



**COURSE:THERMODYNAMICS**  
**CODE: AMEB04**

**Institute of Aeronautical Engineering**  
**( Autonomous)**  
**Dundigal, Hyderabad – 500 043,**

**Prepared by**  
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# COURSE OBJECTIVES:

**The course should enable the students to:**

- 1. Understand the laws of thermodynamics and determine thermodynamic properties, gas laws.**
- 2. Knowledge of properties during various phases of pure substances, mixtures, usage of steam tables and Mollier chart, psychometric charts**
- 3. Understand the direction law and concept of increase in entropy of universe.**

# COURSE LEARNING OUTCOMES (CLOs):

**After completing this course the student must demonstrate the knowledge and ability to:**

- 1. Understand the concepts of conservation of mass, conservation of energy.**
- 2. Demonstrate knowledge of ability to identify & apply fundamentals to solve problems like system properties, amount of work transfer and heat during various processes.**
- 3. Explore knowledge & ability to design the thermal related components in various fields of energy transfer equipment.**
- 4. Derive the first law of Thermodynamics from the concept of conservation of energy.**

## **COURSE LEARNING OUTCOMES (CLOs):**

- 5. Discuss the nature of steady and unsteady processes under the influence of time.**
- 6. Determine entropy changes in a wide range of processes and determine the reversibility or irreversibility of a process from such calculations based on Carnot Cycle.**
- 7. Develop the second law of thermodynamics from the limitations of first law.**
- 8. Knowledge of the Gibbs and Helmholtz free energies as equilibrium criteria, and the statement of the equilibrium condition for closed and open systems.**

## **COURSE LEARNING OUTCOMES (CLOs):**

- 9. Discuss pressure-temperature, volume-temperature, pressure-volume phase diagrams and the steam tables in the analysis of engineering devices and systems.**
- 10. Understand the inter relationship between thermodynamic functions and an ability to use such relationships to solve practical problems.**
- 11. Understand the equation of state, specific and universal gas constants, throttling and free expansion processes.**
- 12. Discuss deviations from perfect gas model, Vander Waals equation of state.**

## **COURSE LEARNING OUTCOMES (CLOs):**

- 13. Understand mole fraction, mass fraction, gravimetric and volumetric analysis, volume fraction**
- 14. Discuss Dalton's law of partial pressure, Avogadro's laws of additive volumes, and partial pressure, equivalent gas constant.**
- 15. Understand enthalpy, specific heats and entropy of mixture of perfect gases.**
- 16. Understand the process of psychrometry that are used in the analysis of engineering devices like air conditioning systems.**

# **COURSE LEARNING OUTCOMES (CLOs):**

- 17. Develop Otto, Diesel, Dual combustion cycles, description and representation on P-V and T-S diagram.**
- 18. Discuss thermal efficiency; mean effective pressures on air standard basis.**
- 19. Understand the comparison of various cycles.**
- 20. Understand introduction to Brayton cycle and Bell Coleman cycle.**

# **MODULE- I**

# **BASIC CONCEPTS AND FIRST LAW**

# **OF THERMODYNAMICS**



# THERMODYNAMICS

**What is Thermodynamics (TD)?**

**Thermodynamics → Therme + Dynamics**  
**(Heat) (power)**

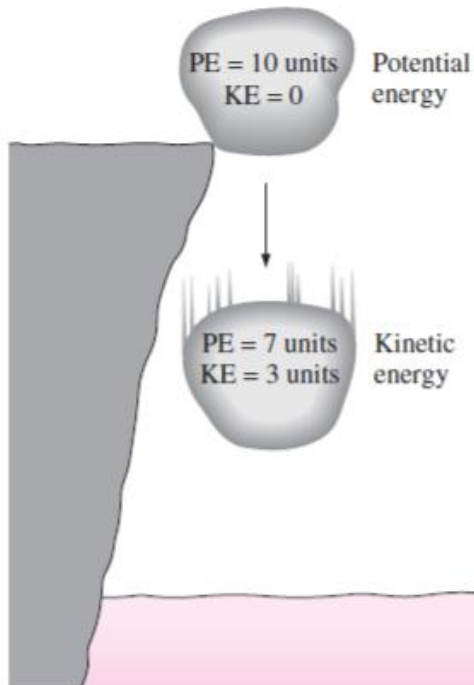
**Man's early effort to convert heat into power.**

**Thermodynamics is a branch of science that deals with  
"ENERGY AND ITS TRANSFORMATION"**

**What is Energy? The ability to cause any changes.**

# ENERGY

- Energy can change from one form to another but the total amount of energy remains constant. That is, energy cannot be created or destroyed.



Energy cannot be created or destroyed;  
it can only change forms

# HISTORY OF THERMODYNAMICS

- ◎ The term Thermodynamics was first used in a publication by Lord Kelvin( William Thomson) in 1849.
- ◎ The first Thermodynamic textbook was written in 1859 by *William Rankine*, a professor at the University of Glasgow.
- ◎ 1<sup>st</sup> and 2<sup>nd</sup> laws of TD were developed around 1850-1870.
- ◎ 1<sup>st</sup> Steam engine developed by Thomas Savery (1697) in England and *Thomas Necomen in (1712)*
- ◎ *James Watt* improved inefficient steam engine further and commercialized in 1776 along with *Mathew Boulton*.

# WHAT IS THE THERMODYNAMICS?

- ⦿ **Thermodynamics is a science dealing with Energy and its Transformation (1<sup>st</sup> Law )**
- ⦿ **Equilibrium process (2<sup>nd</sup> and Zeroth Law)**
- ⦿ **Entropy (3<sup>rd</sup> Law)**

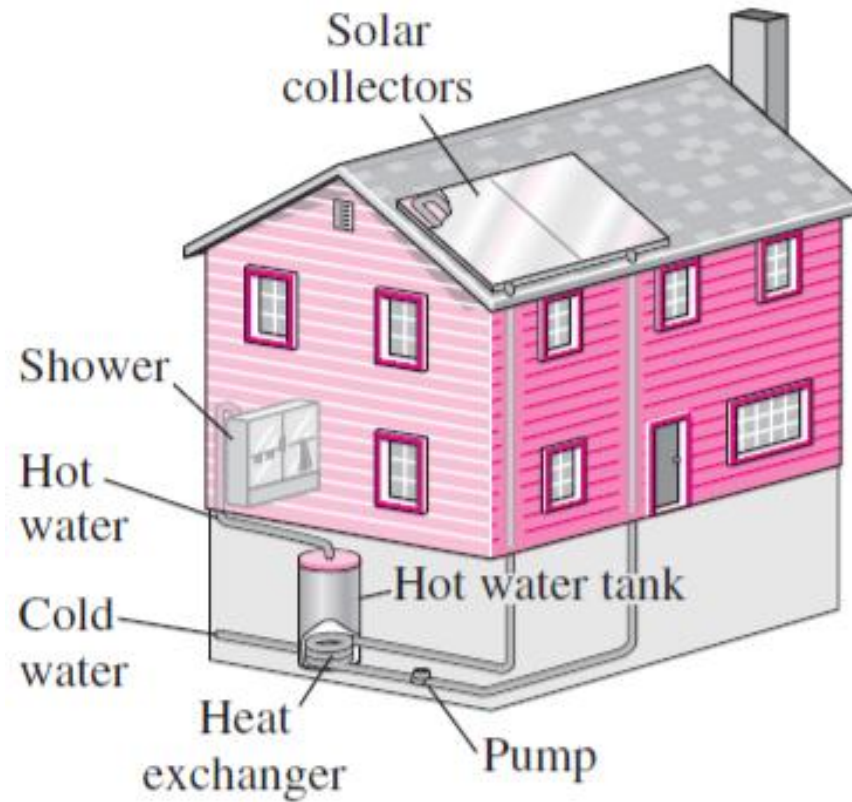
**All these FOUR laws are based on the experimental observations which can not proved directly.**

# APPLICATION OF TD THERMODYNAMICS?

- ◎ **Applications of thermodynamics are right where one lives. An ordinary house is, in some respects, an exhibition hall filled with wonders of thermodynamics. Many ordinary household utensils and appliances are designed, in whole or in part, by using the principles of thermodynamics.**

**Some examples include the electric or gas range, the heating and air-conditioning systems, the refrigerator, the pressure cooker, the water heater, the shower, the iron, and even the computer and the TV.**

# APPLICATION OF TD THERMODYNAMICS?



**The design of many engineering systems, such as this solar hot water system, involves thermodynamics**

# APPLICATION OF TD THERMODYNAMICS?

- **On a larger scale, thermodynamics plays a major part in the design and analysis of automotive engines, rockets, jet engines, and conventional or nuclear power plants, solar collectors, and the design of vehicles from ordinary cars to airplanes. The energy-efficient home that you may be living in, for example, is designed on the basis of minimizing heat loss in winter and heat gain in summer. The size, location, and the power input of the fan of your computer is also selected after an analysis that involves thermodynamics**

# APPLICATION OF TD THERMODYNAMICS?



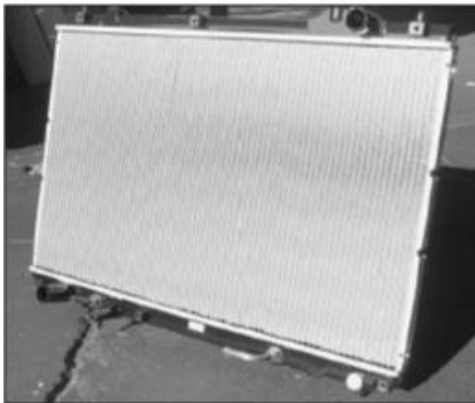
The human body



Air conditioning systems



Airplanes



Car radiators



Power plants



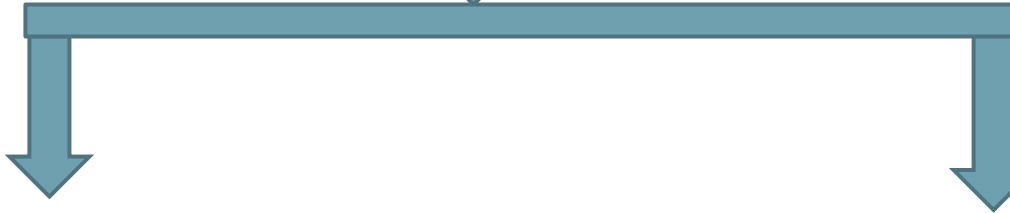
Refrigeration systems

**Figure : Some application areas of thermodynamics.**



# TYPES OF THERMODYNAMICS

**THERMODYNAMICS**



**CLASSICAL THERMODYNAMICS**

**STATISTICAL THERMODYNAMICS**

# TYPES OF THERMODYNAMICS

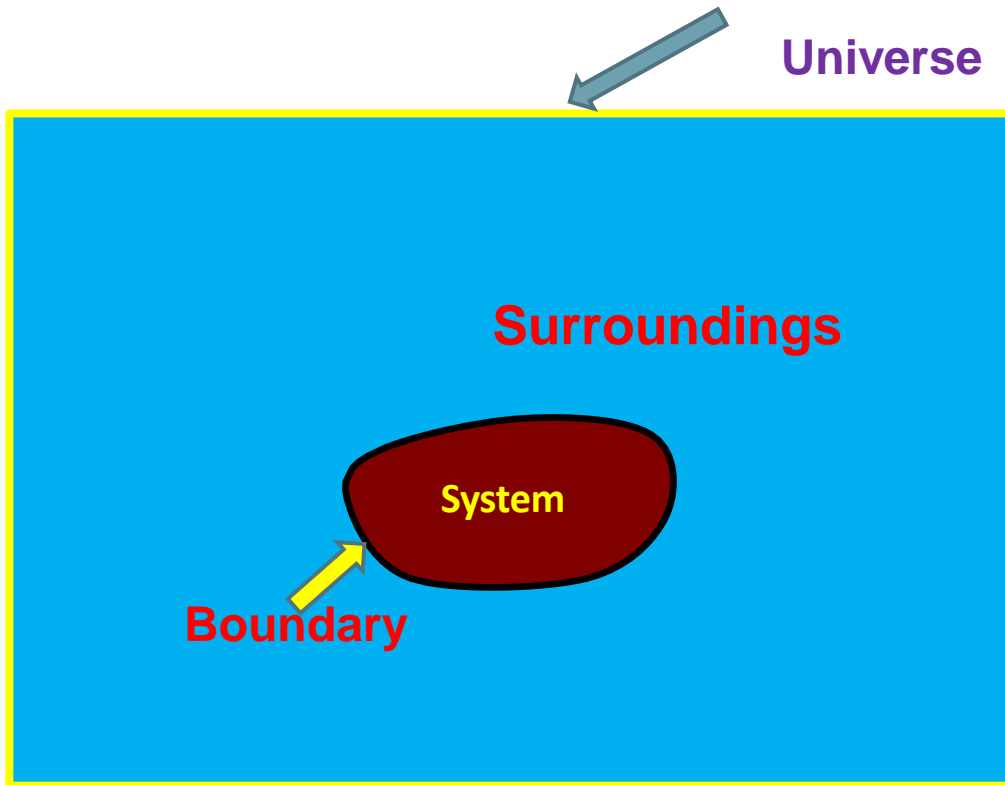
- ⦿ This macroscopic approach to the study of thermodynamics that does not require a knowledge of the behaviour of individual particles is called classical thermodynamics
- ⦿ NO need to consider the structure of the motion.
- ⦿ It provides a direct and easy way to the solution of engineering problems
- ⦿ Few variable are required to describe

## Classical Thermodynamics

- ⦿ A more elaborate approach, based on the average behaviour of large groups of individual particles, is called statistical thermodynamics.
- ⦿ It deals with the matter at molecular level.
- ⦿ The variables can not be measured easily.
- ⦿ Large no of variable to specify of matter.

## Statistical Thermodynamics

# SYSTEM, BOUNDARY, SURROUNDINGS & UNIVERSE



## SYSTEM :

*“A quantity of matter or region in a space” chosen for study.*

## SURROUNDINGS:

*“Everything external to system. or Region outside to the system”.*

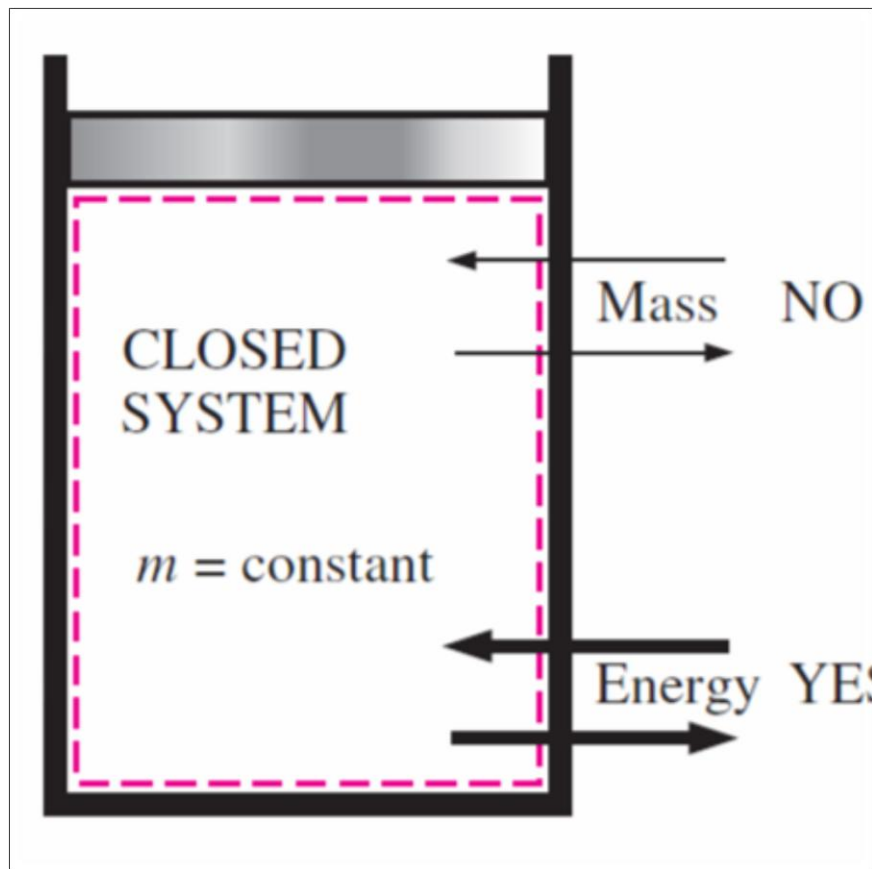
## BOUNDARY:

The real or imaginary surface that separates the SYSTEM and SURROUNDINGS.

# TYPES OF SYSTEMS

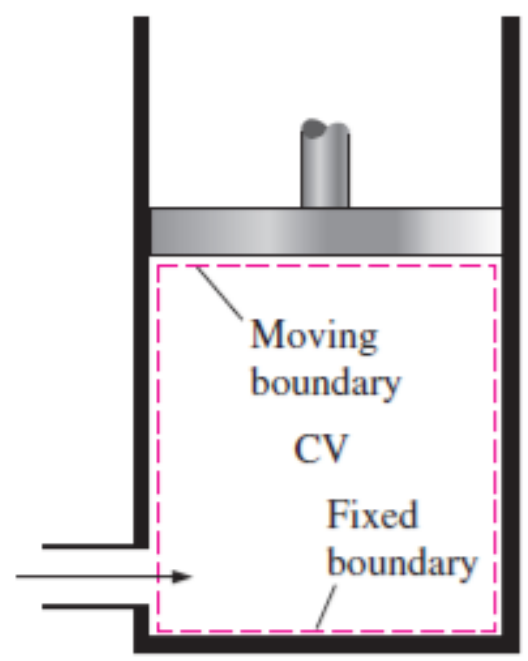
- ⦿ **Closed system**
- ⦿ **Open system**
- ⦿ **Isolated System**

# CLOSED SYSTEM



A closed system (also known as a control mass) consists of a fixed amount of mass, and no mass can cross its boundary. That is, no mass can enter or leave a closed system. But energy, in the form of heat or work, can cross the boundary; and the volume of a closed system does not have to be fixed.

