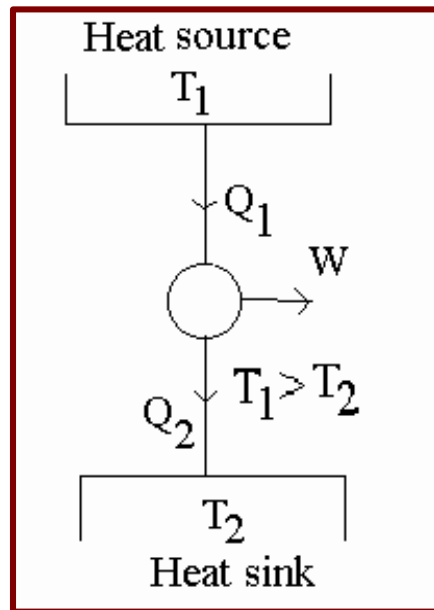
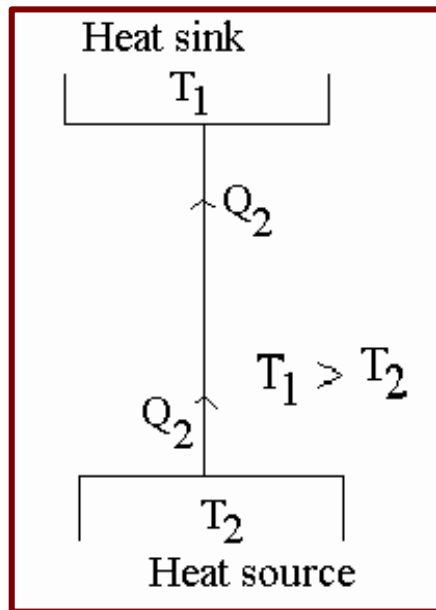
Violation of all 3 laws: try to get everything for nothing

Equivalence of Kelvin-Planck and Clausius statements

II Law basically a negative statement (*like most laws in society*). The two statements look distinct. We shall prove that violation of one makes the other statement violation too.

Let us suspect the Clausius statement-it *may be* possible to transfer heat from a body at colder to a body at hotter temperature without supply of work

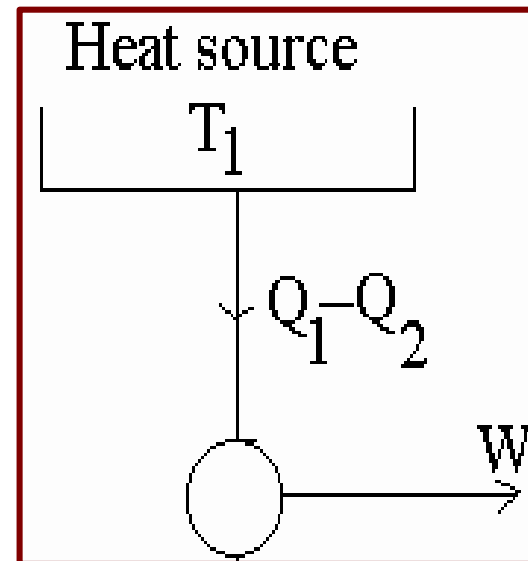
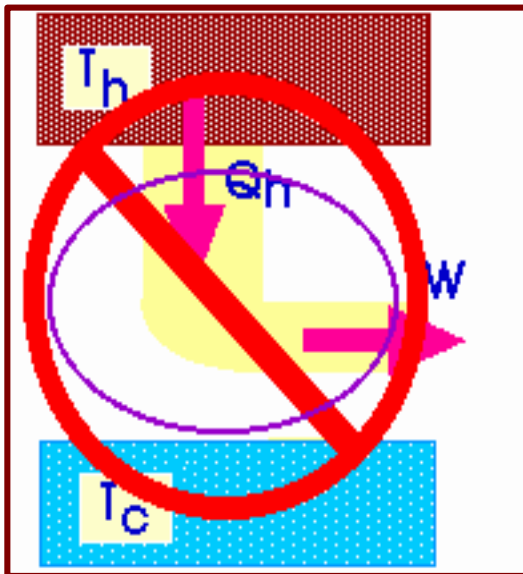
Equivalence of Kelvin-Planck and Clausius statements



Let us have a heat engine operating between T_1 as source and T_2 as a sink. Let this heat engine reject exactly the same Q_2 (as the pseudo-Clausius device) to the reservoir at T_2 . To do this an amount of Q_1 needs to be drawn from the reservoir at T_1 . There will also be a $W = Q_1 - Q_2$

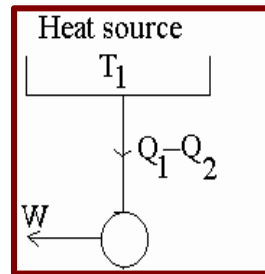
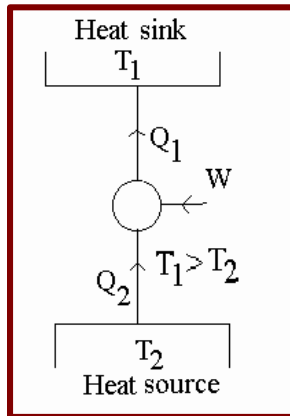
Equivalence of Kelvin-Planck and Clausius statements

Combine the two. The reservoir at T_2 has not undergone any change (Q_2 was taken out and by pseudo-Clausius device and put back by the engine). Reservoir 1 has given out a net $Q_1 - Q_2$. We got work output of W . $Q_1 - Q_2$ is converted to W with no net heat rejection. This is violation of Kelvin-Planck statement.

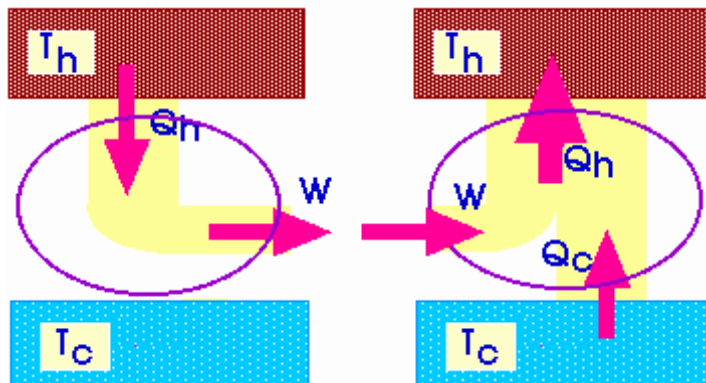


Equivalence of Kelvin-Planck and Clausius statements

- Let us assume that Clausius statement is true and suspect Kelvin-Planck statement



May be possible?



Pseudo Kelvin Planck engine requires only $Q_1 - Q_2$ as the heat interaction to give out W (because it does not reject any heat) which drives the Clausius heat pump

Combining the two yields:

The reservoir at T_1 receives Q_1 but gives out $Q_1 - Q_2$ implying a net delivery of Q_2 to it.

Q_2 has been transferred from T_2 to T_1 without the supply of any work!!

A violation of Clausius statement

Equivalence of Kelvin-Planck and Clausius statements

Moral: If an engine/refrigerator violates one version of II Law,

it violates the other one too.

All reversible engine operating between the same two fixed temperatures will have the same η and COPs.

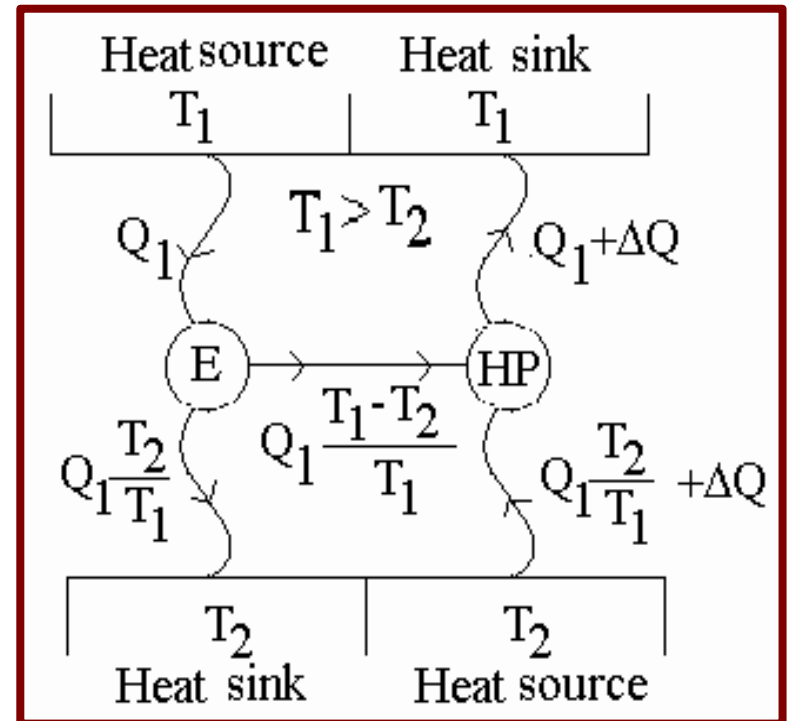
If there exists a reversible engine/ or a refrigerator which can do better than that, it will violate the Clausius statement.

Equivalence of Kelvin-Planck and Clausius statements

Let us presume that the HP is super efficient!!

For the same work given out by the engine E, it can pick up an extra ΔQ from the low temperature source and deliver over to reservoir at T_1 . The net effect is this extra ΔQ has been transferred from T_2 to T_1 with no external work expenditure.

Clearly, *a violation of Clausius statement!!*



Equivalence of Kelvin-Planck and Clausius statements (contd...)

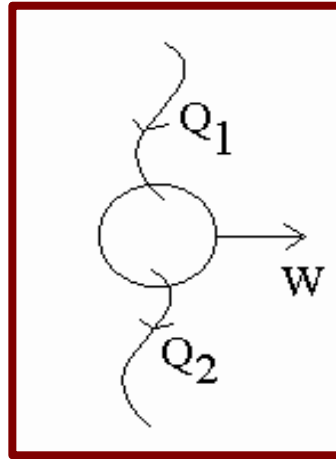
SUM UP

$\frac{3}{4}$ Heat supplied = Q_1 ; Source temperature = T_1 ; Sink temperature = T_2

$\frac{3}{4}$ Maximum possible efficiency = $W/Q_1 = (T_1 - T_2)/T_1$

$\frac{3}{4}$ Work done = $W = Q_1(T_1 - T_2)/T_1$

Equivalence of Kelvin-Planck and Clausius statements (contd...)



Applying I Law

Sum of heat interactions = sum of work interactions

$$Q_1 + Q_2 = W = Q_1 (T_1 - T_2) / T_1$$

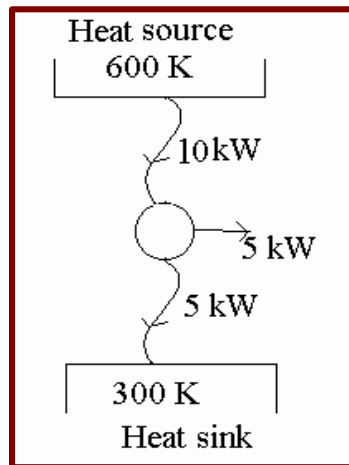
Q_1 is +ve heat interaction; Q_2 is -ve heat interaction

Equivalence of Kelvin-Planck and Clausius statements

$\frac{3}{4}$ Heat rejected = -ve heat interaction = $-Q_2 = (Q_1 - W) =$
 $Q_1 T_2 / T_1$

$\frac{3}{4}$ For a reversible heat engine operating in a cycle $Q_1 / T_1 + Q_2 /$
 $T_2 = 0$

$\frac{3}{4}$ or $S(Q/T) = 0$

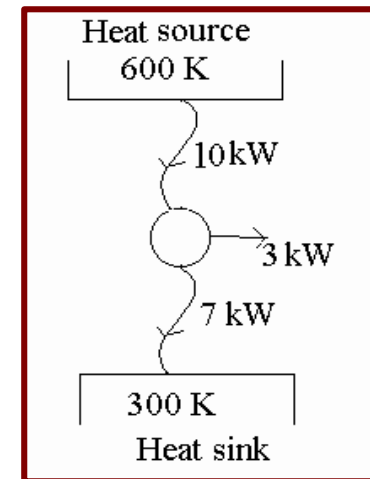


Ideal engine

$$10,000/600 + (-5000/300) = 0$$

Not so efficient engine

$$10,000/600 + (-7000/300) < 0$$



Basics of energy conversation cycles

Heat Engines and Efficiencies

¾ The objective is to build devices which receive heat and produce work (like an aircraft engine or a car engine) or receive work and produce heat (like an air conditioner) in a sustained manner.

¾ All operations need to be cyclic. The cycle comprises of a set of processes during which one of the properties is kept constant (V, p, T etc.)

Heat Engines (contd...)

$\frac{3}{4}$ A minimum of 3 such processes are required to construct a cycle.

$\frac{3}{4}$ All processes need not have work interactions (eg: isochoric)

$\frac{3}{4}$ All processes need not involve heat interactions either (eg: adiabatic process).

Heat Engines (Contd...)

¾A cycle will consist of processes: involving some positive work interactions and some negative.

¾If sum of +ve interactions is $>$ -ve interactions the cycle will produce work

¾If it is the other way, it will need work to operate.

¾On the same lines some processes may have +ve and some -ve heat interactions.

Heat Engines (Contd...)

¾ Commonsense tells us that to return to the same point after going round we need at one path of opposite direction.

¾ I law does not forbid all heat interactions being +ve nor all work interactions being -ve.

¾ But, we know that you can't construct a cycle with all +ve or

¾ All -ve Q's nor with all +ve or all -ve W's

¾ Any cycle you can construct will have some processes with

¾ Q +ve some with -ve.

Heat Engines (Contd...)

¾ Let $Q_1, Q_3, Q_5 \dots$ be +ve heat interactions (Heat supplied)

¾ $Q_2, Q_4, Q_6 \dots$ be -ve heat interactions (heat rejected)

¾ From the first law we have

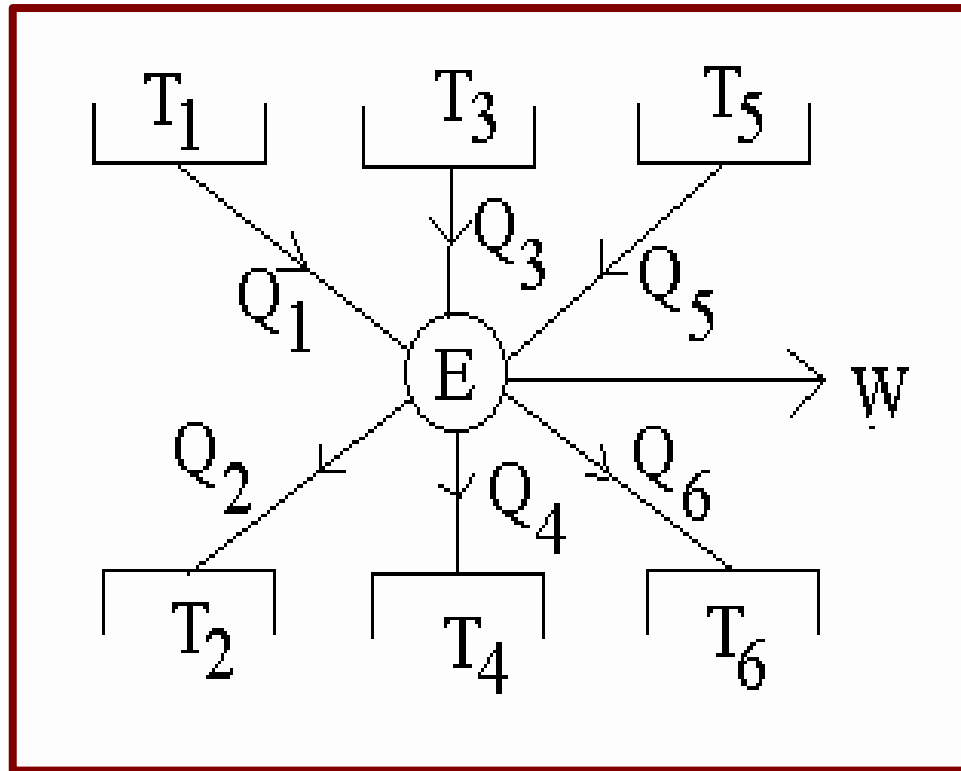
¾ $Q_1 + Q_3 + Q_5 \dots - Q_2 - Q_4 - Q_6 \dots = \text{Net work delivered } (W_{\text{net}})$

¾ $\Sigma Q_{+\text{ve}} - \Sigma Q_{-\text{ve}} = W_{\text{net}}$

¾ The efficiency of the cycle is defined as $\eta = W_{\text{net}} / \Sigma Q_{+\text{ve}}$

¾ Philosophy \rightarrow What we have achieved \div what we have spent to achieve it

Heat Engines (Contd...)