# OPEN SYSTEM



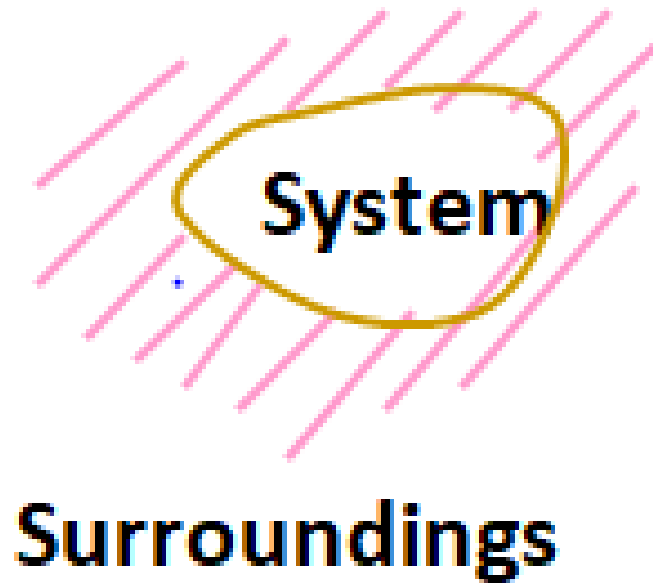
(b) A control volume with fixed and moving boundaries

The open system is one in which matter crosses the boundary of the system. There may be energy transfer also.

Most of the engineering devices are generally open systems.

Ex : Air Compressor

# ISOLATED SYSTEM



**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.**

# PROPERTY

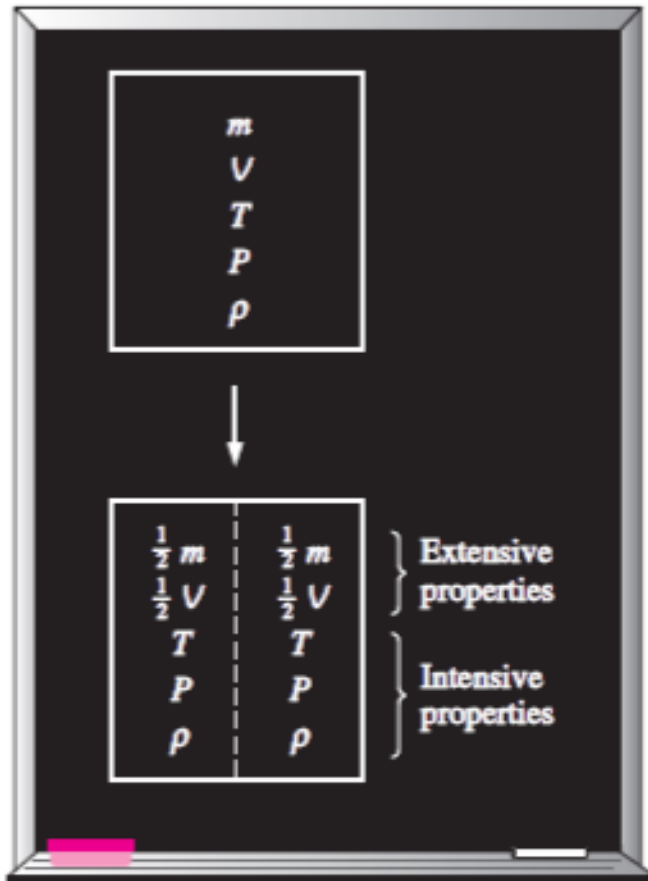
- ◎ Any characteristic of a system is called a property.
- ◎ Some familiar properties are pressure  $P$ , temperature  $T$ , volume  $V$ , and mass  $m$ . The list can be extended to include less familiar ones such as viscosity, thermal conductivity, modulus of elasticity, thermal expansion coefficient, electric resistivity, and even velocity and elevation.
- ◎ Classification of property : Intensive property &  
Extensive property .



# TYPES OF PROPERTY

- ⦿ Properties are considered to be either intensive or extensive.
- ⦿ Intensive properties are those that are *independent of the mass of a system*, such as temperature, pressure, and density.
- ⦿ Extensive properties are those whose values extent—of the system

# TYPES OF PROPERTY



Criterion to differentiate intensive and extensive properties.

# THERMODYNAMIC EQUILIBRIUM

**Thermodynamics deals with equilibrium states.**

**The word equilibrium implies a state of balance. In an equilibrium state there are no unbalanced potentials (or driving forces) within the system.**

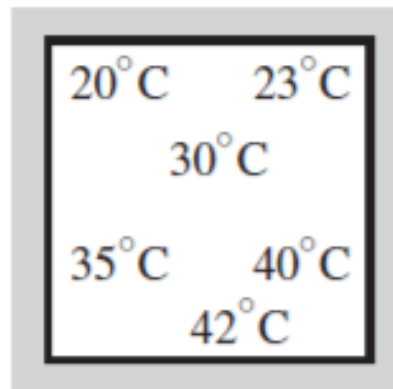
**A system in equilibrium experiences no changes when it is isolated from its surroundings.**

**THERMODYNAMIC EQUILIBRIUM = Thermal equilibrium  
+  
Mechanical equilibrium  
+  
Chemical equilibrium**

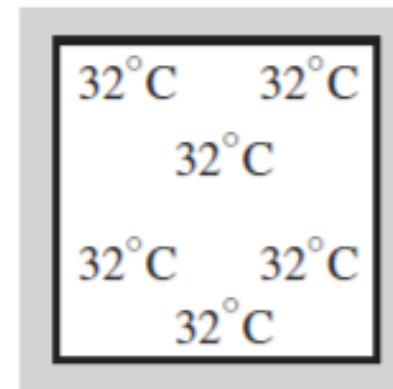
# THERMAL EQUILIBRIUM

## ⦿ Thermal equilibrium:

A system is in thermal equilibrium if the temperature is the same throughout the entire system



(a) Before



(b) After

# THERMODYNAMIC EQUILIBRIUM

- ⦿ **Mechanical Equilibrium**

**Mechanical equilibrium is related to pressure, and a system is in mechanical equilibrium if there is no change in pressure at any point of the system with time.**

- ⦿ **Chemical Equilibrium**

**A system is in chemical equilibrium if its chemical composition does not change with time, that is, no chemical reactions occur. A system will not be in equilibrium unless all the relevant equilibrium criteria are satisfied.**

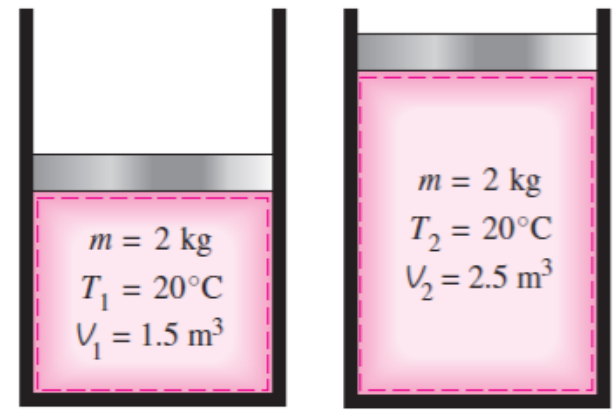
- ⦿ **When the conditions for any one of the three types of equilibrium are not satisfied, a system said to be in a nonequilibrium state.**

# STATE

Consider a system not undergoing any change. At this point, all the properties can be measured or calculated throughout the entire system, which gives us a set of properties that completely **describes the condition, or the state**, of the system. At a given state, all the properties of a system have fixed values.

If the value of even one property changes, the state will change to a different one. Or

Any operation in which one or more of the properties of a system changes is called **CHANGE OF STATE**

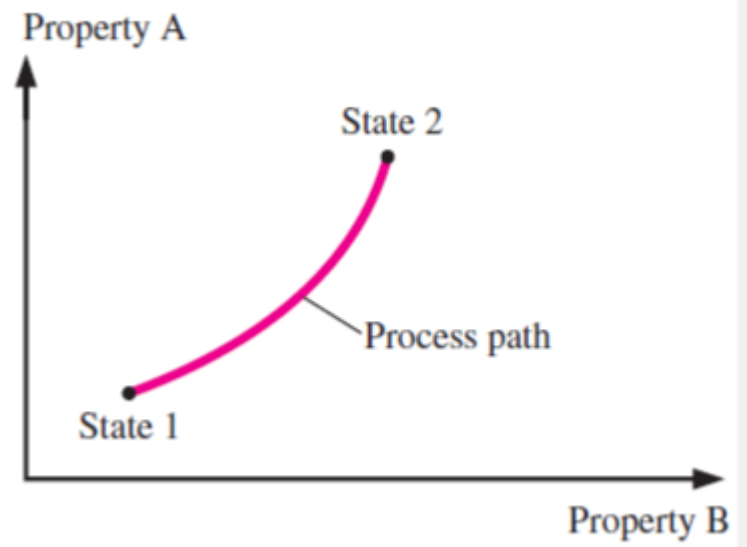


(a) State 1

(b) State 2

# PROCESS & PATH

- ⦿ **PROCESS:**
- ⦿ Any change that a system undergoes from one equilibrium state to another is called a **process**.
- ⦿ The series of states through which a system passes during a process is called the **path of the process**.





# THERMODYNAMIC CYCLE

◎ **THERMODYNAMIC CYCLE:**

When system return back to its initial state.

Or

A series of state changes state changes such that the final state are identical with the initial state.

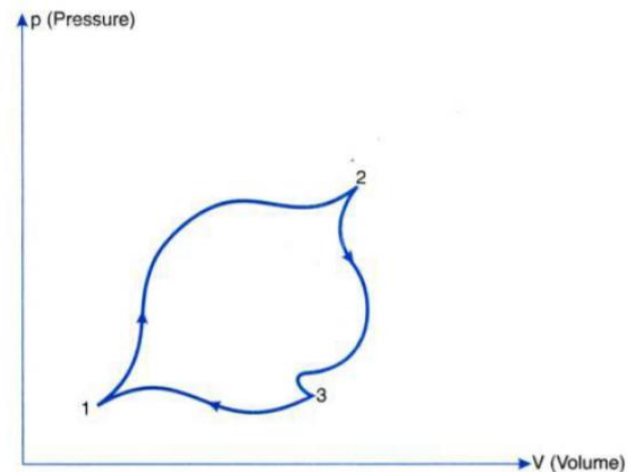


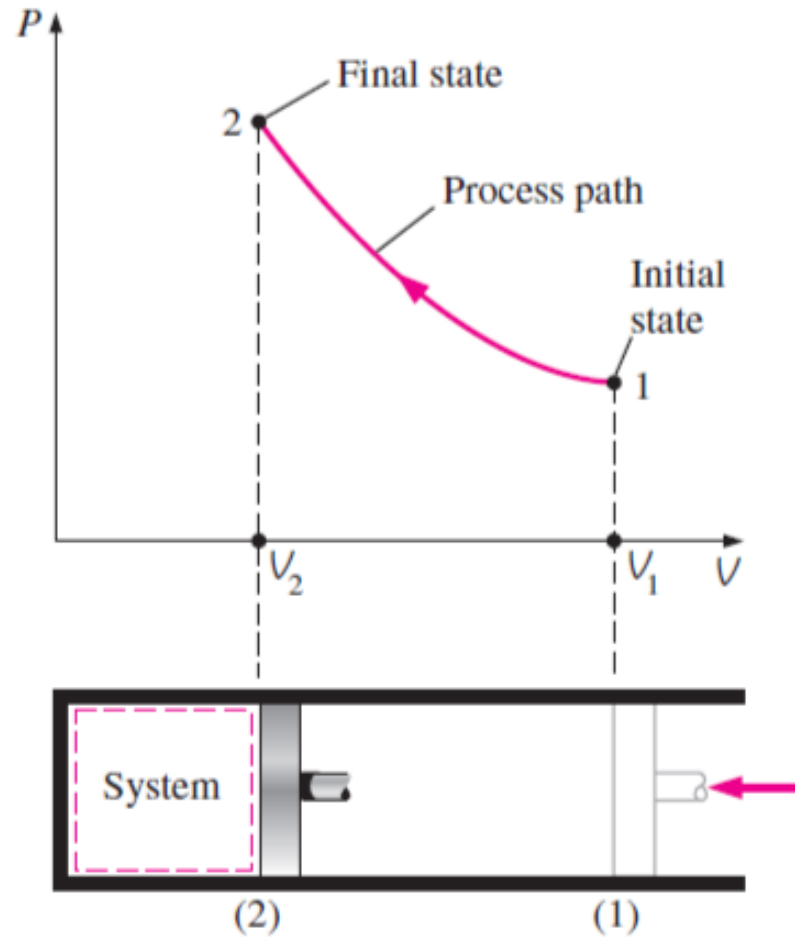
Fig. 1.6. Cycle of operations.

# QUASI STATIC OR QUASI-EQUILIBRIUM PROCESS

If the gas system is isolated, *the departure of the of the state of the system from the thermodynamic equilibrium state will be infinitesimally small.* So every state passed through by the system will be an equilibrium state. such a process, which is but a locus of all the equilibrium points passed through by system, known as a QUASI- STATIC PROCESS.

QUASI meaning “almost”. *Infinite slowness is the characteristics feature of a quasi – static process .* A quasi – static process is thus a succession of equilibrium states.

# QUASI-STATIC PROCESS



The P-V diagram of a compression process.

# CONSTANT PROCESSES

The prefix **iso** - is often used to designate a process for which a particular property remains constant.

**An isothermal process** - T remains constant;

**An isobaric process** - P remains constant &

**isochoric (or isometric) process** - specific volume  $v$  constant.

# WORK AND HEAT

**A closed system interacts with its surroundings in two ways:**

- 1) Work Interaction.**
- 2) Heat Interaction.**

**These may be called as “energy interactions” and these bring about changes in the properties of the system.**

**if the energy crossing the boundary of a closed system is  
not heat, it must be work.**

**Mechanics - “work is the energy transfer associated with a force  
acting through a distance.”**

**A rising piston, a rotating shaft associated with work interactions.**

# WORK

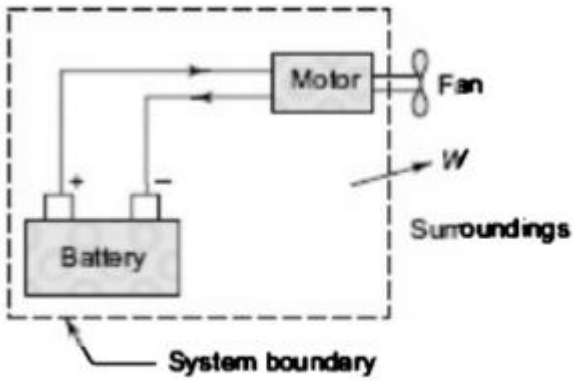


Fig. 3.1 Battery-motor system driving a fan

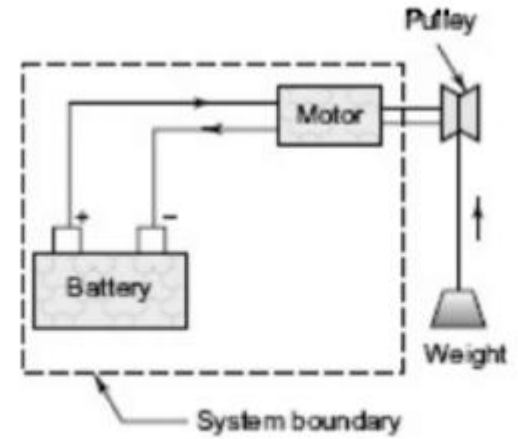


Fig. 3.2 Work transfer from a system

# WORK

**In Thermodynamics, work transfer is considered as occurring between the system and the surroundings. “Work is said to be done by a system if the sole effect on things external to the system can be reduced to the raising of weight”.**