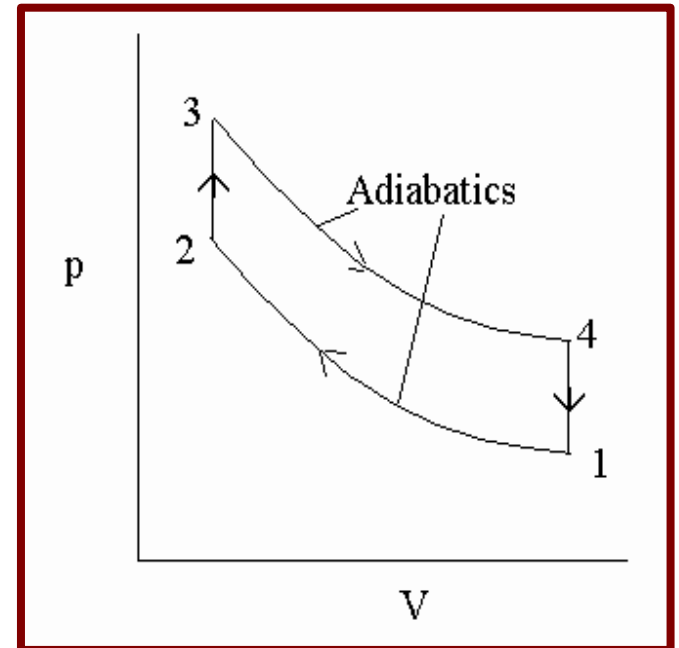


Otto Cycle

Consider the **OTTO Cycle** (on which your car engine works)

It consists of two isochores and two adiabatics

- There is no heat interaction during 1-2 and 3-4
- Heat is added during constant volume heating (2-3) $Q_{2-3} = c_v (T_3 - T_2)$
- Heat is rejected during constant volume cooling (4-1) $Q_{4-1} = c_v (T_1 - T_4)$
- Which will be negative because $T_4 > T_1$



Otto Cycle (Contd...)

¾ Work done = $c_v (T_3 - T_2) + c_v (T_1 - T_4)$

¾ The efficiency = $[c_v(T_3 - T_2) + c_v(T_1 - T_4)] / [c_v(T_3 - T_2)]$

$$= [(T_3 - T_2) + (T_1 - T_4)] / [(T_3 - T_2)]$$

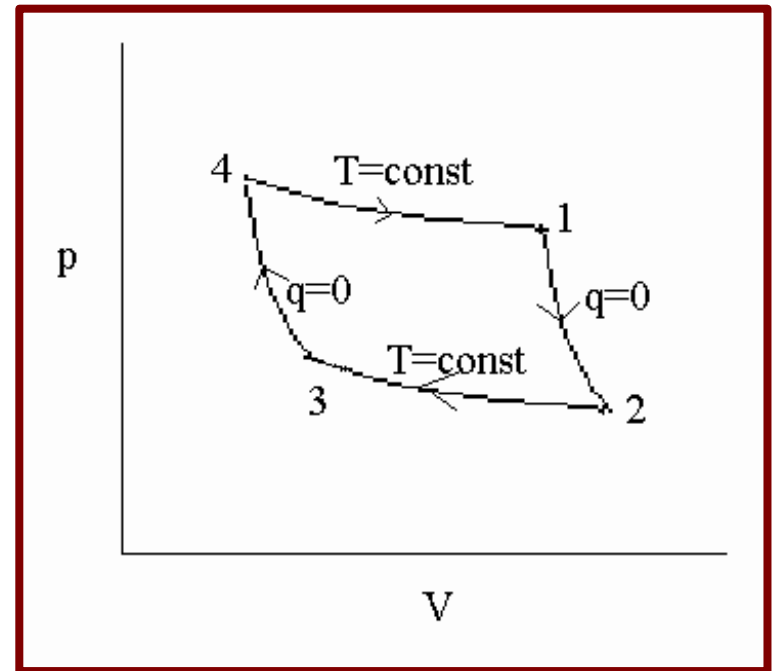
$$= 1 - [(T_4 - T_1) / (T_3 - T_2)]$$

Carnot Cycle

Consider a **Carnot cycle** - against which all other cycles are compared

It consists of two isotherms and two adiabatics

- Process 4-1 is heat addition because $v_4 < v_1$
- Process 2-3 is heat rejection because $v_3 < v_2$



Carnot Cycle (contd..)

Process	Work	Heat
1-2	$(p_1v_1 - p_2v_2)/(g-1)$	0
2-3	$p_2v_2 \ln (v_3/v_2)$	$p_2v_2 \ln (v_3/v_2)$
3-4	$(p_3v_3 - p_4v_4)/(g-1)$	0
4-1	$p_4v_4 \ln (v_1/v_4)$	$p_4v_4 \ln (v_1/v_4)$
Sum	$(p_1v_1 - p_2v_2 + p_3v_3 - p_4v_4)/(g-1)$	
	$+ RT_2 \ln (v_3/v_2)$	$RT_2 \ln (v_3/v_2)$
	$+ RT_1 \ln (v_1/v_4)$	$+ RT_1 \ln (v_1/v_4)$

But, $p_1v_1 = p_4v_4$ and $p_2v_2 = p_3v_3$

Therefore the first term will be 0

!!We reconfirm that I law works!!

Carnot Cycle (contd..)

We will show that $(v_2/v_3) = (v_1/v_4)$

1 and 2 lie on an adiabetic

so do 3 and 4

$$p_1 v_1^\gamma = p_2 v_2^\gamma$$

$$p_4 v_4^\gamma = p_3 v_3^\gamma$$

Divide one by the other
 $/p_3 v_3^\gamma$ (A)

$$(p_1 v_1^\gamma / p_4 v_4^\gamma) = (p_2 v_2^\gamma / p_3 v_3^\gamma)$$

$$(p_1/p_4) (v_1^\gamma / v_4^\gamma) = (p_2/p_3) (v_2^\gamma / v_3^\gamma)$$

But $(p_1/p_4) = (v_4/v_1)$ because 1 and 4 are on the same isotherm

Similarly $(p_2/p_3) = (v_3/v_2)$ because 2 and 3 are on the same isotherm

Carnot Cycle (contd..)

Therefore A becomes $(v_1 / v_4)^{\gamma-1} = (v_2/v_3)^{\gamma-1}$
which means $(v_2/v_3) = (v_1/v_4)$

$$\begin{aligned}\text{Work done in Carnot cycle} &= RT_1 \ln (v_1/v_4) + RT_2 \ln (v_3/v_2) \\ &= RT_1 \ln (v_1/v_4) - RT_2 \ln (v_2/v_3) \\ &= R \ln (v_1/v_4) (T_1 - T_2)\end{aligned}$$

$$\text{Heat supplied} = R \ln (v_1/v_4) T_1$$

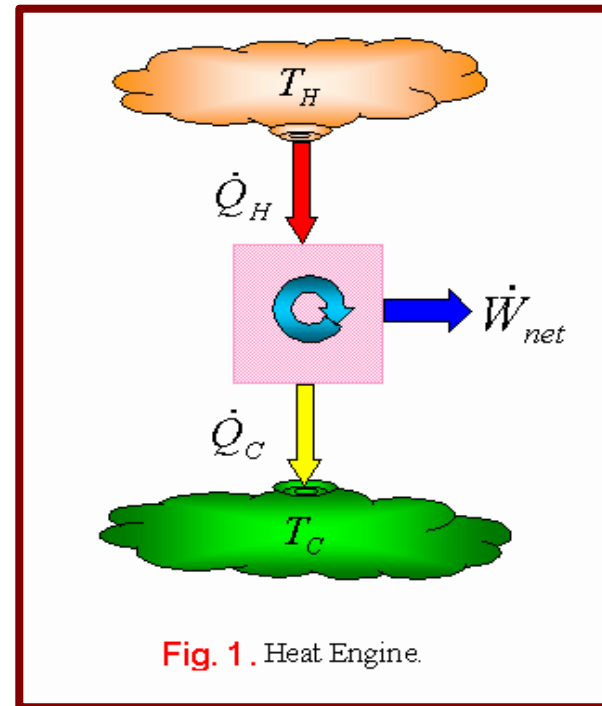
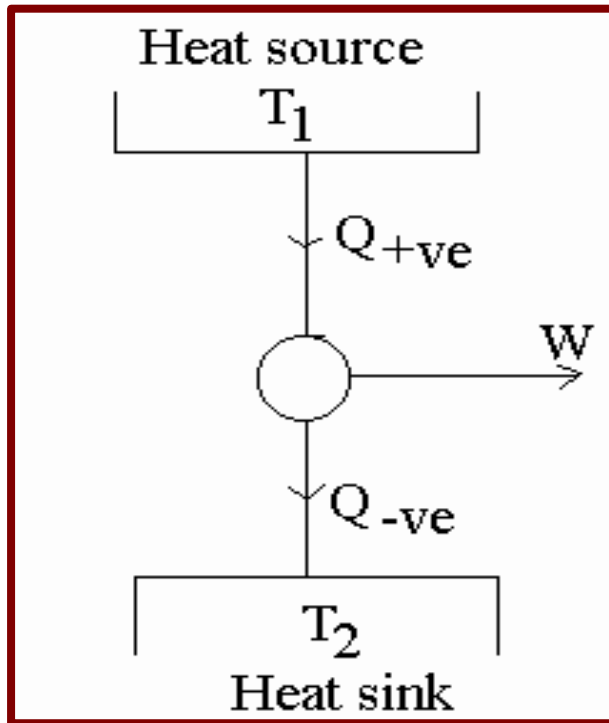
$$\text{The efficiency} = (T_1 - T_2)/T_1$$

In all the cycles it also follows that Work done = Heat supplied
- heat rejected

Carnot Cycle (contd..)

Carnot engine has one Q +ve process and one Q -ve process. This engine has a single heat source at T_1 and a single sink at T_2 .

If Q +ve $>$ Q -ve; W will be +ve It is a heat engine



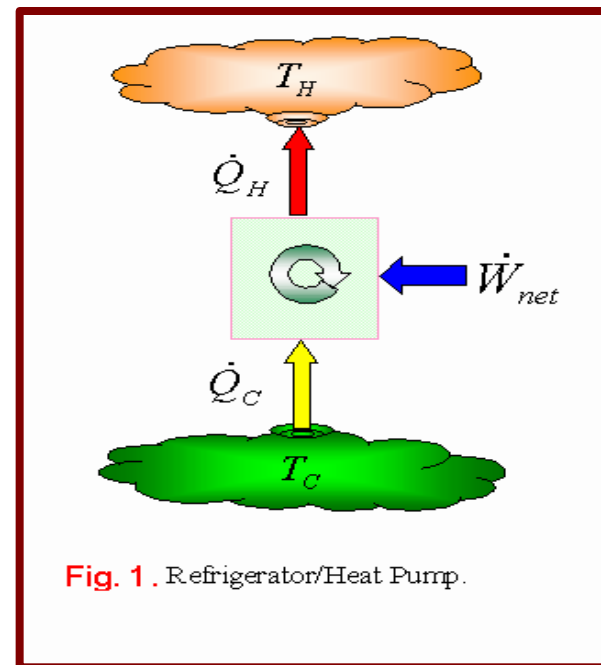
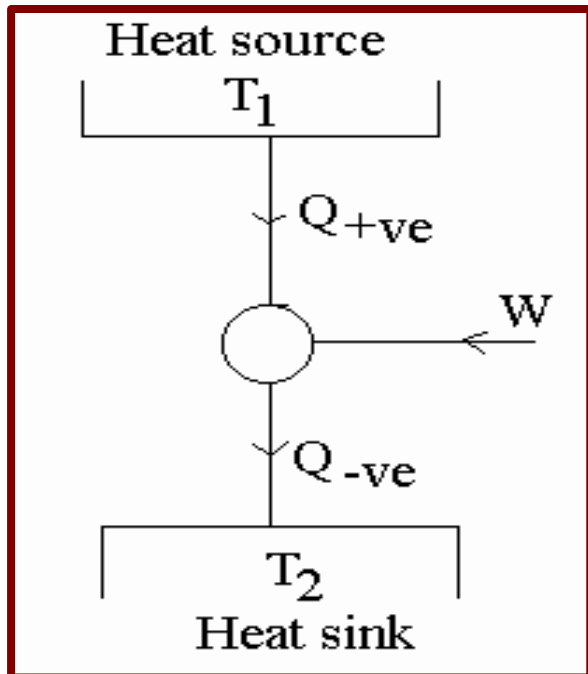
Carnot Cycle (contd..)

It will turn out that Carnot efficiency of $(T_1 - T_2)/T_1$ is the best we can get for any cycle operating between two fixed temperatures.

Carnot Cycle (contd..)

$Q_{+ve} < Q_{-ve}$ W will be -ve It is not a heat engine

Efficiency is defined only for a work producing heat engine
not a work consuming cycle



Carnot Cycle (contd..)

Note: We can't draw such a diagram for an Otto cycle because there is no single temperature at which heat interactions occur

Pure substances and
Steam tables and ideal
and real gases

Properties Of Gases

¾ In thermodynamics we distinguish between

a) perfect gases

b) Ideal gases

c) real gases

¾ The equation $pV/T = \text{constant}$ was derived assuming that

Molecules of a gas are point masses

¾ There are no attractive nor repulsive forces between the molecules

¾ Perfect gas is one which obeys the above equation.

Perfect Gas(contd...)

¾ Various forms of writing perfect gas equation of state

¾ $pV = mR_u T / M$ (p in Pa; V in m^3 ; m in kg ; T in K; M kg/kmol)

¾ $pv = RT$

¾ $p = rRT$

¾ $pV = n R_u T$

¾ $\rho = \text{density (kg/ m}^3\text{)}$ $n = \text{number of moles}$

¾ $R_u = \text{Universal Gas Constant} = 8314 \text{ J/kmol K}$

Perfect Gas (Contd...)

$\frac{3}{4}$ R = Characteristic gas constant = R_u/M
J/kg K

$\frac{3}{4}$ N_A = Avogadro's constant = 6.022×10^{26} k
mol⁻¹

$\frac{3}{4}$ k_B = Boltzmann constant = 1.380×10^{-23} J/K

$\frac{3}{4}$ $R_u = N_A k_B$

Deductions

For a perfect gas a constant pv process is also a constant temperature process; ie., it is an isothermal process.

Eg 1: *Calculate the density of nitrogen at standard atmospheric condition.*

$$p=1.013 \times 10^5 \text{ Pa}, T=288.15 \text{ K}; R=8314/28 \text{ J/kg K}$$

$$\begin{aligned} \rho &= p/RT = 1.013 \times 10^5 / [288.15 \times (8314/28)] \\ &= 1.184 \text{ kg/ m}^3 \end{aligned}$$

Perfect Gas (contd...)

Eg 2: What is the volume occupied by 1 mole of nitrogen at normal atmospheric condition?

1 mole of nitrogen has $m=0.028$ kg. $p=1.013 \times 10^5$ Pa, $T=273.15$ K, $R=8314/28$ J/kg K

$$V = mRT/p = 0.028 \times (8314/28) \times 273.15 / 1.013 \times 10^5 = 0.0224183 \text{ m}^3$$

$$\text{Alternately } V = nR_u t/p = 1 \times 8314 \times 273.15 / 1.013 \times 10^5 = 0.0224183 \text{ m}^3$$

This is the familiar rule that a mole of a gas at NTP will occupy about 22.4 litres.

Note: NTP refers to 273.15 K and STP to 288.15 K; $P=1.013 \times 10^5$ pa

Perfect Gas (contd...)

When can a gas be treated as a perfect gas?

A) At low pressures and temperatures far from critical point

B) At low densities

$\frac{3}{4}$ A perfect gas has constant specific heats.

$\frac{3}{4}$ An **ideal gas** is one which obeys the above equation, but whose specific heats are functions of temperature alone.

Real Gas

A real gas obviously does not obey the perfect gas equation because, the molecules have a finite size (however small it may be) and they do exert forces among each other. One of the earliest equations derived to describe the real gases is the van der Waal's equation

$$(P + a/v^2)(v - b) = RT;$$

Constant a takes care of attractive forces; B the finite volume of the molecule.

Real Gas (contd...)

¾ There are numerous equations of state.

¾ The world standard to day is the Helmholtz free energy based equation of state.

¾ For a real gas $pv \neq RT$;

¾ The quantity $pv/RT = z$ and is called the “COMPRESSIBILITY”.

¾ For a perfect gas always $z=1$.

Definitions

¾ Specific heat at constant volume $c_v = (\partial u / \partial T)_v$

¾ enthalpy $h = u + pv$

¾ Specific heat at constant pressure $c_p = (\partial h / \partial T)_p$

¾ u , h , c_v and c_p are all properties.

¾ Implies partial differentiation.

¾ The subscript denotes whether v or p is kept constant.

Definitions (contd...)