# WORK

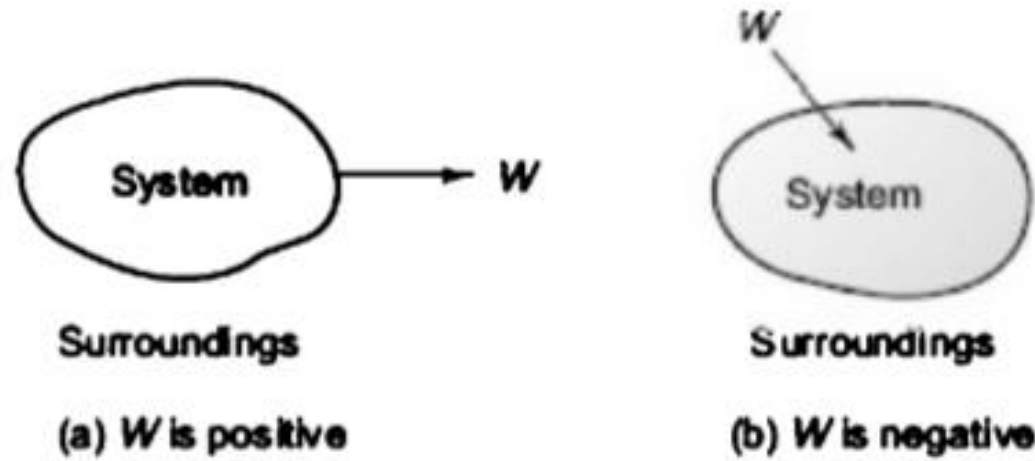
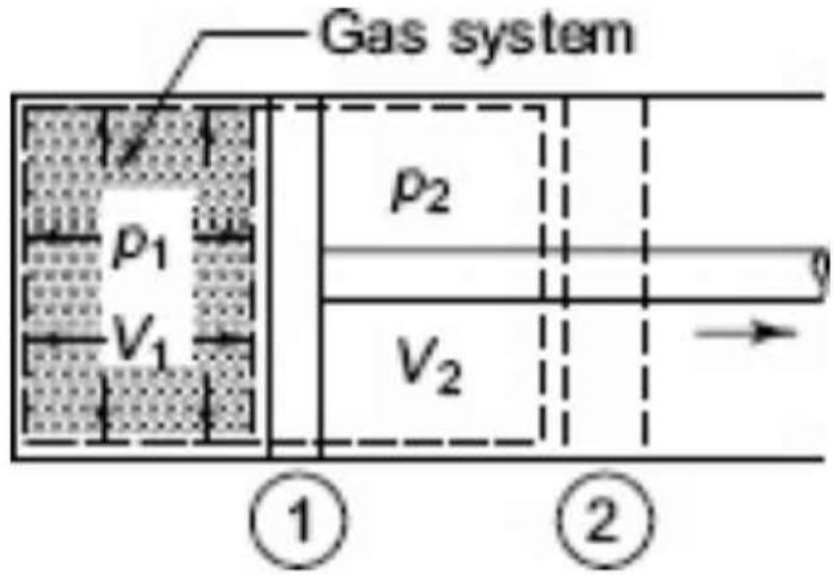


Fig. 3.3 *Work interaction between a system and the surroundings*

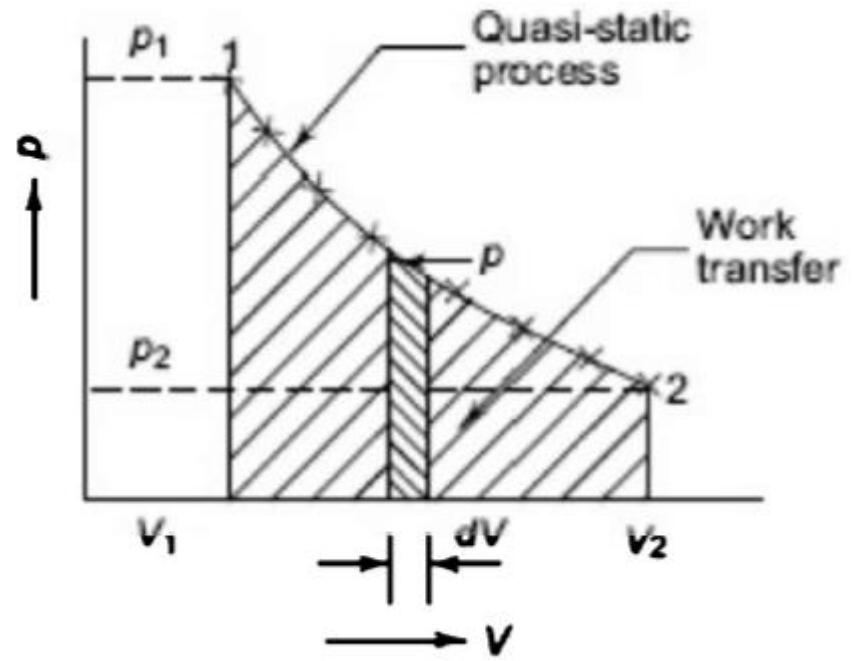
**Unit of work is N.m or Joule [1 Nm = 1 Joule]**

**Power:** The rate at which work is done by, or upon, the system. The unit of power is J/s or Watt

# DISPALCEMENT WORK OR pdV WORK



**pdV work**



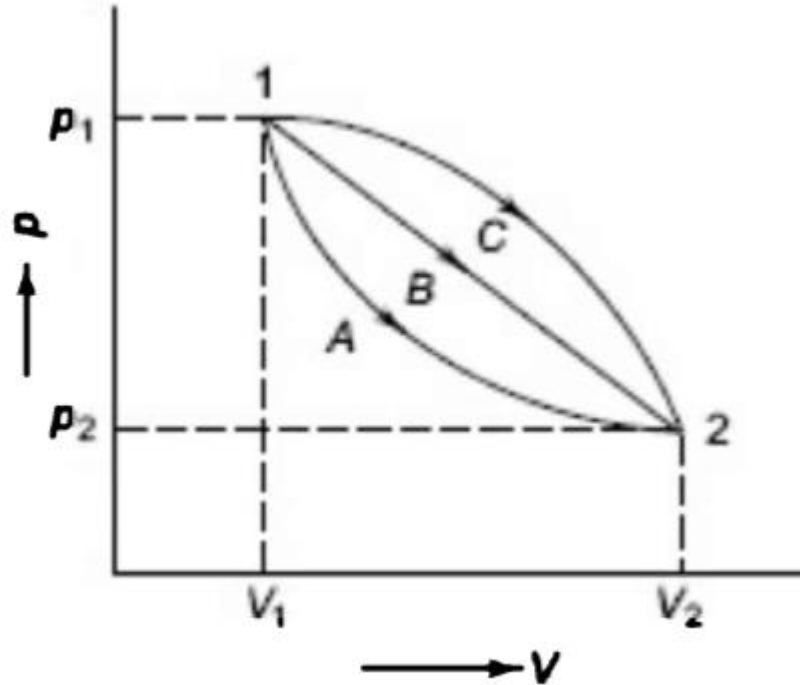
**QUASI-STATIC pdV Work**

Infinitesimal amount of work done by gas  $dW = F \cdot dl = p \cdot a \cdot dl = pdV$

Amount of work  $W$  done by the system

$$W_{1-2} = \int_{V_1}^{V_2} p dV$$

# PATH FUNCTION & POINT FUNCTION



**Work done by a system is a path function, not a point function. Its not a property Of the system. Energy is stored in a system, but not work. Work is energy transit and can be identified only when the system undergoes a process.**

# PATH FUNCTION & POINT FUNCTION

On the other hand, work done in a quasi-static process between two given states depends on the path followed.

$$\int_1^2 dW \neq W_2 - W_1$$

Rather,

$$\int_1^2 dW = W_{1 \rightarrow 2} \quad \text{or} \quad {}_1W_2$$

# PATH FUNCTION & POINT FUNCTION

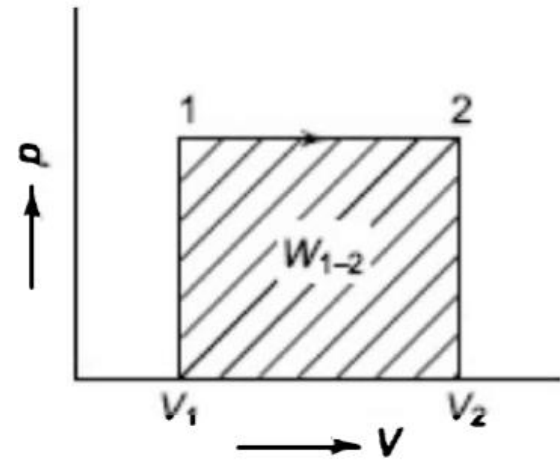
$$\oint dV = 0, \oint dp = 0, \oint dT = 0 \quad (3.3)$$

where the symbol  $\oint$  denotes the cyclic integral for the closed path. Therefore, *the cyclic integral of a property is always zero.*

# pdV WORK IN VARIOUS QUASI\_STATIC PROCESS

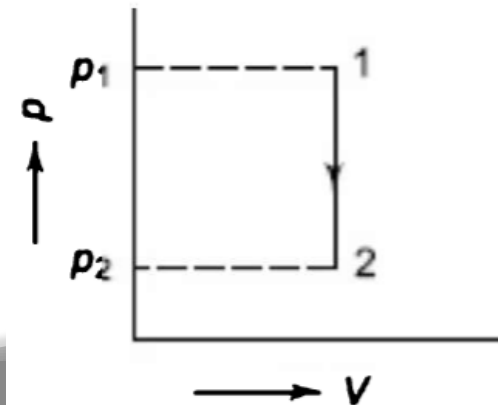
## 1. Constant pressure process (isobaric process)

$$W_{1-2} = \int_{V_1}^{V_2} p dV = p(V_2 - V_1)$$



## 2. Constant volume process (isochoric process)

$$W_{1-2} = \int p dV = 0$$



# pdV WORK IN VARIOUS QUASI-STATIC PROCESS

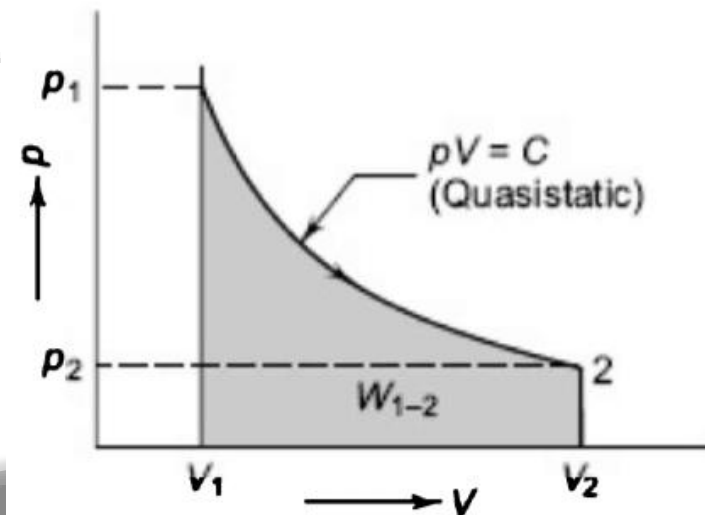
- ⊙ Process in which  $pV=C$

$$W_{1-2} = \int_{V_1}^{V_2} p dV$$

$$pV = p_1 V_1 = C$$

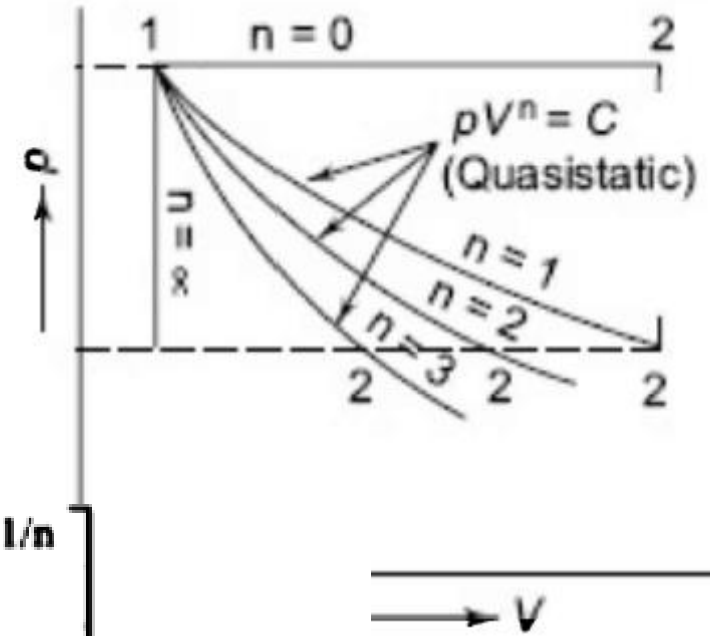
$$p = \frac{(p_1 V_1)}{V}$$

$$\begin{aligned} W_{1-2} &= p_1 V_1 \int_{V_1}^{V_2} \frac{dV}{V} = p_1 V_1 \ln \frac{V_2}{V_1} \\ &= p_1 V_1 \ln \frac{p_1}{p_2} \end{aligned}$$



# pdV WORK IN VARIOUS QUASI-STATIC PROCESS

- Process in which  $pV^n = C$ ,  
Where n=constant



$$= \frac{p_1 V_1 - p_2 V_2}{n-1} = \frac{p_1 V_1}{n-1} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{n-1/n} \right]$$

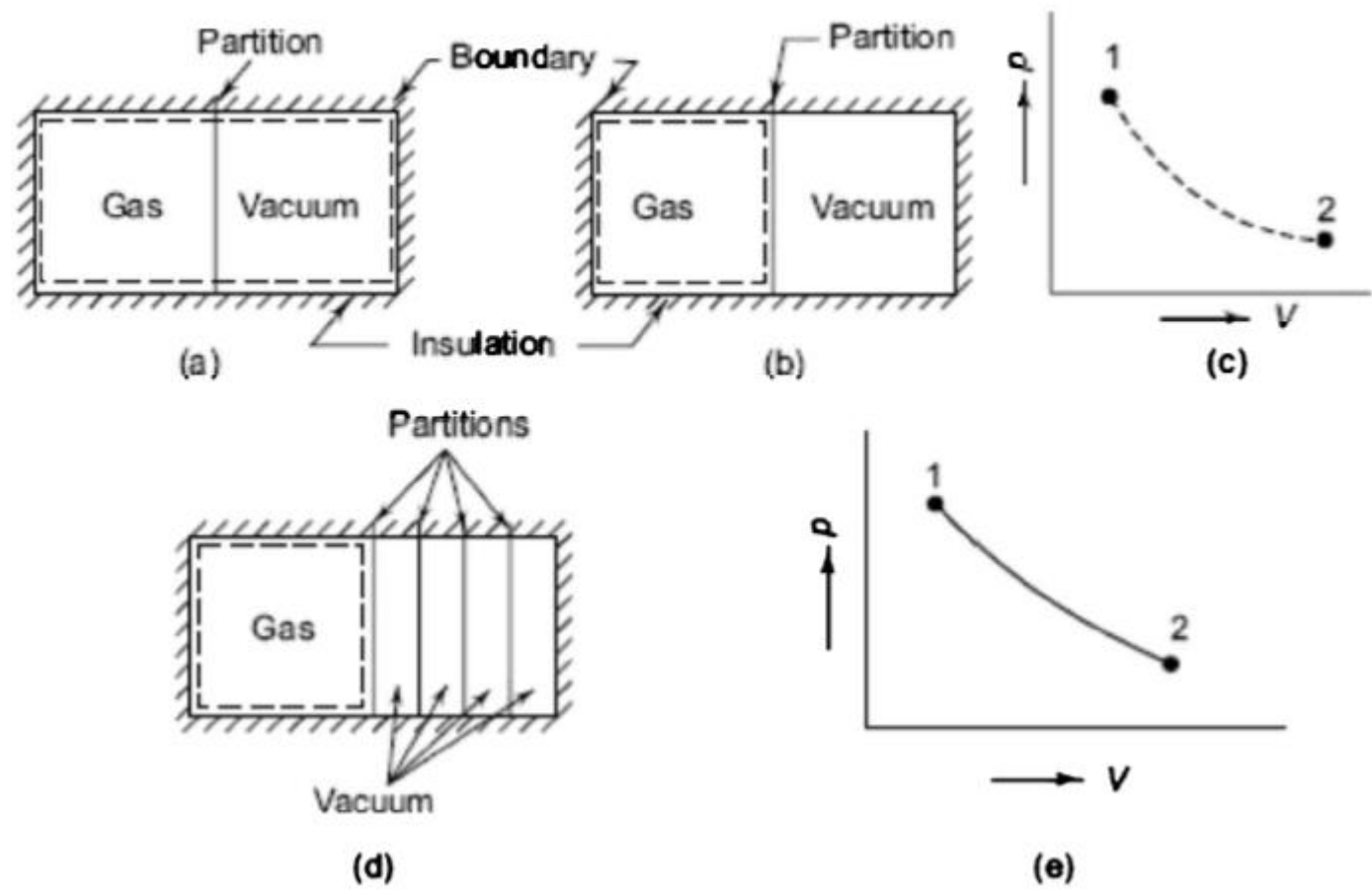
Similarly, for process in which  $pV^\gamma = c$ , where  $\gamma = c_p / c_v$ .

$$W_{1-2} = \frac{p_1 V_1}{\gamma-1} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} \right]$$



# FREE EXPANSION WITH ZERO WORK TRANSFER

- Expansion of gas against vacuum called *free expansion*



# NET WORK DONE BY A SYSTEM

- ⊙  **$W=0$ ; because the expansion of the gas is not restrained by an equal but opposing forces at moving boundary.**
- ⊙ **No external force is moved through any distance.**
- ⊙  **$W=0$  →  $W$  free expansion = 0**

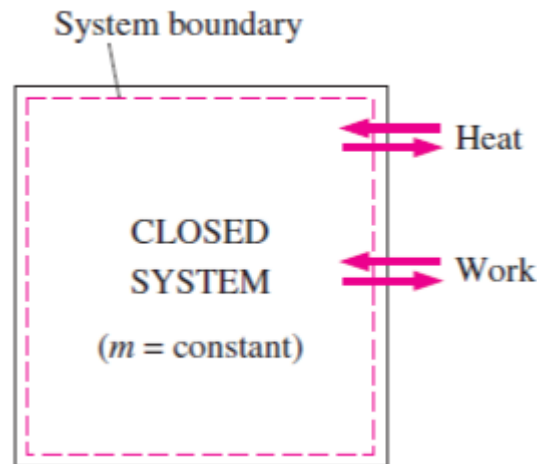
# NET WORK DONE BY A SYSTEM

- Often different forms of work transfer occur simultaneously during a process executed by system. When all these work interactions have been evaluated, the total or net work done by the system would be equal to algebraic sum of these a given below:

$$W_{\text{total}} = W_{\text{displacement}} + W_{\text{shear}} + W_{\text{electrical}} + W_{\text{stirring}} + \dots$$

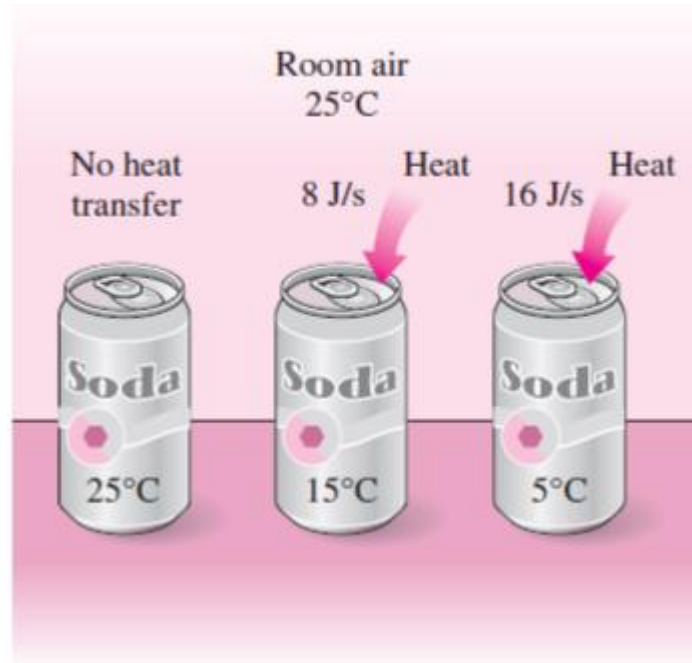
# HEAT

Heat is defined as the form of *energy that is transferred between two systems* (or a system and its surroundings) by virtue of a temperature difference.