¾ For a perfect gas since c_v and c_p are constants and do not depend on any other property, we can write $c_v = du/dT$ and $c_p = dh/dT$

¾ Since $h = u + pv$ $dh/dT = du/dT + d(pv)/dT$ 1

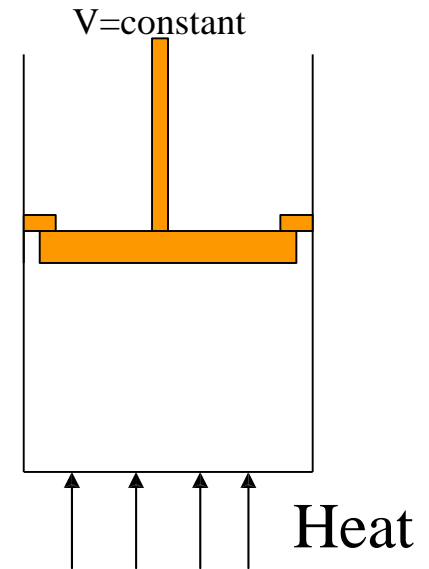
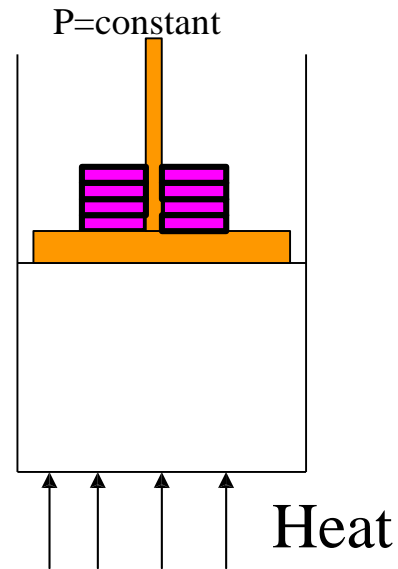
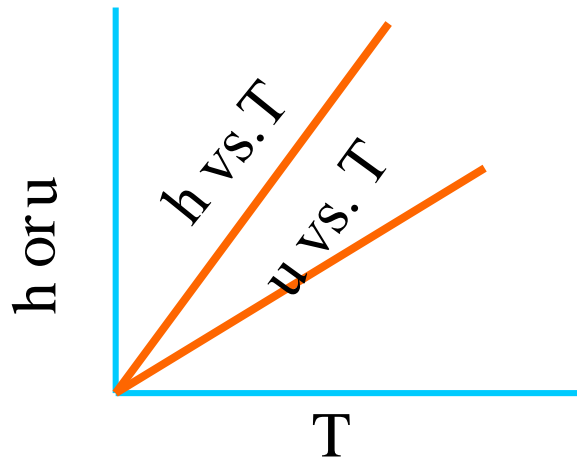
¾ But $pv = RT$ for a perfect gas. Therefore, $d(pv)/dT = d(RT)/dT = R$

¾ Eq. 1 can be rewritten as $c_p = c_v + R$

¾ R is a positive quantity. Therefore, for any perfect gas $c_p > c_v$

¾ Note: **Specific heats and R have the same units J/kg K**

Alternate Definitions From Physics



Alternate Definitions

From Physics (contd...)

$\frac{3}{4}c_p$ = amount of heat to be added to raise the temperature of unit mass of a substance when the pressure is kept constant

$\frac{3}{4}c_v$ = amount of heat to be added to raise the temperature of unit mass of a substance when the volume is kept constant

$\frac{3}{4}$ Physical interpretation of why $c_p > c_v$?

Alternate Definitions

From Physics(contd...)

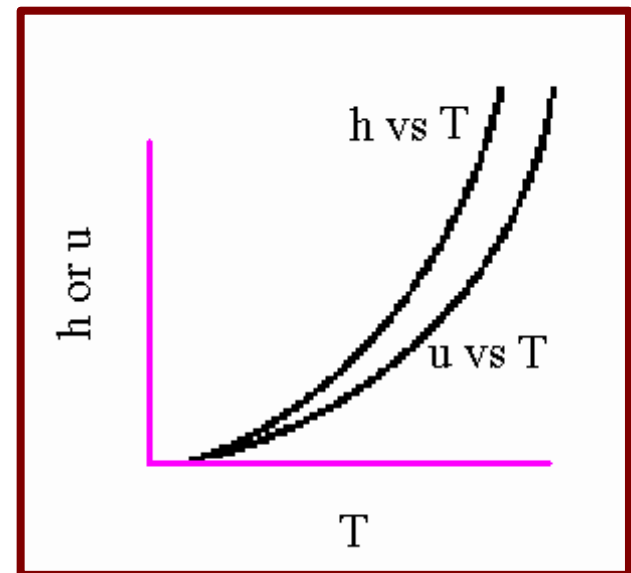
¾ When heat is added at const. p , a part of it goes to raising the piston (and weights) thus doing some work. Therefore, heat to be added to rise system T by 1K must account for this. Consequently, more heat must be added than in $v=\text{const.}$ case (where the piston does not move).

Alternate Definitions From Physics (contd...)

¾ When heat is added at const v the whole amount subscribes to increase in the internal energy.

¾ The ratio c_p/c_v is designated as γ .

¾ c_p and c_v increase with temperature



Alternate Definitions

From Physics (contd...)

Volume Fractions of Components in Sea Level Dry Air
and their ratio of specific heats

		γ			γ
N ₂	0.78084	1.40	O ₂	0.209476	1.40
Ar	9.34x10 ⁻³	1.67	CO ₂	3.14x10 ⁻⁴	1.30
Ne	1.818x10 ⁻⁵	1.67	He	5.24x10 ⁻⁶	1.67
Kr	1.14x10 ⁻⁶	1.67	Xe	8.7x10 ⁻⁸	1.67
CH ₄	2x10 ⁻⁶	1.32	H ₂	5x10 ⁻⁷	1.41

Implications of an Adiabatic Process for a Perfect Gas in a Closed System

¾ The First Law for a closed system going through an adiabatic process is

¾ $-w = du$ or $-pdv = c_v dT$ for a perfect gas

¾ From the relation $c_p - c_v = R$ and $\gamma = c_p / c_v$

¾ $c_v = R / (\gamma - 1)$ $c_p = \gamma R / (\gamma - 1)$

¾ Therefore $-pdv = R dT / (\gamma - 1)$ (A)

¾ From the perfect gas relation $pv = RT$;

Implications (Contd...)

¾ Since During an adiabatic process p, v and T can change simultaneously let dp, dv and dT be the incremental changes.

¾ Now the perfect gas relation will be

$$(p+dp)(v+dv) = R(T+dT)$$

¾ Which on expansion become $pv + vdp + pdv + dp dv = RT + RdT$

Implications (Contd...)

¾Using the condition $pV=RT$ and the fact that product of increments $dp dv$ can be ignored in relation to the other quantities

¾we get

$$vdp + pdv = RdT$$

¾Substitute for RdT in eq. (A)

$$-pdv = [vdp + pdv] / (\gamma - 1)$$

¾Rearrange terms

$$-pdv \{ 1 + 1 / (\gamma - 1) \} = vdp / (\gamma - 1)$$

¾or $-\gamma pdv = vdp$ or $-\gamma dv/v = dp/p$

Implications (Contd...)

¾ We will integrate it to obtain

$$\text{¾ const} - \gamma \ln(v) = \ln(p)$$

$$\text{¾ const} = \ln(p) + \gamma \ln(v) = \ln(p) + \ln(v^\gamma) = \ln(pv^\gamma)$$

$$\text{¾ or} \quad pv^\gamma = \text{another constant (B)}$$

Implications (Contd...)

Note: This is an idealised treatment. A rigorous treatment needs the Second Law of Thermodynamics. Eq (B) holds good when the process is also reversible. The concept of reversibility will be introduced later.

The work done during an adiabatic process between states 1-2 will be

$$W_{1-2} = (p_1 V_1 - p_2 V_2) / (g - 1)$$

Implications (Contd...)

Recapitulate: $pV^\gamma = \text{constant}$

1. Is not an equation of state, but a description of the path of a specific process - adiabatic and reversible
2. Holds only for a perfect gas

Pure Substance

- $\frac{3}{4}$ Pure Substance is one with uniform and invariant chemical composition.
- $\frac{3}{4}$ Eg: Elements and chemical compounds are pure substances. (water, stainless steel)
- $\frac{3}{4}$ Mixtures are not pure substances. (eg: Humid air)

Pure Substance (contd...)

- ¾ Exception!! Air is treated as a pure substance though it is a mixture of gases.
- ¾ In a majority of cases a minimum of two properties are required to define the state of a system. The best choice is an extensive property and an intensive property

Properties Of Substance

¾ Gibbs Phase Rule determines what is expected to define the state of a system

$$\text{¾ } F = C + 2 - P$$

¾ F = Number of degrees of freedom (i.e., no. of properties required)

¾ C = Number of components P = Number of phases

¾ E.g.: Nitrogen gas $C=1$; $P=1$. Therefore, $F=2$

Properties of substance (Contd...)

- ¾ To determine the state of the nitrogen gas in a cylinder two properties are adequate.
- ¾ A closed vessel containing water and steam in equilibrium:
 $P=2, C=1$
- ¾ Therefore, $F=1$. If any one property is specified it is sufficient.
- ¾ A vessel containing water, ice and steam in equilibrium
- ¾ $P=3, C=1$ therefore $F=0$. The triple point is uniquely defined.

Properties of Liquids

The most common liquid is water. It has peculiar properties compared to other liquids.

$\frac{3}{4}$ Solid phase is less dense than the liquid phase (ice floats on water)

$\frac{3}{4}$ Water expands on cooling (a fully closed vessel filled with water will burst if it is cooled below the freezing point).

$\frac{3}{4}$ The largest density of water near atmospheric pressure is at 4°C.

Properties of Liquids (contd...)

¾ The zone between the saturated liquid and the saturated vapour region is called the two phase region - where the liquid and vapour can co-exist in equilibrium.

¾ Dryness fraction: It is the mass fraction of vapour in the mixture.

¾ Normally designated by 'x'.

¾ On the saturated liquid line $x=0$

¾ On the saturated vapour line $x=1$

¾ x can have a value only between 0 and 1

Properties of Liquids (contd...)

¾ Data tables will list properties at the two ends of saturation.

¾ To calculate properties in the two-phase region:

¾ p, T will be the same as for saturated liquid or saturated vapour

$$v = x v_g + (1-x) v_f$$

$$h = x h_g + (1-x) h_f$$

$$u = x u_g + (1-x) u_f$$

Properties of Liquids

(contd...)

¾ One of the important properties is the change in enthalpy of phase transition h_{fg} also called the latent heat of vaporisation or latent heat of boiling. It is equal to $h_g - h_f$.

¾ Similarly u_{fg} -internal energy change due to evaporation and v_{fg} - volume change due to evaporation can be defined (but used seldom).

Properties of Liquids (contd...)

¾The saturation phase depicts some very interesting properties:

¾The following saturation properties depict a maximum:

- | | | | | |
|-----------------|-------------------|-----------------------------------|---------------|-------------------|
| 1. T | 2. ρ_f | 3. $T (\rho_f - \rho_g)$ | 4. $T h_{fg}$ | 5. $T_c(p_c - p)$ |
| 6. $p(T_c - T)$ | 7. $p(v_g - v_f)$ | 8. $T (\rho_c^2 - \rho_f \rho_g)$ | 9. h_g | |

¾The equation relating the pressure and temperature along the saturation is called the vapour pressure curve.

¾Saturated liquid phase can exist only between the triple point and the critical point.

Characteristics of the critical point

1. It is the highest temperature at which the liquid and vapour phases can coexist.
 2. At the critical point h_{fg} , u_{fg} and v_{fg} are zero.
 3. Liquid vapour meniscus will disappear.
 4. Specific heat at constant pressure is infinite.
- ¾A majority of engineering applications (eg: steam based power generation; Refrigeration, gas liquefaction) involve thermodynamic processes close to saturation.

Characteristics of the critical point (contd...)

¾ The simplest form of vapour pressure curve is

¾ $\ln p = A + B/T$ valid only near the triple point. (Called Antoine's equation)

¾ The general form of empirical vapour pressure curve is

¾ $\ln p = \ln p_c + [A_1(1 - T/T_c) + A_2(1 - T/T_c)^{1.5} + A_3(1 - T/T_c)^2 + \dots] / (T/T_c)$ (Called the Wagner's equation)

¾ Definitions: Reduced pressure $p_r = p/p_c$;

¾ Reduced temperature $T_r = T/T_c$

Characteristics of the critical point (contd...)

¾ For saturated phase often its enthalpy is an important property.

¾ Enthalpy-pressure charts are used for refrigeration cycle analysis.

¾ Enthalpy-entropy charts for water are used for steam cycle analysis.

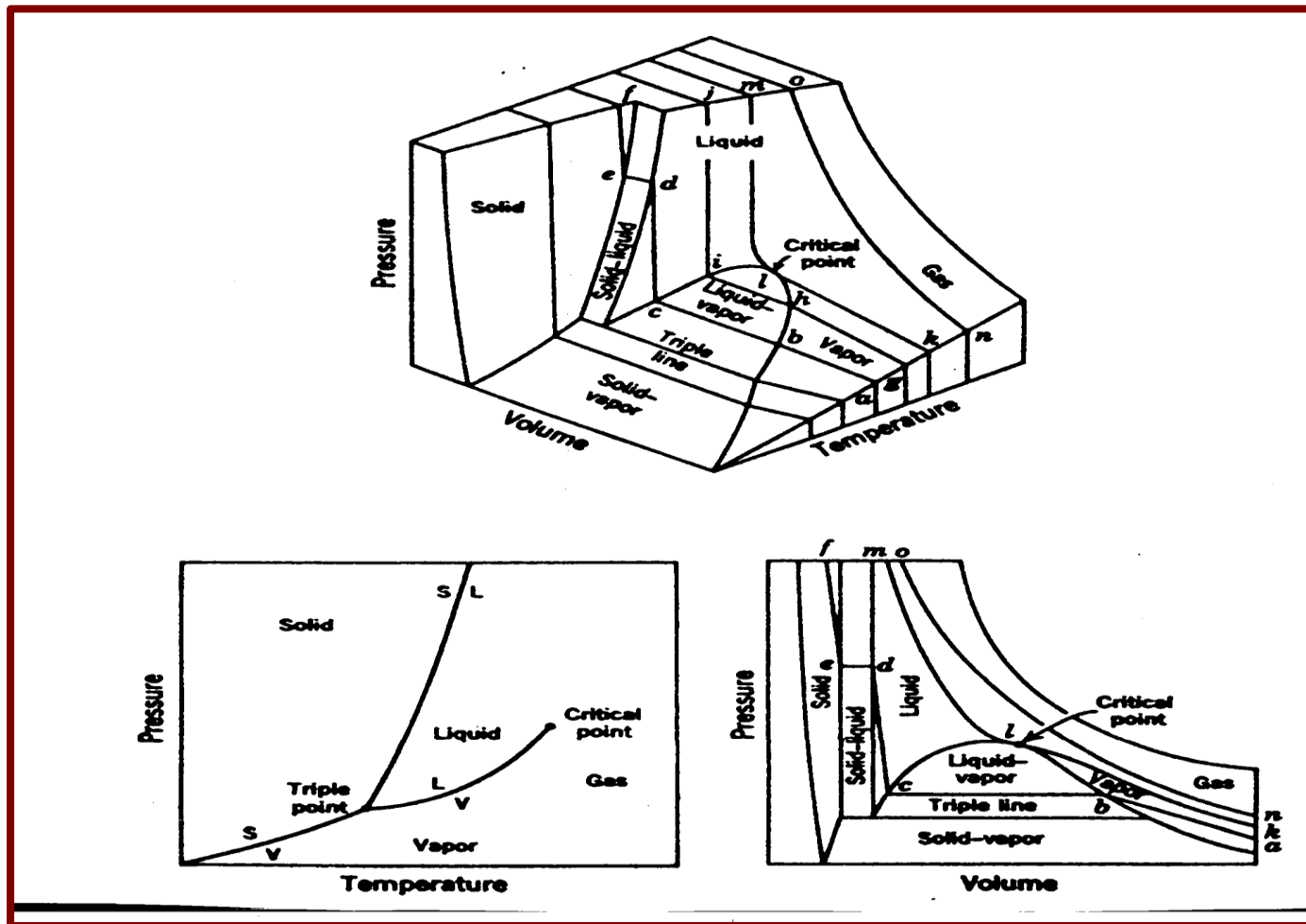
¾ Note: Unlike pressure, volume and temperature which have specified numbers associated with it, in the case of internal energy, enthalpy (and entropy) only changes are required. Consequently, a base (or datum) is defined - as you have seen in the case of water.

Characteristics of the critical point (contd...)