Energy can cross the boundaries of a closed system in the form of heat and work.

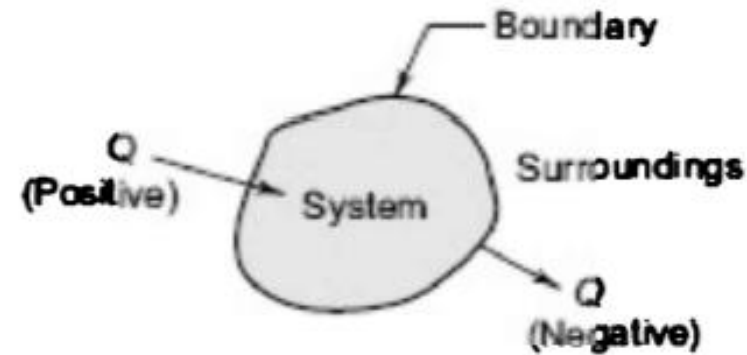
# HEAT



**Temperature difference is the driving force for heat transfer. The larger the temperature difference, the higher is the rate of heat transfer.**

# Heat

The transfer of **heat into a system** is (positive )  
 frequently referred to as **heat addition** and  
 the transfer of **heat out of a system**  
 (negative) as **heat rejection**.



The symbol  $Q$  is used for heat transfer,  
 i.e The Quantity of heat transferred within a certain time.

Unit of HEAT is Joule,

The rate of Heat transfer is given in KW or W

# ADIABATIC PROCESS

A process during which there is **no heat transfer** is called an adiabatic process. The word adiabatic comes from the Greek word *adiabatos*, which means not to be passed. There are two ways a process can be adiabatic:

Either the system is **well insulated** so that only a negligible amount of heat can pass through the boundary, or both the system and the surroundings are at the **same temperature** and therefore there is no driving force (temperature difference) for heat transfer.

**Diathermic wall:** where as a wall which permits the flow of heat a diathermic wall

# SPECIFIC HEAT

- ◎ The specific heat of a substance is defined as the amount of heat required to raise a unit mass of the substance through a unit rise in temperature.
- ◎ The symbol  $c$  will be used for specific heat.

$$c = \frac{Q}{m \cdot \Delta t} \text{ J/kg K}$$

- ◎ Where  $Q$  is the amount of heat transfer(J),
- ◎  $m$  is the mass of substance (kg) and
- ◎  $\Delta t$  the rise in temperature(K).



# HEAT CAPACITY

- ⦿ The product of mass and specific heat( $mc$ ) is called the Heat capacity ( $C$ ) substance.
- ⦿ Capital letter  $C, C_p$  or  $C_v$  is used for heat capacity
- ⦿ For gases, if the
- ⦿ process is constant pressure,  $c_p$
- ⦿ process is constant pressure,  $c_v$

# LATENT HEAT

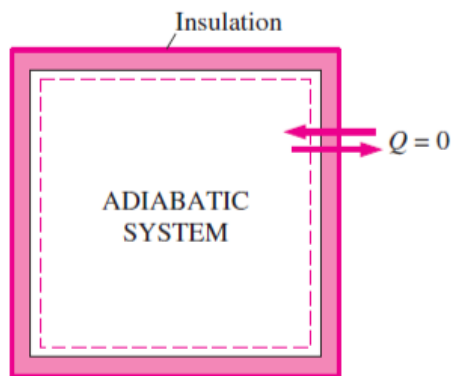
- ◎ The amount of heat transfer required to **cause a phase change in unit mass of substance at a constant pressure and temperature.**
- ◎ There is three phase s in which matter can exits:
- ◎ Solid, liquid and vapour or gas.
- ◎ Latent heat fusion : The amount of heat transferred to melt unit mass of solid into liquid or freeze unit mass of liquid to solid.

# LATENT HEAT

- ⦿ **Latent heat of vaporization: the quantity of heat required to vaporise unit mass of liquid into vapour or condense unit mass of vapour into liquid.**
- ⦿ **Latent heat of sublimation: the amount of heat transferred to convert unit mass of solid to vapour or vice versa.**

# HEAT

As a form of energy, heat has energy units, kJ being the most common one. The amount of heat transferred during the process between two states (states 1 and 2) is denoted by  $Q_{12}$ , or just  $Q$ . Heat transfer per unit mass of a system is denoted  $q$  and is determined from



$$q = \frac{Q}{m} \quad (\text{kJ/kg})$$

**During an adiabatic process, a system exchanges no heat with its surroundings.**

if the energy crossing the boundary of a closed system is

**not heat, it must be work.**

**work is the energy transfer associated with a force acting through a distance.**

**A rising piston, a rotating shaft associated with work interactions.**

# WORK

Work is also a form of energy transferred like heat and, therefore, has energy units such as kJ. The work done during a process between states 1 and 2 is denoted by  $W_{12}$ , or simply  $W$ . The work done per unit mass of a system is denoted by  $w$  and is expressed as

$$w = \frac{W}{m} \quad (\text{kJ/kg})$$

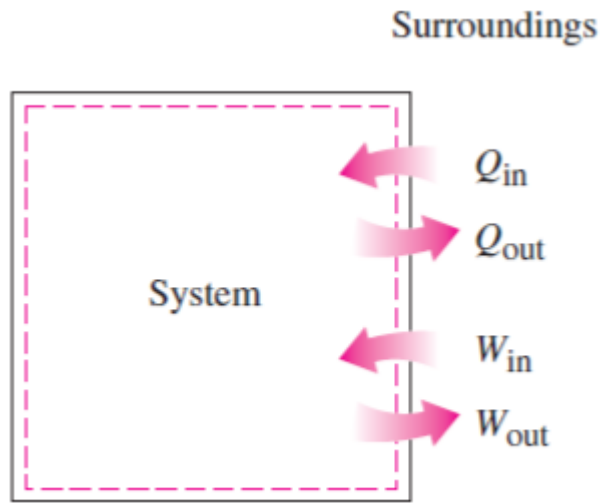
The **work done per unit** time is called **power** and is denoted  $W$   
 The unit of power is kJ/s, or kW.

# HEAT AND WORK ARE DIRECTIONAL QUANTITIES

Heat and work are directional quantities

The complete description of a heat or work interaction requires the specification of both the magnitude and direction.

**Formal sign convention**



Heat transfer **to a system** and work **done by a system** are **Positive**.

Heat transfer **from a system** and **work done on a system** are **negative**

# ZEROth LAW OF THERMODYNAMICS

When a **body A** is in thermal equilibrium with a **body B**, and also separately with a **body C**, then **B and C** will be in thermal equilibrium with each other. This is known as Zeroth law of thermodynamics.



# MEASUREMENT OF TEMPERATURE – REFERENCE POINTS



$\theta(X) = aX$ , where  $a$  is an arbitrary constant.

If  $X_1$  corresponds to  $\theta(X_1)$ , then  $X_2$  will correspond to

$$\frac{\theta(X_1)}{X_1} \cdot X_2$$

that is

$$\theta(X_2) = \frac{\theta(X_1)}{X_1} \cdot X_2 \quad (2)$$

Two temperatures on the linear  $X$  scale are to each other as the ratio of the corresponding  $X$ 's.

# MEASUREMENT OF TEMPERATURE – REFERENCE POINTS



- ⦿ **Triple point of water, the state at which ice, liquid water, and water vapour co- exist in equilibrium.**
- ⦿ **The temperature at which this state exists is arbitrarily assigned the value of 273.16 degree kelvin or 273.16K.**

# MEASUREMENT OF TEMPERATURE – REFERENCE POINTS



$$\theta_t = aX_t$$

$$a = \frac{\theta_t}{X_t} = \frac{273.16}{X_t}$$

$$\theta = aX = \frac{273.16}{X_t} \cdot X$$

$$\theta = 273.16 \frac{X}{X_t}$$

- ⊙ **a= arbitrary constant**
- ⊙ triple point of water by  $\theta_t$ ,
- ⊙ whose temperature  $\theta$  is to be measured

**Table 2.1** *Thermometers and thermometric properties*

<i>Thermometer</i>	<i>Thermometric property</i>	<i>Symbol</i>
1. Constant volume gas thermometer	Pressure	$P$
2. Constant pressure gas thermometer	Volume	$V$
3. Electrical resistance thermometer	Resistance	$R$
4. Thermocouple	Thermal e.m.f.	$e$
5. Mercury-in-glass thermometer	Length	$L$

## 2.3 COMPARISON OF THERMOMETERS

Applying the above principle to the five thermometers listed in Table 2.1, the temperatures are given as follows:

1. Constant volume gas thermometer  $\theta(P) = 273.16 \frac{P}{P_i}$

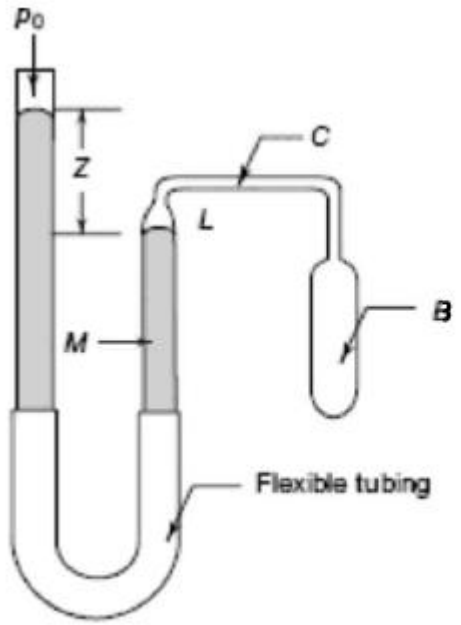
2. Constant pressure gas thermometer  $\theta(V) = 273.16 \frac{V}{V_i}$

3. Electric resistance thermometer  $\theta(R) = 273.16 \frac{R}{R_i}$

4. Thermocouple  $\theta(\epsilon) = 273.16 \frac{\epsilon}{\epsilon_i}$

5. Liquid-in-glass thermometer  $\theta(L) = 273.16 \frac{L}{L_i}$

# GAS THERMOMETER



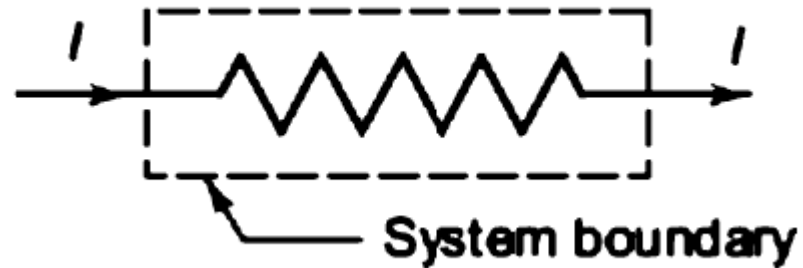
Constant volume gas thermometer

$$\Delta T = \frac{V}{R} \Delta P$$

$$\Delta T = \frac{P}{R} \Delta V$$

# OTHER TYPES OF WORK TRANSFER

## ⊙ Electrical work



$$dW = E \cdot dC$$

$$= EI d\tau$$

$$I = \frac{dC}{d\tau}$$

$$W = \int_1^2 EI d\tau$$

where  $C$  is the charge in coulombs and  $\tau$  is time in seconds. Thus  $dC$  is the charge crossing a boundary during time  $d\tau$ . If  $E$  is the voltage potential, the work is

# OTHER TYPES OF WORK TRANSFER

## ◎ Shaft work

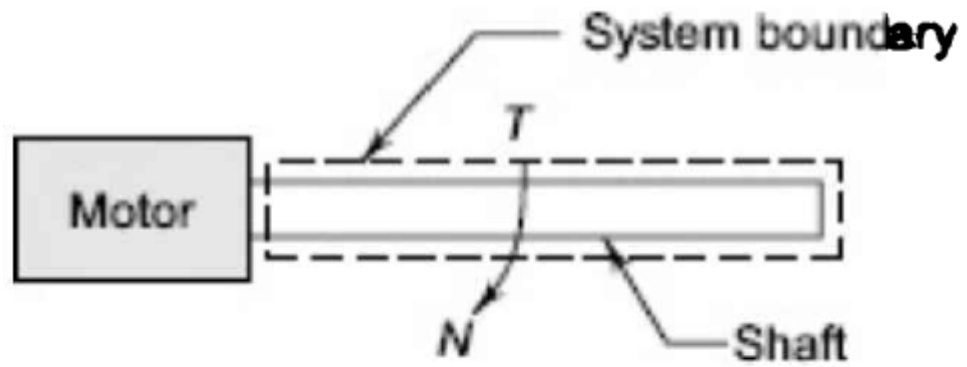


Fig. 3.14(A) Shaft work

$$W = \int_1^2 T d\theta$$

the shaft power is

$$W = \int_1^2 T \frac{d\theta}{d\tau} = T\omega$$

where  $\omega$  is the angular velocity and  $T$  is considered a constant



# OTHER TYPES OF WORK TRANSFER

$$\int p dV = 0.$$

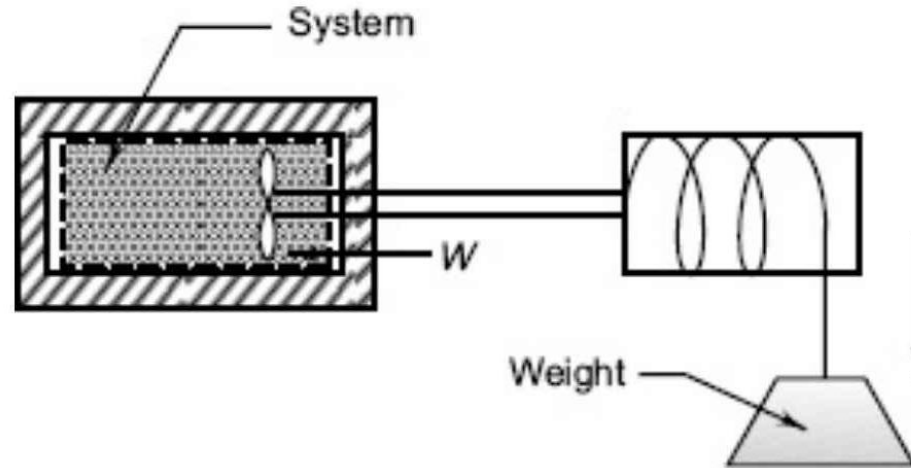


Fig. 3.15 Paddle-wheel

the differential work transfer to the fluid  $dW = mgdz = Td\theta$

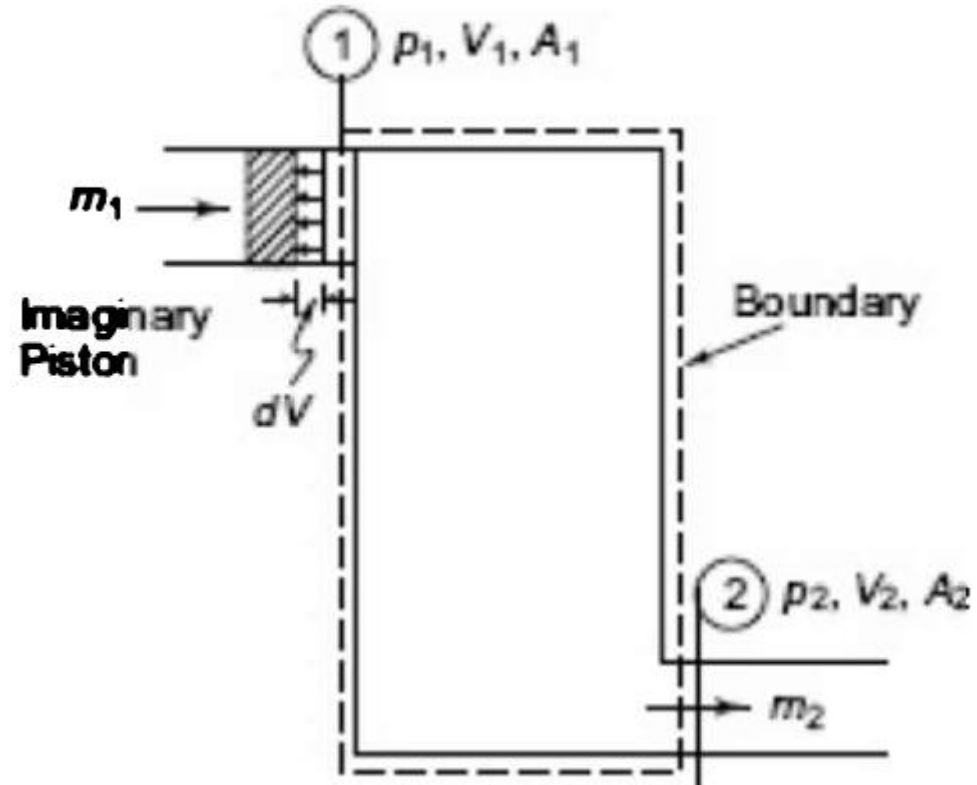
the total work transfer is

$$W = \int_1^2 mgdz = \int_1^2 W' dz = \int_1^2 Td\theta$$

$W'$  is the weight lowered.