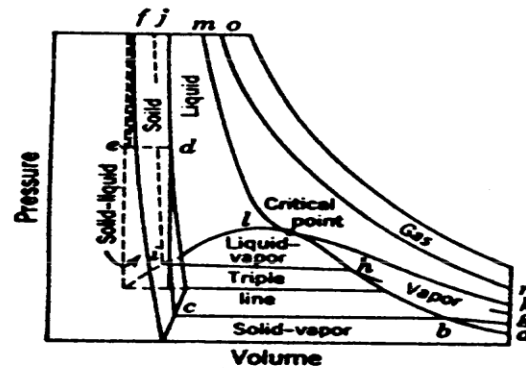
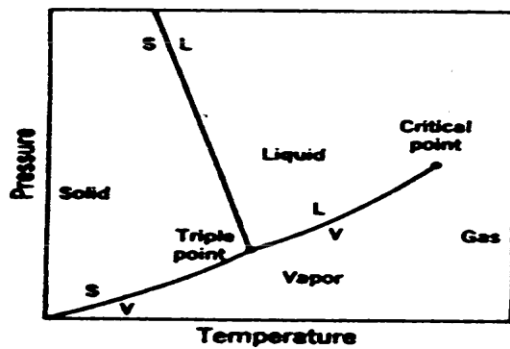
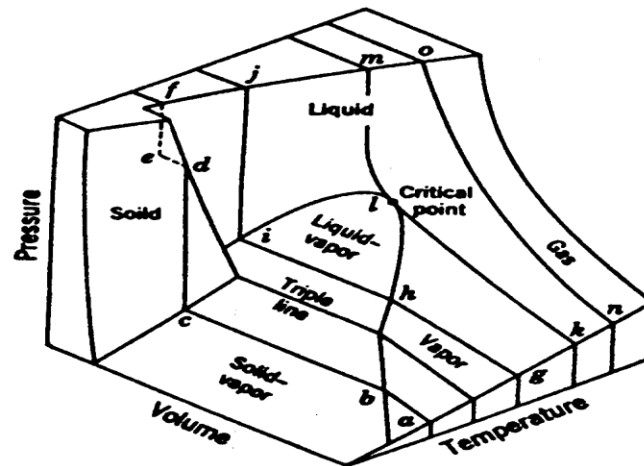
¾For example for NIST steam tables $u=0$ for water at triple point. (You can assign any number you like instead of 0). [Don't be surprised if two different sets of steam tables give different values for internal energy and enthalpy].

¾Since, p and v for water at triple point are known you can calculate h for water at triple point (it will not be zero).

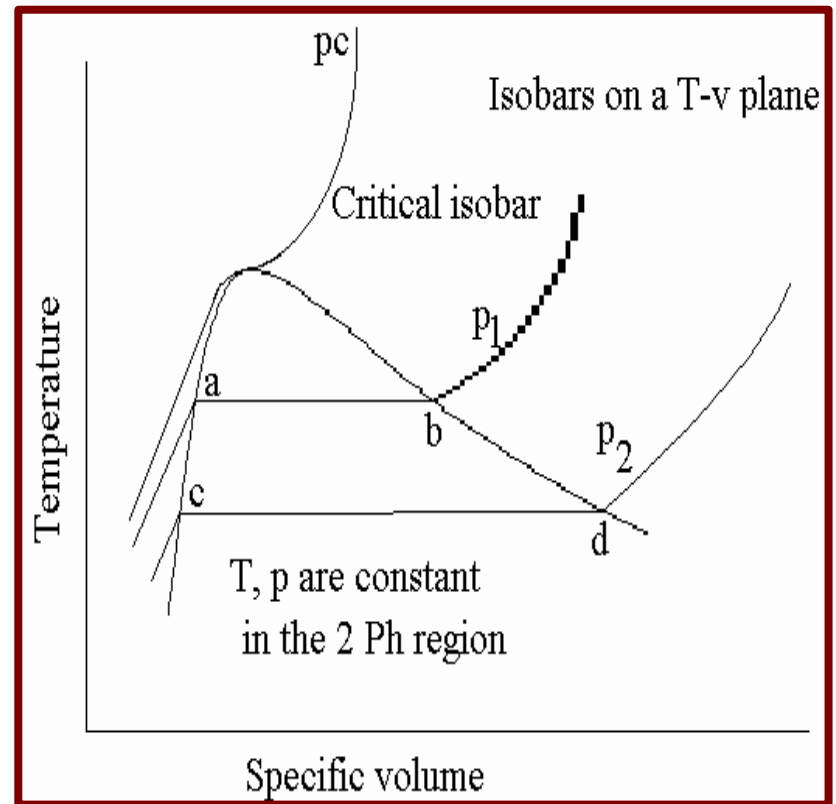
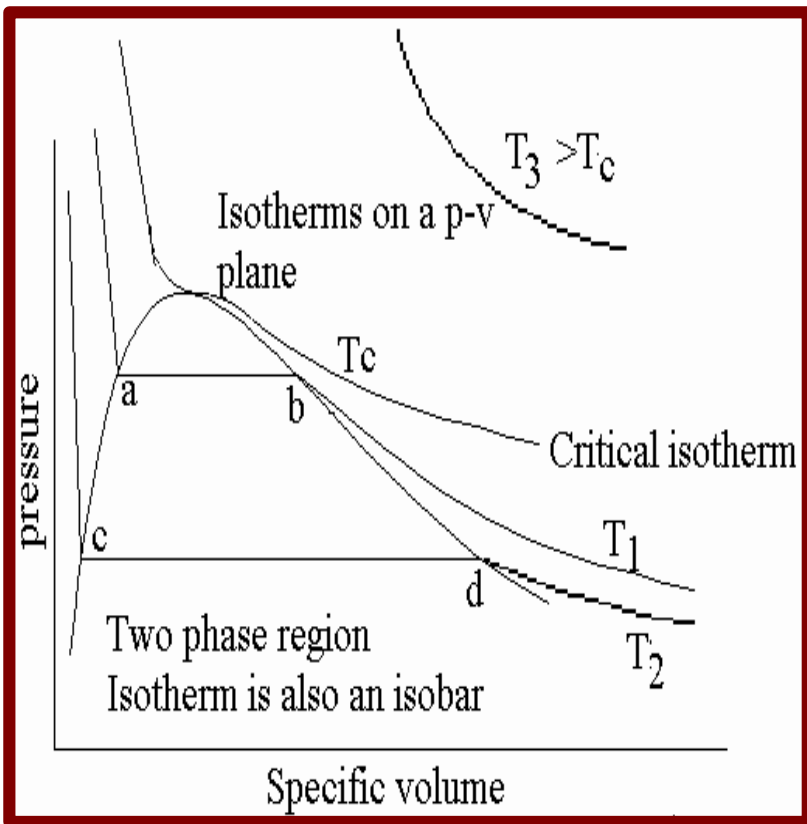
¾If you like you can also specify $h=0$ or 200 or 1000 kJ/kg at the triple point and hence calculate u .



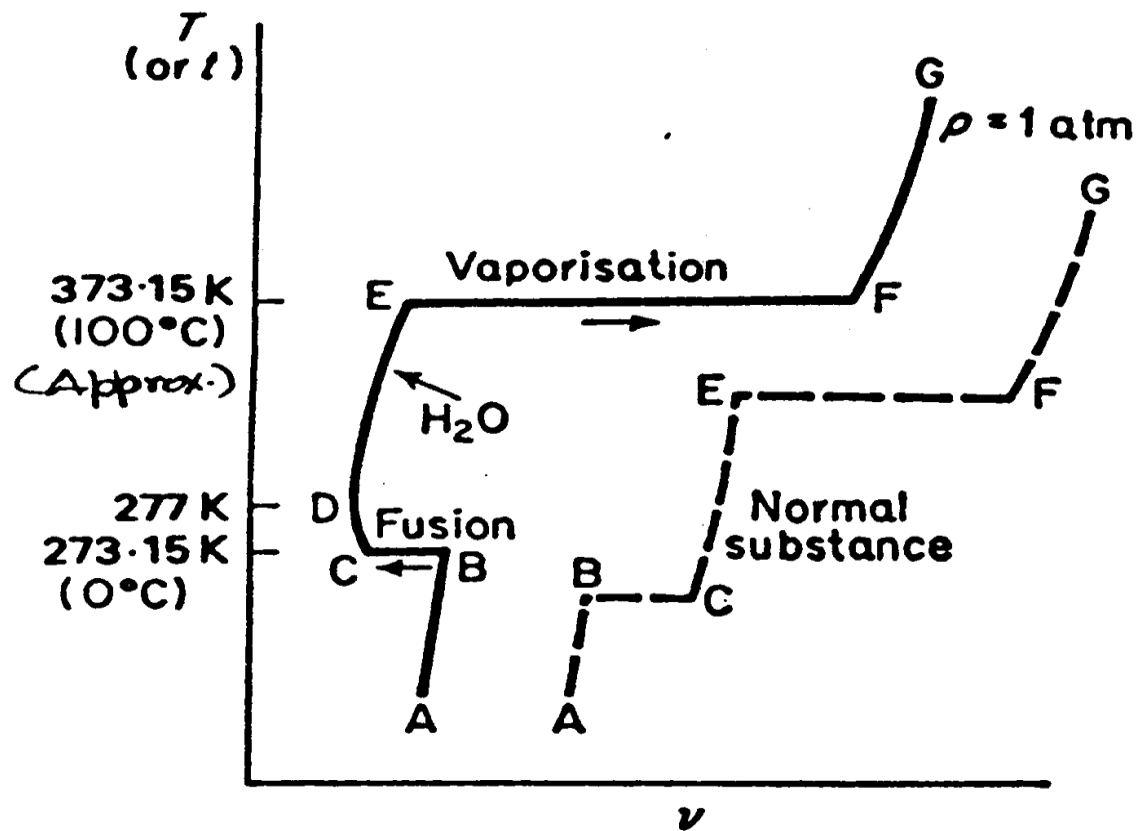
Pressure-volume-temperature surface
for a substance that contracts on freezing