# OTHER TYPES OF WORK TRANSFER

## Flow work



# OTHER TYPES OF WORK TRANSFER

the work done in time  $d\tau$  becomes

$$(\dot{W}_{\text{flow}})_{\text{in}} = p_1 v_1 dm_1$$

Similarly, flow work of the fluid element leaving the system is

$$(\dot{W}_{\text{flow}})_{\text{out}} = p_2 v_2 dm_2$$

The flow work per unit mass is thus

$$\dot{W}_{\text{flow}} = pv$$

It is the displacement work done at the moving system boundary.

# OTHER TYPES OF WORK TRANSFER

## ◎ WORK DONE IN CHANGING THE ARE OF A SURFACE FILM

an infinitesimal amount  $dA$  is

$$dW = -\sigma dA$$

where  $\sigma$  is the surface tension (N/m).

$$\therefore W = - \int_1^2 \sigma dA$$

# OTHER TYPES OF WORK TRANSFER

## ⊙ Magnetization of a paramagnetic solid

$$dW = -HdI$$

$$W_{1-2} = -\int_{I_1}^{I_2} HdI$$

where  $H$  is the field strength, and  $I$  is the component of the magnetisation field in the direction of the field. The minus sign provides that an increase in magnetisation (positive  $dI$ ) involves negative work.

# OTHER TYPES OF WORK TRANSFER

- Work done in stretching a wire

$$W = - \int_1^2 \mathcal{F} dL$$

$$\mathcal{F} = sA = E\epsilon A, \text{ since } \frac{s}{\epsilon} = E$$

$$d\epsilon = \frac{dL}{L}$$

$$dW = - \mathcal{F} dL = - E\epsilon AL d\epsilon$$

$$W = - AEL \int_1^2 \epsilon d\epsilon = - \frac{AEL}{2} (\epsilon_2^2 - \epsilon_1^2)$$

# OTHER TYPES OF WORK TRANSFER

Displacement  
work (compressible fluid)

$$W = \int_1^2 p dV$$

Electrical work

$$W = \int_1^2 E dC - \int_1^2 EI d\tau$$

Shaft work

$$W = \int_1^2 T d\theta$$

Surface film

$$\int_1^2 \delta W = 0, \quad \text{although} \quad \int_1^2 p dV \neq 0 \quad (3.25)$$

Stretched wire

$$W = \int_1^2 F dL$$

Magnetised solid

$$W = \int_1^2 H dI$$

# Choice of the System and Boundaries Are at Our convenience

- **We must choose the system for each and every problem we work on, so as to obtain best possible information on how it behaves.**
- **In some cases the choice of the system will be obvious and in some cases not so obvious.**
- **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

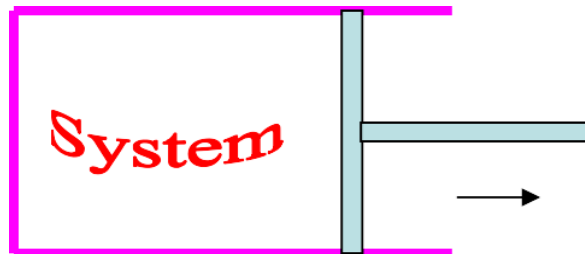
**The boundaries may be real physical surfaces or they may be imaginary for the convenience of analysis.**

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

# Choice of the System and Boundaries Are at Our Convenience

- 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.**

➤ **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.**

➤ **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.**

# PROPERTY

- It is some characteristic of the system to which some physically meaningful numbers can be assigned without knowing the history behind it.
- These are macroscopic in nature.
- Invariably the properties must enable us to identify the system.
- 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!!.
- All of them are properties of and. But you pick and choose a set of his traits which describe him best for a given situation.
- 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

## ➤ 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.

## ➤ Intensive property:

whose value is independent of the size or extent of the system. eg: pressure, temperature (p, T).

## PROPERTY (CONTD..)

- **Specific property:**

- **It is the value of an extensive property per unit mass of system. (lower case letters as symbols) eg: specific volume, density ( $v$ ,  $\rho$ ).**
- **It is a special case of an intensive property.**
- **Most widely referred properties in thermodynamics:**
- **Pressure; Volume; Temperature; Entropy; Enthalpy; Internal energy.**

# STATE & PHASE

## ➤ **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.

## ➤ **Phase:**

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

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

# 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:**

- A system may undergo changes in some or all of its properties.**
- 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

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

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

➤ Complete the cycle by regaining the initial state

• Isothermal (T)

• Isobaric (p)

• Isochoric (v)

• Isentropic (s)

• Isenthalpic (h)

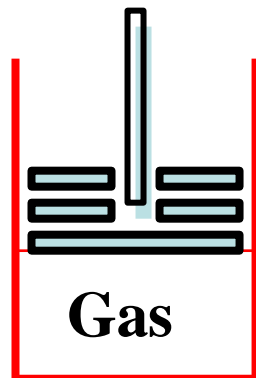
• Isosteric (concentration)

• 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

- The deviation from thermodynamic equilibrium is infinitesimal.
- All states of the system passes through are equilibrium states.



# QUASI-STATIC PROCESSES

- If we remove the weights slowly one by one the pressure of the gas will displace the piston gradually. It is quasistatic.
- 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 sustained manner
- In both cases the systems have undergone a change of state.
- 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

**A system is said to be in an equilibrium state if its properties Will not change without some perceivable effect in the surroundings.**

- **Equilibrium generally requires all properties to be uniform throughout the system.**
- **There are mechanical, thermal, phase, and chemical equilibrium.**
- **Nature has a preferred way of directing changes. eg:**
  - **water flows from a higher to a lower level**
  - **Electricity flows from a higher potential to a lower one.**

# TYPES OF EQUILIBRIUM

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

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

No interactions between them occur. They are said to be in equilibrium.

# ➤ DEFINITION OF TEMPERATURE AND ZEROth LAW OF THERMODYNAMICS



➤ **Temperature is a property of a system which determines the degree of hotness.**

➤ **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 in empirical scale.**

# ZEROth LAW OF THERMODYNAMICS (CONTD...)

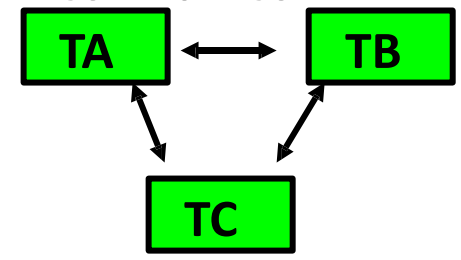
- **Two systems are said to be equal in temperature, when there is no change in their respective observable properties when they are brought together. In other words, “when two systems are at the same temperature they are in thermal equilibrium” (They will not exchange heat).**
- **If two systems (say 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 ZEROETH LAW

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

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

➤ B and C are in thermal equilibrium.



Consequence of of '0'th law

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

➤ Looks very logical

➤ All temperature measurements are based on this LAW.



# TRAITS OF ENGINEERS

➤ 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

➤ Next, we have to do it in a sustained manner (we cant use fly by night techniques!!)

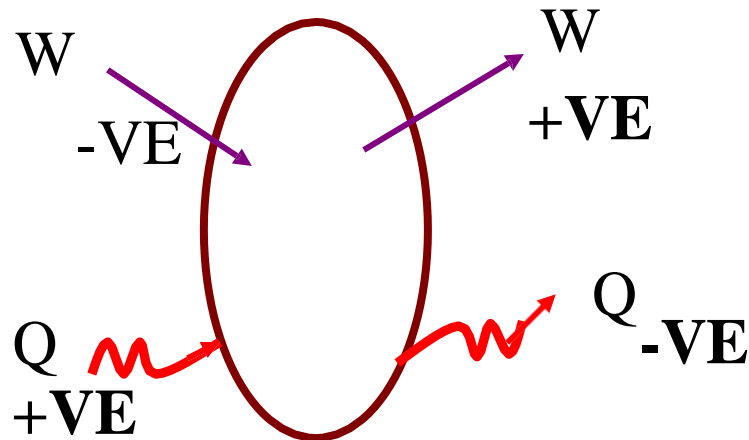
➤ We require a combination of processes.

➤ Sustainability is ensured from a cycle

➤ A system is said to have gone through a cycle if the initial state has been regained after a series of processes

# SIGN CONVENTIONS

- **Work done BY the system is +ve**
- **Obviously work done ON the system is -ve**
- **Heat given TO the system is +ve**
- **Obviously Heat rejected by the system is -ve**



# Types of Work Interaction

## Types of work interaction

- **Expansion and compression work (displacement work)**
- **Work of a reversible chemical cell**
- **Work in stretching of a liquid surface**
- **Work done on elastic solids**
- **Work of polarization and magnetization**

- **All temperature changes need not be due to heat alone**

**eg: Friction**

- **All heat interaction need not result in changes in temperature eg: condensation or evaporation**

# VARIOUS TYPES OF WORK

➤ **Displacement work (pdV work)**

➤ **Force exerted,  $F = p \cdot A$**

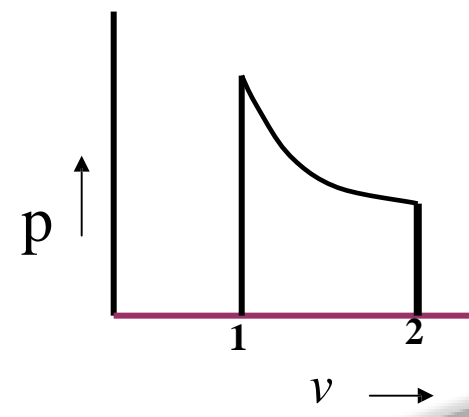
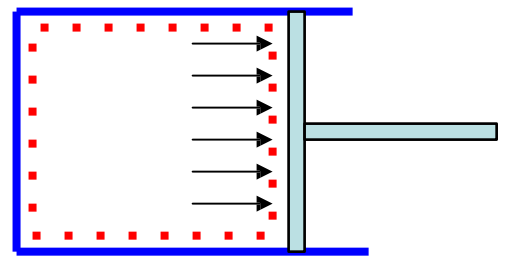
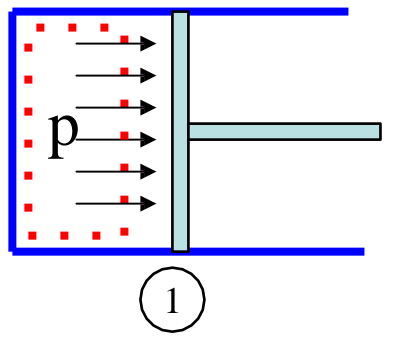
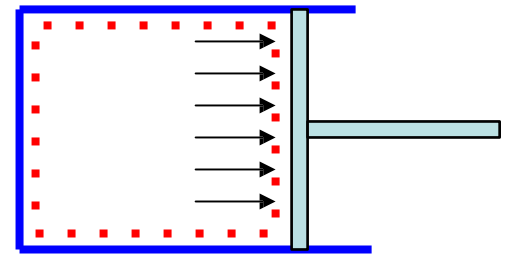
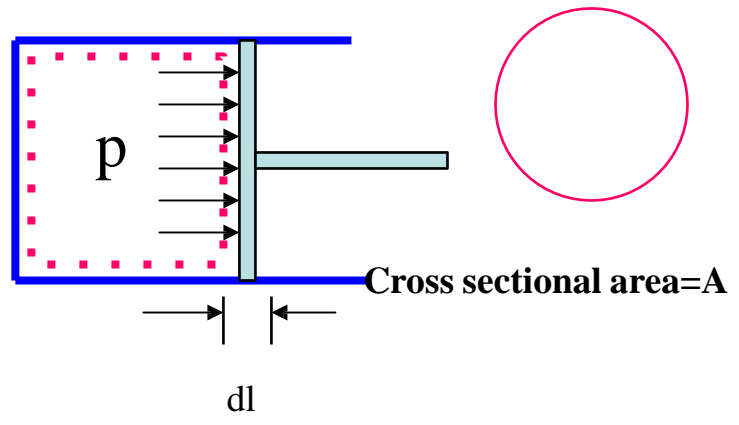
➤ **Work done**

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

➤ **If the piston moves through a finite distance say 1-2, Then work done has to be evaluated by integrating**

$$\int W = \int p dV$$

# Work (Contd...)

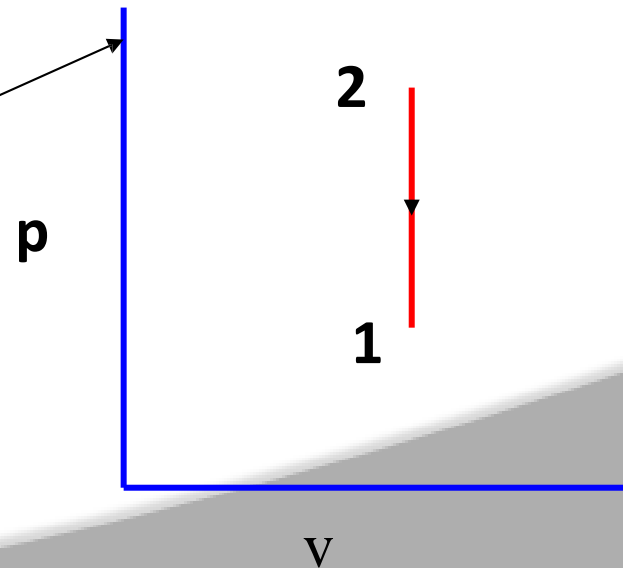
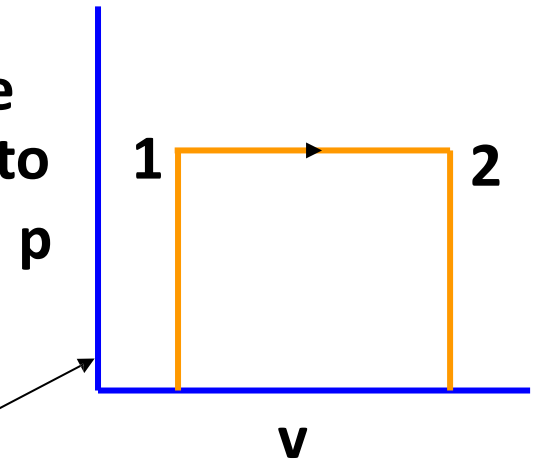


# DISCUSSION ON WORK CALCULATION

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:

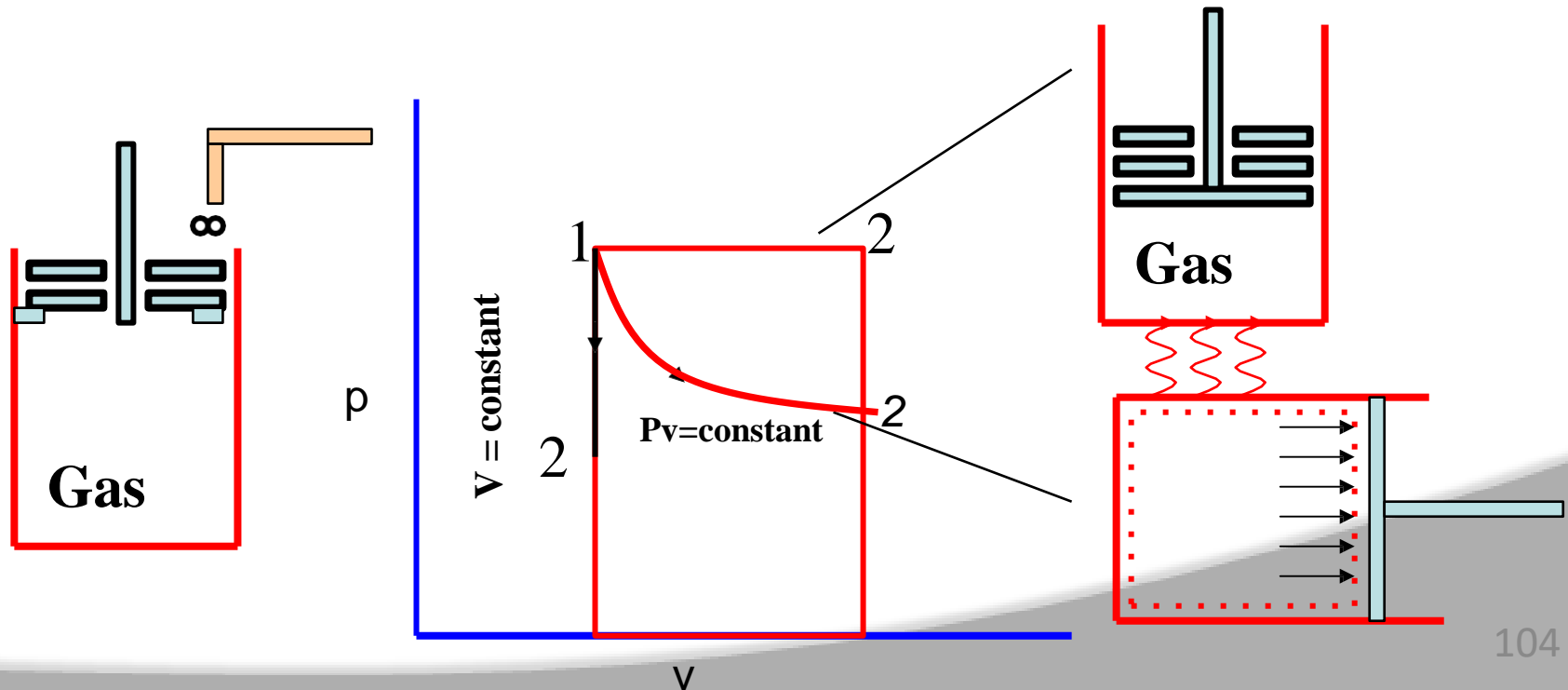
- Pressure might have remained constant  
or
  - It might have undergone a change as per a relation  $p(V)$   
or
  - The volume might have remained constant
- In general the area under the process on  $p$ - $V$  plane gives the work



# OTHER POSSIBLE PROCESS

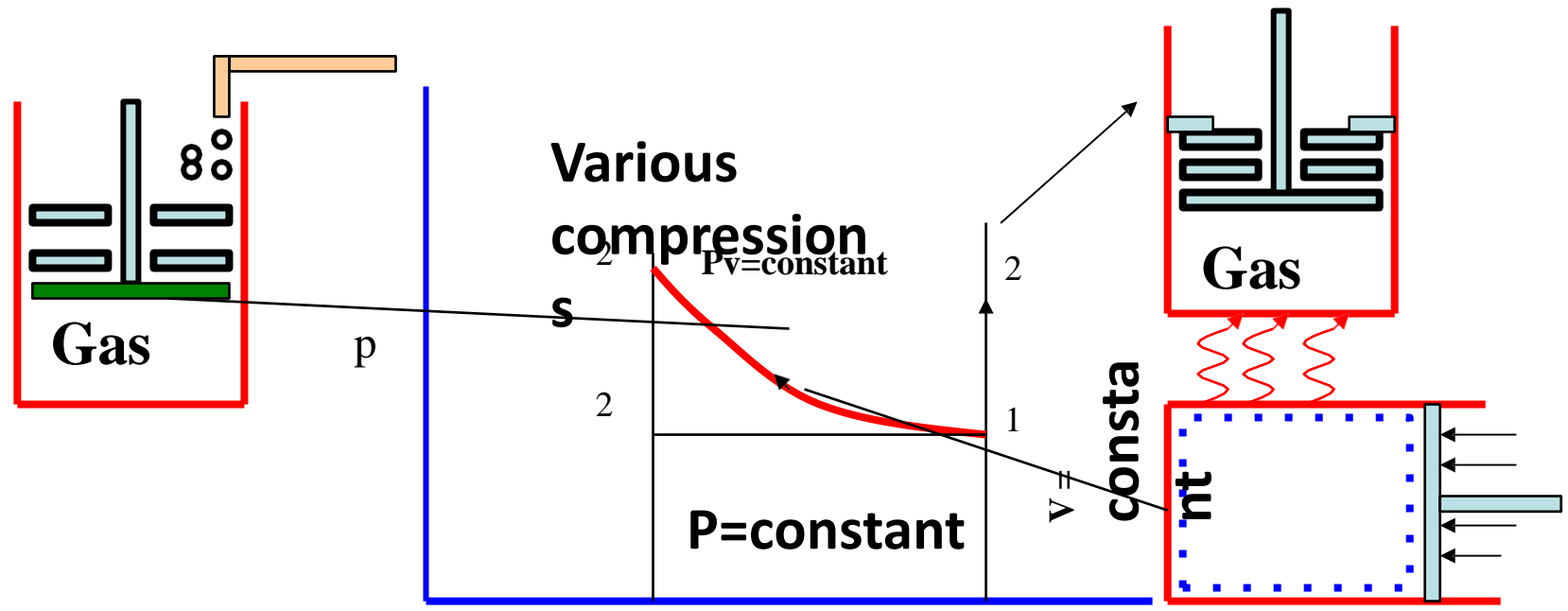
- $pV = \text{constant}$  (it will be a rectangular hyperbola)
- In general  $pV^n = \text{constant}$

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





# OTHER POSSIBLE PROCESS



- $n=0$  Constant pressure  
( $V_2 > V_1$  - expansion)
- $n=1$   $p_v = \text{constant}$   
( $p_2 < p_1$  ;  $V_2 > V_1$  - expansion) ( $p_2 < p_1$  - cooling)
- $n = ?$  Constant volume

# 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  $dA$ .  $dW = \gamma dA$

where  $\gamma$  is the surface tension.

## THE SECOND LAW OF THERMODYNAMICS

# SECOND LAW OF THERMODYNAMICS

**The second law of thermodynamics states that processes occur in a certain direction, not in just any direction. Physical processes in nature can proceed toward equilibrium spontaneously:**

**Water flows down a waterfall.**

**Gases expand from a high pressure to a low pressure.**

**Heat flows from a high temperature to a low temperature.**

**Once it has taken place, a spontaneous process can be reversed, but it will not reverse itself spontaneously. Some external inputs, energy, must be expended to reverse the process.**

# SECOND LAW OF THERMODYNAMICS

**The first law is concerned with the conversion of energy from one form to another. Joule's experiments showed that energy in the form of heat could not be completely converted into work; however, work energy can be completely converted into heat energy. Evidently heat and work are not completely interchangeable forms of energy. Furthermore, when energy is transferred from one form to another, there is often a degradation of the supplied energy into a less “useful” form. We shall see that it is the second law of thermodynamics that controls the direction processes may take and how much heat is converted into work.**

# HEAT (THERMAL) RESERVOIR

## Some Definitions

- **To express the second law in a workable form, we need the following definitions.**
- **Heat (thermal) reservoir**
- **A heat reservoir is a sufficiently large system in stable equilibrium to which and from which finite amounts of heat can be transferred without any change in its temperature.**
- **A high temperature heat reservoir from which heat is transferred is sometimes called a heat source. A low temperature heat reservoir to which heat is transferred is sometimes called a heat sink.**

# WORK RESERVOIR THERMODYNAMIC CYCLE

## **Work reservoir:**

**A work reservoir is a sufficiently large system in stable equilibrium to which and from which finite amounts of work can be transferred adiabatically without any change in its pressure.**

## **Thermodynamic cycle :**

**A system has completed a thermodynamic cycle when the system undergoes a series of processes and then returns to its original state, so that the properties of the system at the end of the cycle are the same as at its beginning.**

**Thus, for whole numbers of cycles**

# HEAT ENGINE

## Heat engine

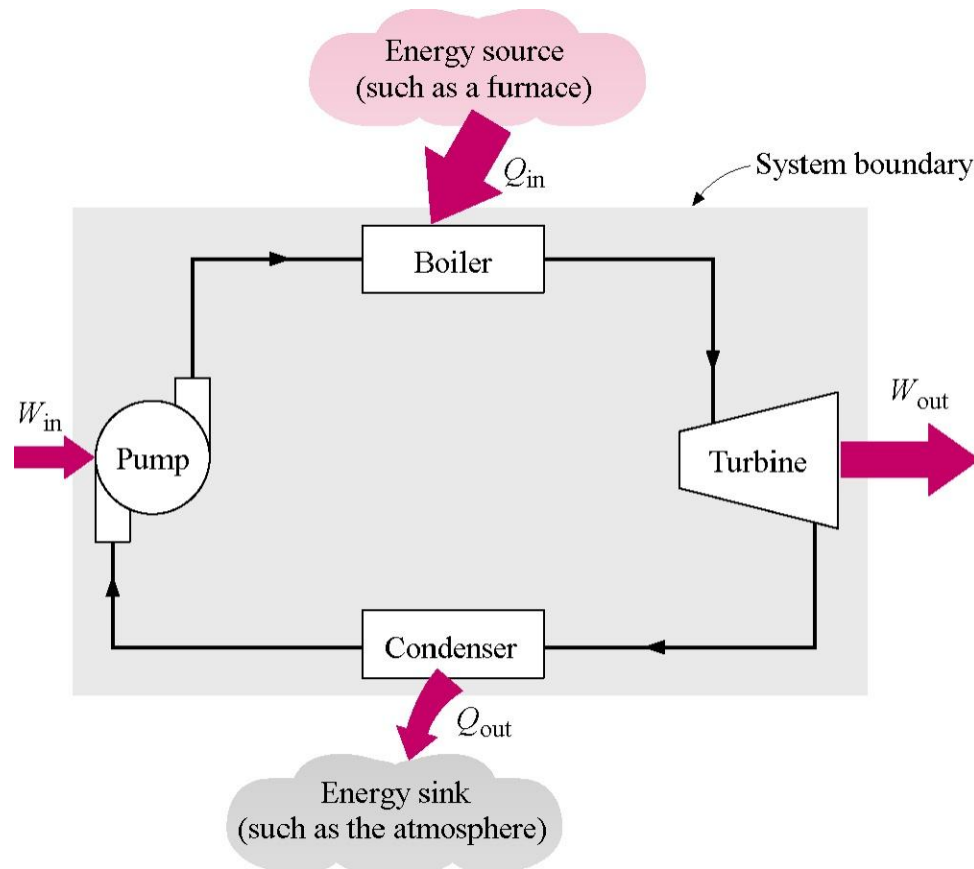
**A heat engine is a thermodynamic system operating in a thermodynamic cycle to which net heat is transferred and from which net work is delivered.**

**The system, or working fluid, undergoes a series of processes that constitute the heat engine cycle.**



# HEAT ENGINE

The following figure illustrates a steam power plant as a heat engine operating in a thermodynamic cycle.



# THERMAL EFFICIENCY,

## Thermal Efficiency, $\eta_{th}$

The thermal efficiency is the index of performance of a work-producing device or a heat engine and is defined by the ratio of the net work output (the desired result) to the heat input (the costs to obtain the desired result).

For a heat engine the desired result is the net work done and the input is the heat supplied to make the cycle operate. The thermal efficiency is always less than 1 or less than 100 percent.

$$\eta_{th} = \frac{W_{net, out}}{Q_{in}}$$

# THERMAL EFFICIENCY

where

$$W_{net, out} = W_{out} - W_{in}$$

$$Q_{in} \neq Q_{net}$$

Here the use of the *in* and *out* subscripts means to use the magnitude (take the positive value) of either the work or heat transfer and let the minus sign in the net expression take care of the direction.

↗ 0 (Cyclic)

Now apply the first law to the cyclic heat engine.

$$Q_{net, in} - W_{net, out} = \Delta U$$

$$W_{net, out} = Q_{net, in}$$

$$W_{net, out} = Q_{in} - Q_{out}$$

The cycle thermal efficiency may be written as

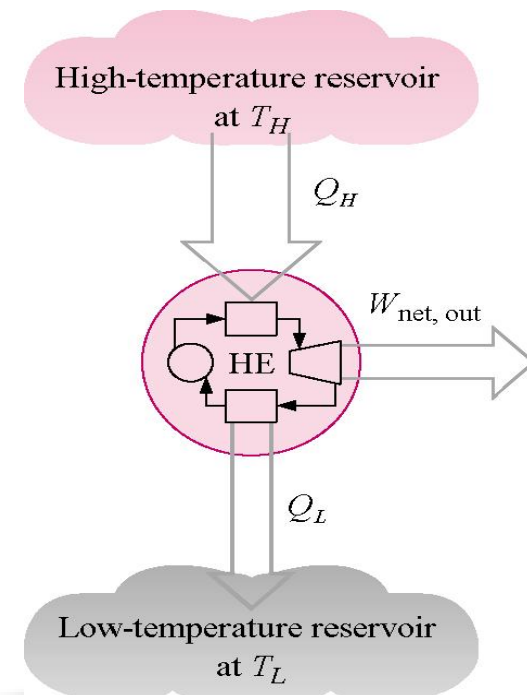
# THERMAL EFFICIENCY

$$\begin{aligned}\eta_{th} &= \frac{W_{net, out}}{Q_{in}} \\ &= \frac{Q_{in} - Q_{out}}{Q_{in}} \\ &= 1 - \frac{Q_{out}}{Q_{in}}\end{aligned}$$

Cyclic devices such as heat engines, refrigerators, and heat pumps often operate between a high-temperature reservoir at temperature  $T_H$  and a low-temperature reservoir at temperature  $T_L$ .

The thermal efficiency of the above device becomes

$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$



## Example

A steam power plant produces 50 MW of net work while burning fuel to produce 150 MW of heat energy at the high temperature. Determine the cycle thermal efficiency and the heat rejected by the cycle to the surroundings.

$$\eta_{th} = \frac{W_{net, out}}{Q_H}$$

$$= \frac{50 \text{ MW}}{150 \text{ MW}} = 0.333 \quad \text{or} \quad 33.3\%$$

$$W_{net, out} = Q_H - Q_L$$

$$Q_L = Q_H - W_{net, out}$$

$$= 150 \text{ MW} - 50 \text{ MW}$$

$$= 100 \text{ MW}$$

# HEAT PUMP

## Heat Pump

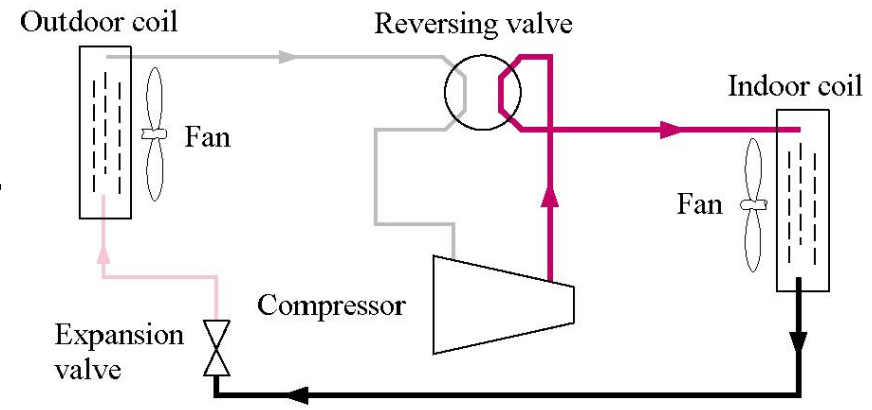
**A heat pump is a thermodynamic system operating in a thermodynamic cycle that removes heat from a low-temperature body and delivers heat to a high-temperature body. To accomplish this energy transfer, the heat pump receives external energy in the form of work or heat from the surroundings.**

**While the name “heat pump” is the thermodynamic term used to describe a cyclic device that allows the transfer of heat energy from a low temperature to a higher temperature, we use the terms “refrigerator” and “heat pump” to apply to particular devices**

# HEAT PUMP SYSTEMS

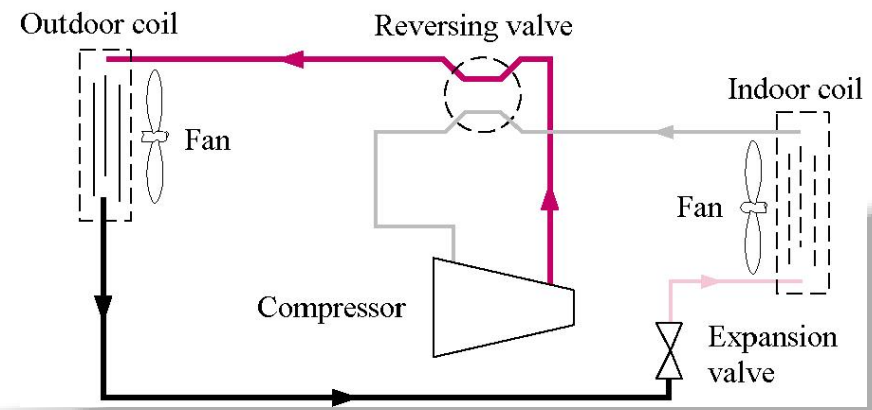
A typical heat pump system is shown here. In the heating mode high pressure vapor refrigerant is sent to the indoor heat exchanger coil. The refrigerant gives up its energy to the inside air and condenses to a liquid. The liquid is throttled to a low pressure and temperature to the outdoor coil and receives energy from the from the outside air. The refrigerant vaporizes, enters the compressor to be compressed to the high pressure, and the cycle is completed.

HEAT PUMP OPERATION – HEATING MODE



- High-pressure liquid
- Low-pressure liquid-vapor
- Low-pressure vapor
- High-pressure vapor

HEAT PUMP OPERATION – COOLING MODE



# Coefficient of Performance, COP

## Coefficient of Performance, COP

The index of performance of a refrigerator or heat pump is expressed in terms of the coefficient of performance, COP, the ratio of desired result to input. This measure of performance may be larger than 1, and we want the COP to be as large as possible.

$$COP = \frac{\text{Desired Result}}{\text{Required Input}}$$



# Parameters of Performance and Second Law Statements

## Heat Pump and Air Conditioner Ratings

Heat pumps and air conditioners are rated using the SEER system. SEER is the seasonal adjusted energy efficiency (bad term for HP and A/C devices) rating. The SEER rating is the amount of heating (cooling) on a seasonal basis in Btu/hr per unit rate of power expended in watts, W.

The heat transfer rate is often given in terms of tons of heating or cooling. One ton equals  $12,000 \text{ Btu/hr} = 211 \text{ kJ/min}$ .

A discussion on how to maintain the SEER rating of heat pumps and air conditioners may be found at

# SECOND LAW STATEMENTS & KELVIN-PLANCK STATEMENT

## Second Law Statements

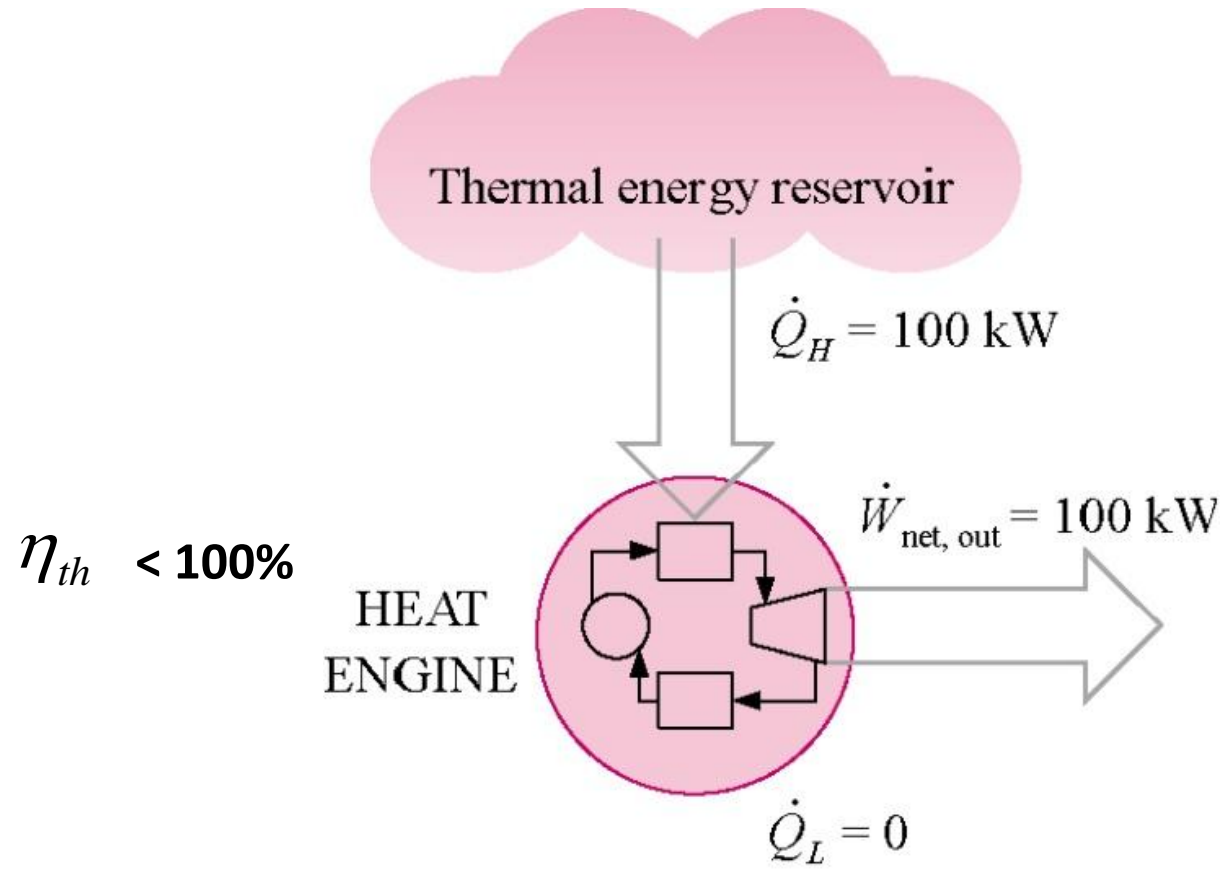
The second law of thermodynamics states that the total entropy of an isolated system can never decrease over time. The total entropy of a system and its surroundings can remain constant in ideal cases where the system is in thermodynamic equilibrium, or is undergoing a (fictive) reversible process.

## **Kelvin-Planck statement of the second law**

**It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work.**

**The Kelvin-Planck statement of the second law of thermodynamics states that no heat engine can produce a net amount of work while exchanging heat with a single reservoir only. In other words, the maximum possible efficiency is less than 100 percent.**

# KELVIN-PLANCK STATEMENT OF THE SECOND LAW



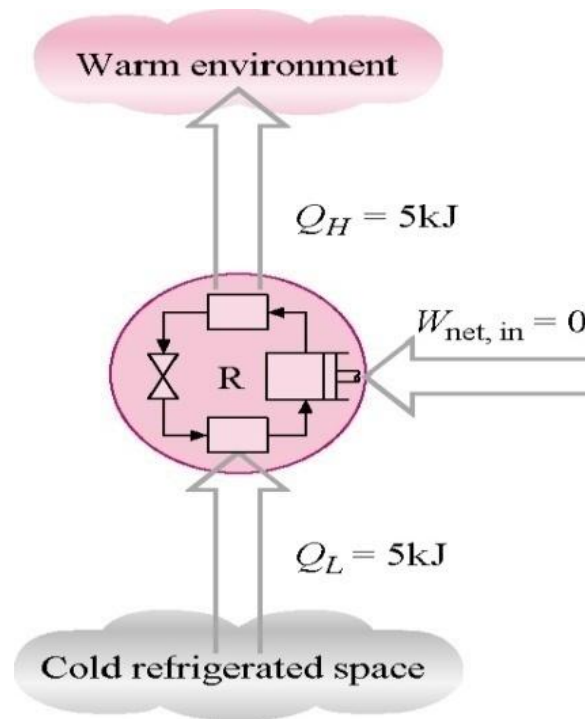
**Heat engine that violates the Kelvin-Planck statement of the second law**

# CLAUSIUS STATEMENT OF THE SECOND LAW

## Clausius statement of the second law

The Clausius statement of the second law states that it is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.

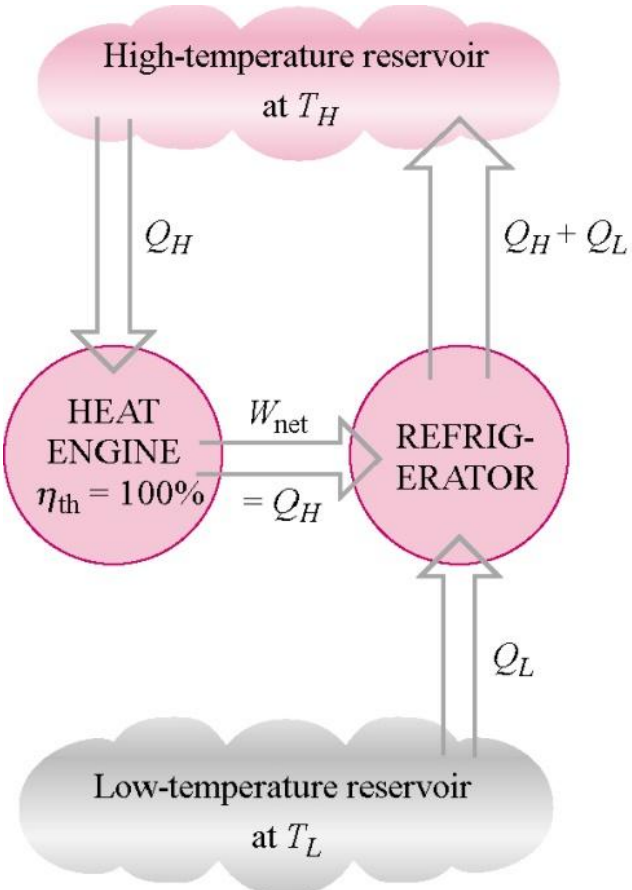
# CLAUSIUS STATEMENT OF THE SECOND LAW



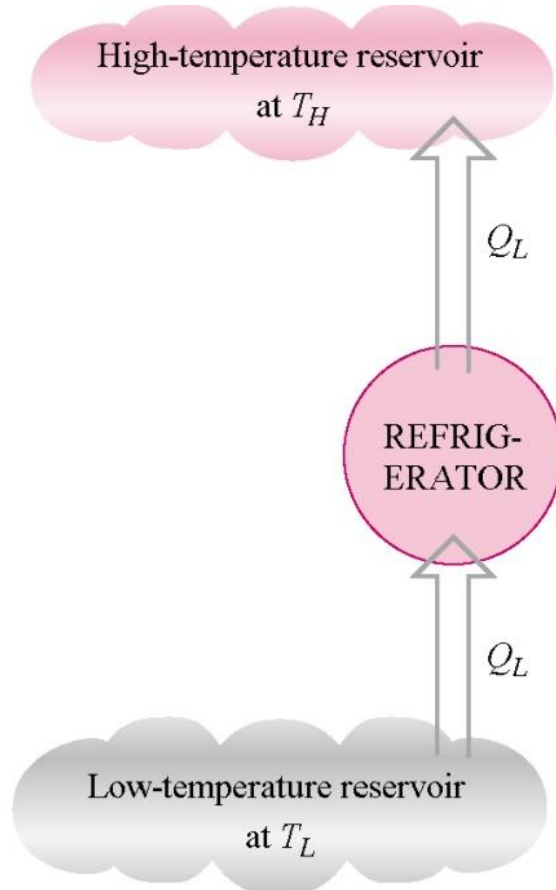
# CLAUSIUS STATEMENT OF THE SECOND LAW

A violation of either the Kelvin-Planck or Clausius statements of the second law implies a violation of the other. Assume that the heat engine shown below is violating the Kelvin-Planck statement by absorbing heat from a single reservoir and producing an equal amount of work  $W$ . The output of the engine drives a heat pump that transfers an amount of heat  $Q_L$  from the low-temperature thermal reservoir and an amount of heat  $Q_H + Q_L$  to the high-temperature thermal reservoir. The combination of the heat engine and refrigerator in the left figure acts like a heat pump that transfers heat  $Q_L$  from the low-temperature reservoir without any external energy input

# CLAUSIUS STATEMENT OF THE SECOND LAW



(a) A refrigerator which is powered by a 100% efficient heat engine



(b) The equivalent refrigerator



## Perpetual-Motion Machines

**Any device that violates the first or second law of thermodynamics is called a perpetual-motion machine. If the device violates the first law, it is a perpetual-motion machine of the first kind. If the device violates the second law, it is a perpetual-motion machine of the second kind.**

## Reversible Processes

**A reversible process is a quasi-equilibrium, or quasi-static, process with a more restrictive requirement.**

# REVERSIBLE PROCESS

## **Internally reversible process**

The internally reversible process is a quasi-equilibrium process, which, once having taken place, can be reversed and in so doing leave no change in the system. This says nothing about what happens to the surroundings about the system.

## **Totally or externally reversible process**

The externally reversible process is a quasi-equilibrium process, which, once having taken place, can be reversed and in so doing leave no change in the system or surroundings.

# IRREVERSIBLE PROCESS

## Irreversible Process

**An irreversible process is a process that is not reversible.**

**All real processes are irreversible. Irreversible processes occur because of the following:**

**Friction**

**Unrestrained expansion of gases**

**Heat transfer through a finite temperature difference**

**Mixing of two different substances**

**Hysteresis effects**

**$I^2R$  losses in electrical circuits**

# CARNOT CYCLE

## The Carnot Cycle

French military engineer Nicolas Sadi Carnot (1769-1832) was among the first to study the principles of the second law of thermodynamics. Carnot was the first to introduce the concept of cyclic operation and devised a reversible cycle that is composed of four reversible processes, two isothermal and two adiabatic.

Process 1-2: Reversible isothermal heat addition at high temperature,  $T_H > T_L$ , to the working fluid in a piston-cylinder device that does some boundary work.

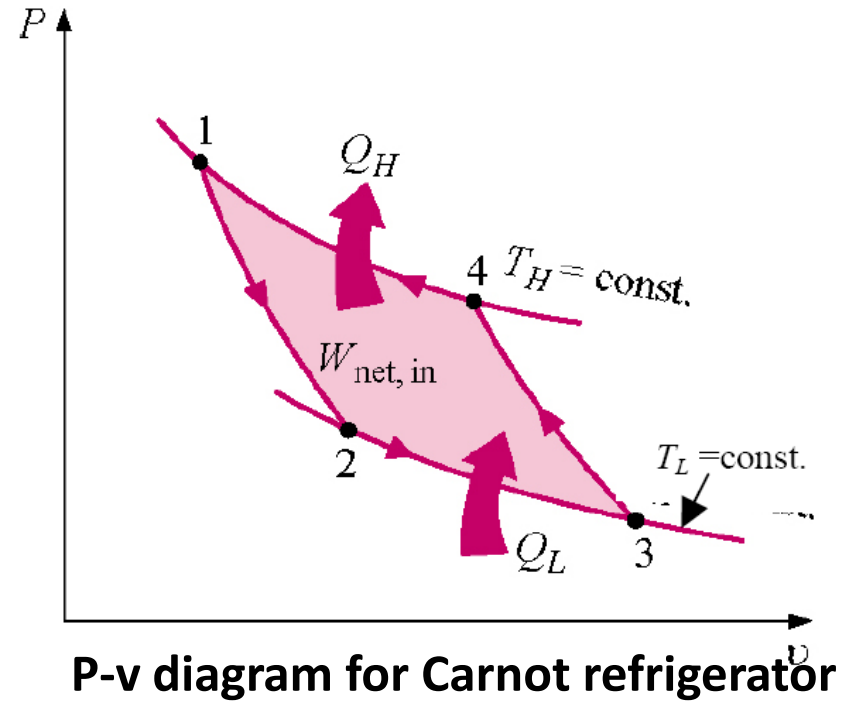
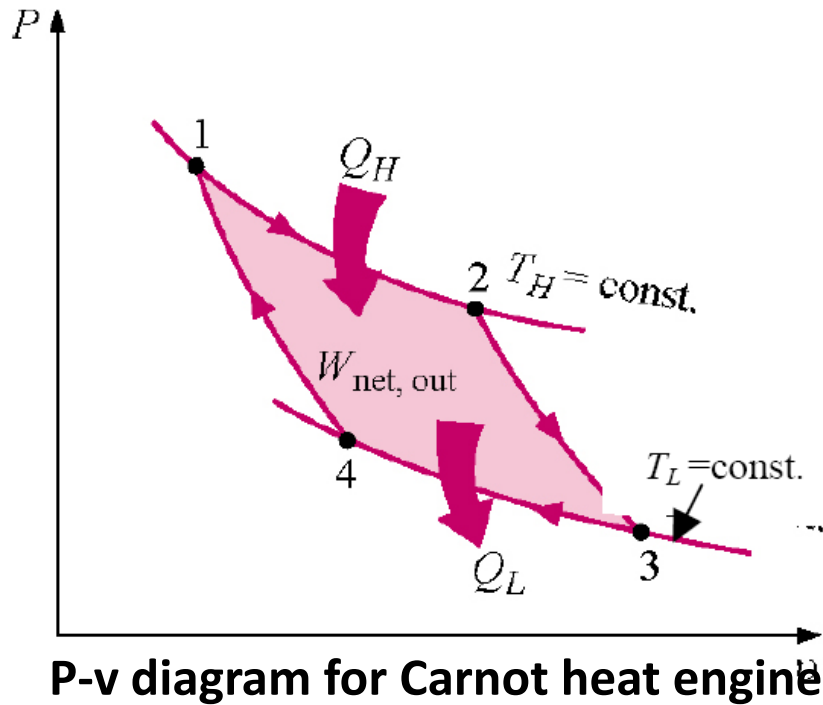
# CARNOT CYCLE

## Carnot Cycle

**Process 3-4:** The system is brought in contact with a heat reservoir at  $T_L < T_H$  and a reversible isothermal heat exchange takes place while work of compression is done on the system.

**Process 4-1:** A Reversible adiabatic compression process increases the working fluid temperature from  $T_L$  to  $T_H$

# CARNOT CYCLE



You may have observed that power cycles operate in the clockwise direction when plotted on a process diagram. The Carnot cycle may be reversed, in which it operates as a refrigerator. The refrigeration cycle operates in the counterclockwise direction.

# CARNOT PRINCIPLE

## Carnot Principles

The second law of thermodynamics puts limits on the operation of cyclic devices as expressed by the Kelvin-Planck and Clausius statements. A heat engine cannot operate by exchanging heat with a single heat reservoir, and a refrigerator cannot operate without net work input from an external source.

$$\eta_{th} < \eta_{th, Carnot}$$

Consider heat engines operating between two fixed temperature reservoirs at  $T_H > T_L$ . We draw two conclusions about the thermal efficiency of reversible and irreversible heat engines, known as the Carnot principles.