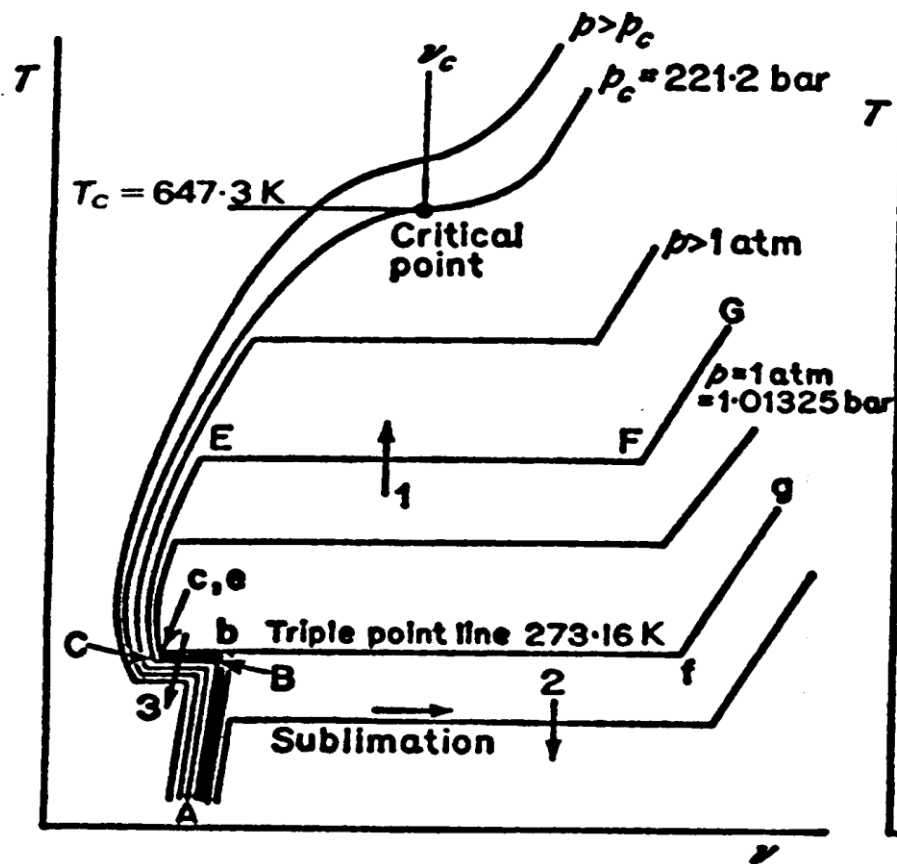


Pressure-volume-temperature surface for a substance that expands on freezing.

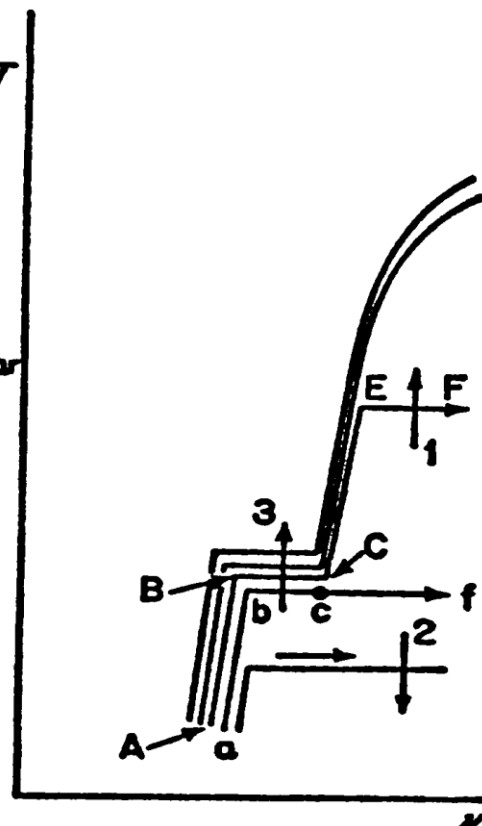


Note that there is a discontinuity at the phase boundaries
(points a,b,c,d etc.)

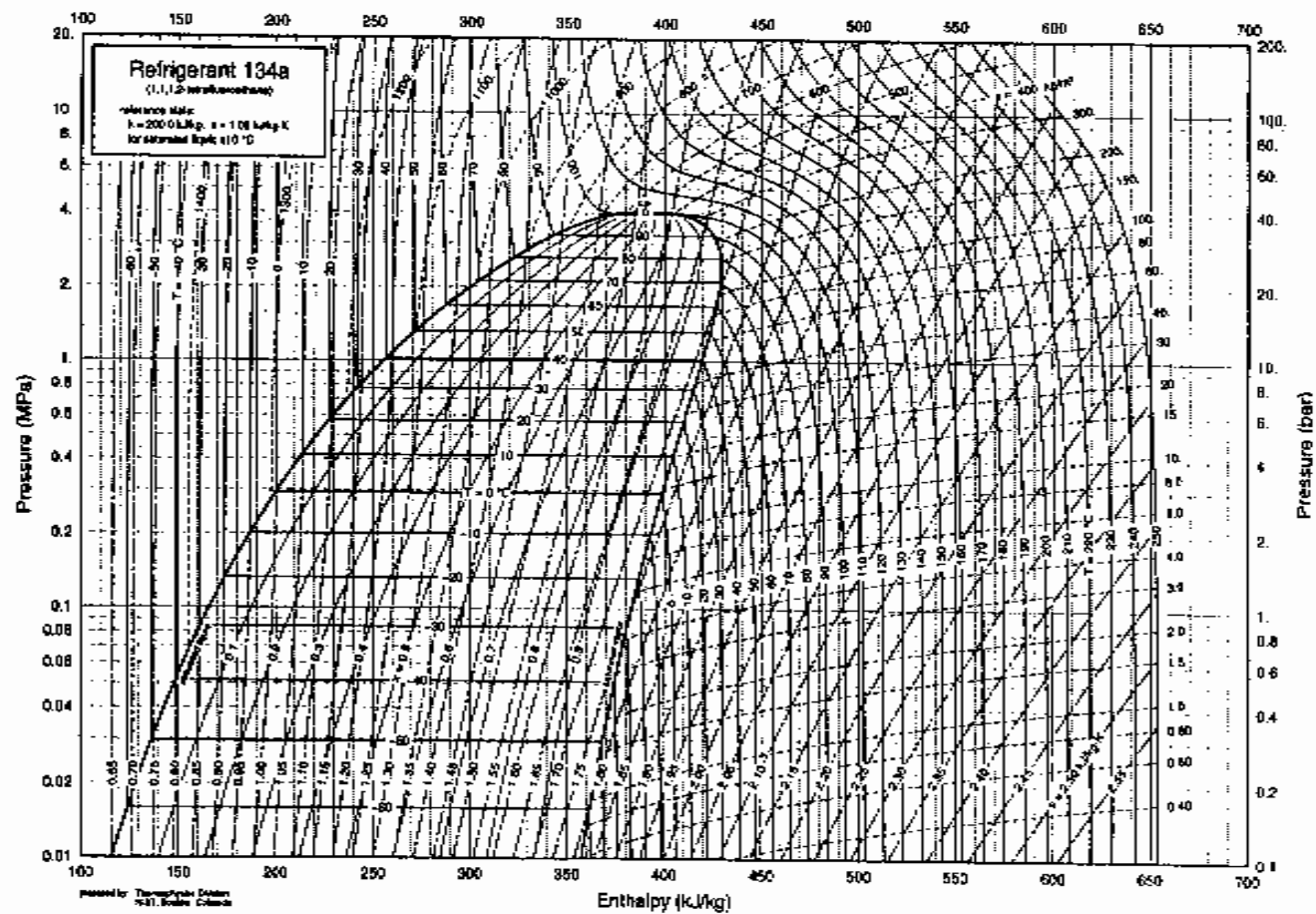




(a) Water



(b) Normal substance



International Association for the Properties of Water and Steam (IAPWS) has provided two formulations to calculate the thermodynamic properties of ordinary water substance,

- i) “The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use” (IAPWS-95) and
- ii) “The IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam” (IAPWS-IF97).