# CARNOT PRINCIPLE

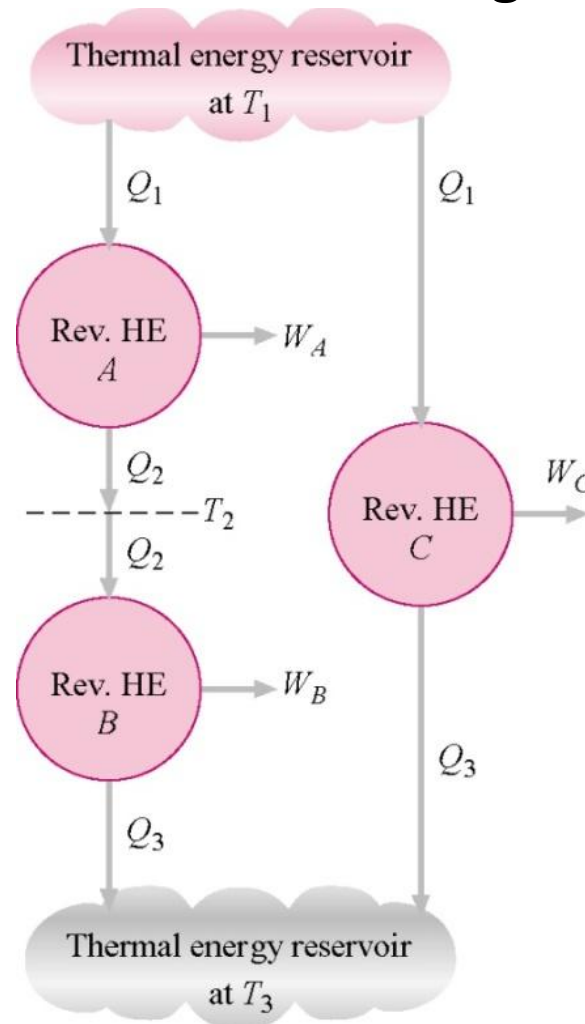
**(a) The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs.**

**(b) The efficiencies of all reversible heat engines operating between the same two constant-temperature heat reservoirs have the same efficiency.**

**As the result of the above, Lord Kelvin in 1848 used energy as a thermodynamic property to define temperature and devised a temperature scale that is independent of the thermodynamic substance.**

# LORD KELVIN'S CARNOT HEAT ENGINE ARRANGEMENT.

The following is Lord Kelvin's Carnot heat engine arrangement.



# LORD KELVIN'S CARNOT HEAT ENGINE ARRANGEMENT.

Since the thermal efficiency in general is  $\eta_{th} = 1 - \frac{Q_L}{Q_H}$

For the Carnot engine, this can be written as  $\eta_{th} = g(T_L, T_H) = 1 - f(T_L, T_H)$

Considering engines A, B, and C  $\frac{Q_1}{Q_3} = \frac{Q_1}{Q_2} \frac{Q_2}{Q_3}$

This looks like  $f(T_1, T_3) = f(T_1, T_2) f(T_2, T_3)$

# LORD KELVIN'S CARNOT HEAT ENGINE ARRANGEMENT.

One way to define the  $f$  function is

$$f(T_1, T_3) = \frac{\theta(T_2)}{\theta(T_1)} \frac{\theta(T_3)}{\theta(T_2)} = \frac{\theta(T_3)}{\theta(T_1)}$$

The simplest form of  $\theta$  is the absolute temperature itself.

$$f(T_1, T_3) = \frac{T_3}{T_1}$$

The Carnot thermal efficiency becomes

$$\eta_{th, rev} = 1 - \frac{T_L}{T_H}$$

This is the maximum possible efficiency of a heat engine operating between two heat reservoirs at temperatures  $T_H$  and  $T_L$ . Note that the temperatures are absolute temperatures.

# LORD KELVIN'S CARNOT HEAT ENGINE ARRANGEMENT.

These statements form the basis for establishing an absolute temperature scale, also called the Kelvin scale, related to the heat transfers between a reversible device and the high- and low-temperature heat reservoirs by

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

Then the  $Q_H/Q_L$  ratio can be replaced by  $T_H/T_L$  for reversible devices, where  $T_H$  and  $T_L$  are the absolute temperatures of the high- and low-temperature heat reservoirs, respectively. This result is only valid for heat exchange across a heat engine operating between two constant temperature heat reservoirs. These results do not apply when the heat exchange is occurring with heat sources and sinks that do not have constant temperature.

## Reversed Carnot Device Coefficient of Performance

If the Carnot device is caused to operate in the reversed cycle, the reversible heat pump is created. The COP of reversible refrigerators and heat pumps are given in a similar manner to that of the Carnot

heat engine as

$$\begin{aligned}
 COP_R &= \frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1} \\
 &= \frac{T_L}{T_H - T_L} = \frac{1}{\frac{T_H}{T_L} - 1}
 \end{aligned}$$

$$\begin{aligned}
 COP_{HP} &= \frac{Q_H}{Q_H - Q_L} = \frac{\frac{Q_H}{Q_L}}{\frac{Q_H}{Q_L} - 1} \\
 &= \frac{T_H}{T_H - T_L} = \frac{\frac{T_H}{T_L}}{\frac{T_H}{T_L} - 1}
 \end{aligned}$$

**Again, these are the maximum possible COPs for a refrigerator or a heat pump operating between the temperature limits of  $T_H$  and  $T_L$ .**

**The coefficients of performance of actual and reversible (such as Carnot) refrigerators operating between the same temperature limits compare as follows:**

**A similar relation can be obtained for heat pumps by replacing all values of  $\text{COP}_R$  by  $\text{COP}_{HP}$  in the above relation.**

## Example Carnot engine

A Carnot heat engine receives 500 kJ of heat per cycle from a high-temperature heat reservoir at  $652^{\circ}\text{C}$  and rejects heat to a low-temperature heat reservoir at  $30^{\circ}\text{C}$ . Determine

- a. b.

(a) The thermal efficiency of this Carnot engine.

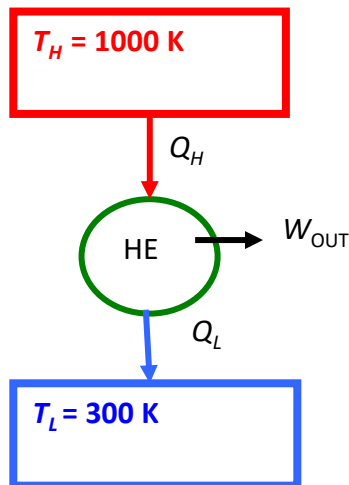
(b) The amount of heat rejected to the low-temperature

heat reservoir.



# Example Carnot engine

An inventor claims to have invented a heat engine that develops a thermal efficiency of 80 percent when operating between two heat reservoirs at 1000 K and 300 K. Evaluate his claim.

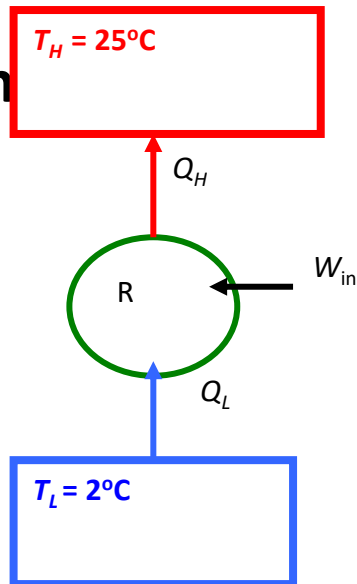


$$\begin{aligned}
 \eta_{th, rev} &= 1 - \frac{T_L}{T_H} \\
 &= 1 - \frac{300K}{1000K} \\
 &= 0.70 \quad \text{or} \quad 70\%
 \end{aligned}$$

The claim is false since no heat engine may be more efficient than a Carnot engine operating between the heat reservoirs.

# Example Carnot engine

An inventor claims to have developed a refrigerator that maintains the refrigerated space at  $2^{\circ}\text{C}$  while operating in a room where the temperature is  $25^{\circ}\text{C}$  and has a COP of 13.5. Is there any truth to his claim

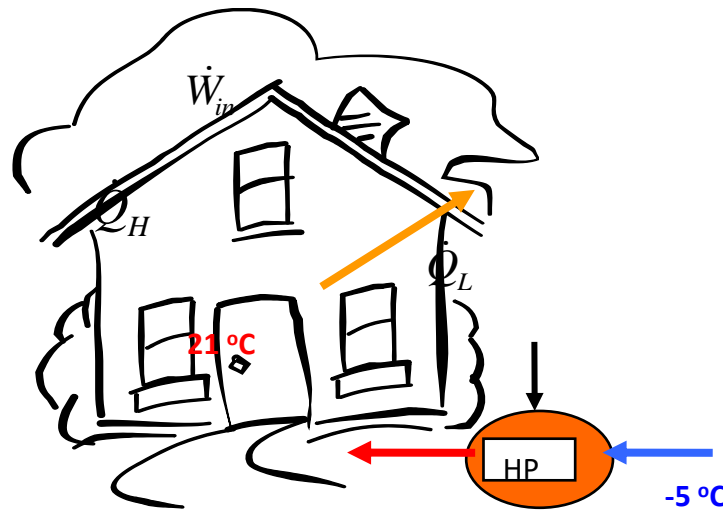


$$\begin{aligned}
 COP_R &= \frac{Q_L}{Q_H - Q_L} = \frac{T_L}{T_H - T_L} \\
 &= \frac{(2 + 273) K}{(25 - 2) K} \\
 &= 11.96
 \end{aligned}$$

The claim is false since no refrigerator may have a COP larger than the COP for the reversed Carnot device.

## Example Carnot engine

A heat pump is to be used to heat a building during the winter. The building is to be maintained at  $21^{\circ}\text{C}$  at all times. The building is estimated to be losing heat at a rate of  $135,000 \text{ kJ/h}$  when the outside temperature drops to  $-5^{\circ}\text{C}$ . Determine the minimum power required to drive the heat pump unit for this outside temperature.



The heat lost by the building has to be supplied by the heat pump.

# Example Carnot engine

$$\dot{Q}_H = \dot{Q}_{Lost} = 135000 \frac{kJ}{h}$$

$$\begin{aligned} COP_{HP} &= \frac{\dot{Q}_H}{\dot{Q}_H - \dot{Q}_L} = \frac{T_H}{T_H - T_L} \\ &= \frac{(21 + 273)K}{(21 - (-5))K} \\ &= 11.31 \end{aligned}$$

Using the basic definition of the COP

$$COP_{HP} = \frac{\dot{Q}_H}{\dot{W}_{net, in}}$$

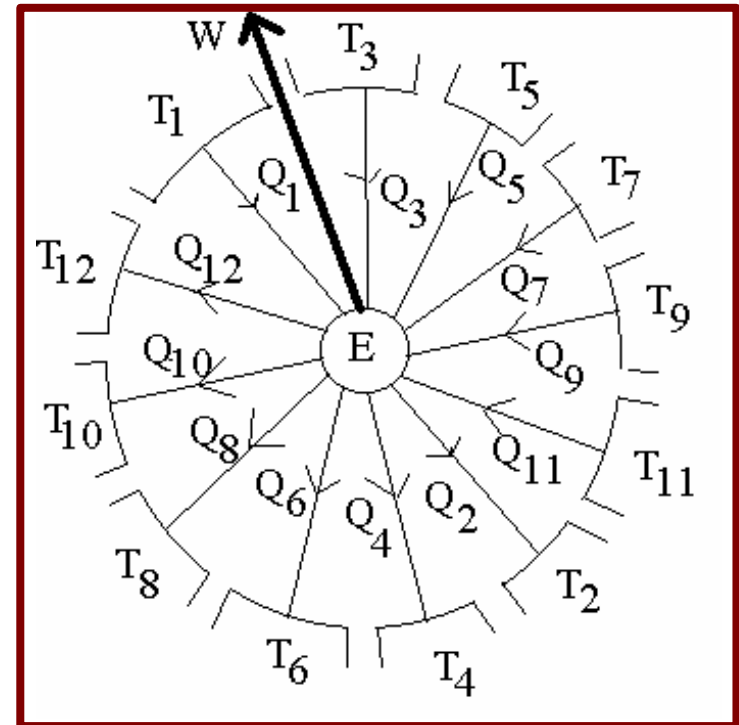
$$\dot{W}_{net, in} = \frac{\dot{Q}_H}{COP_{HP}}$$

$$\begin{aligned} &= \frac{135,000 kJ / h}{11.31} \frac{1h}{3600s} \frac{1kW}{kJ / s} \\ &= 3.316 kW \end{aligned}$$

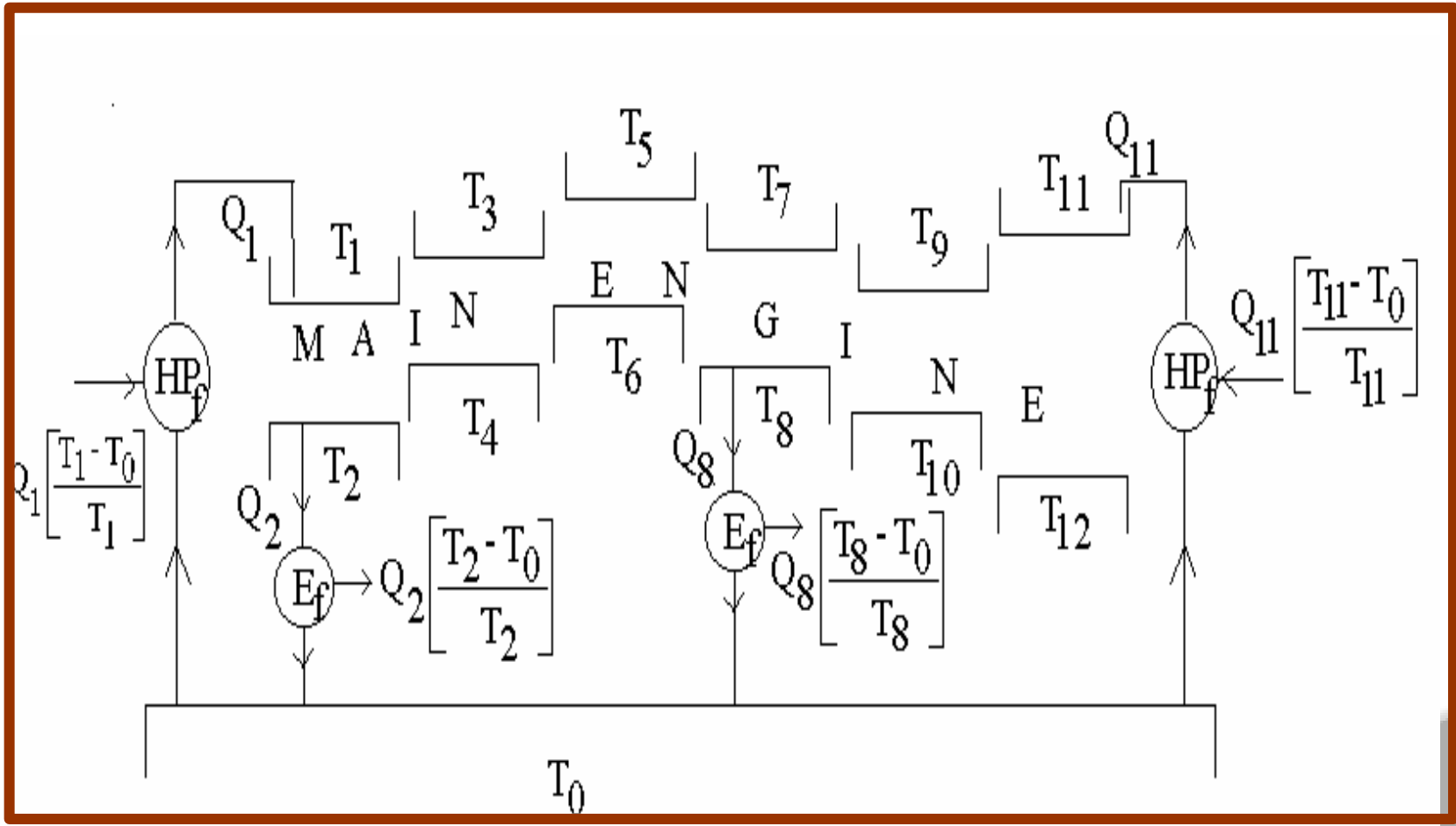
# CLAUSIUS INEQUALITY

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

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....



# CLAUSIUS INEQUALITY (CONTD...)



# CLAUSIUS INEQUALITY (CONTD...)

➤ Sum of work inputs for =

All fictitious heat pumps  $Q_1, Q_3, \dots + Q_1 T_0 / T_1 + Q_3 T_0 / T_3, \dots$

➤ Sum of work outputs of =  $Q_2 + Q_4, \dots - Q_2 T_0 / T_2 - Q_4 T_0 / T_4, \dots$

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

But we know that for the main engine at the centre

- $W = Q_1 + Q_3 - Q_2 - Q_4$  [after taking the sign into account]
- 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

- To  $[Q_1 / T_1 + Q_3 / T_3 \dots - Q_2 / T_2 - Q_4 / T_4 \dots] = 0$
- which implies that  $Q_1 / T_1 + Q_3 / T_3 \dots - Q_2 / T_2 - Q_4 / T_4 \dots = 0$
- In general,  $S(Q/T) = 0$  provided the engine is perfectly reversible.

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

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

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

# CLAUSIUS INEQUALITY (CONTD...)

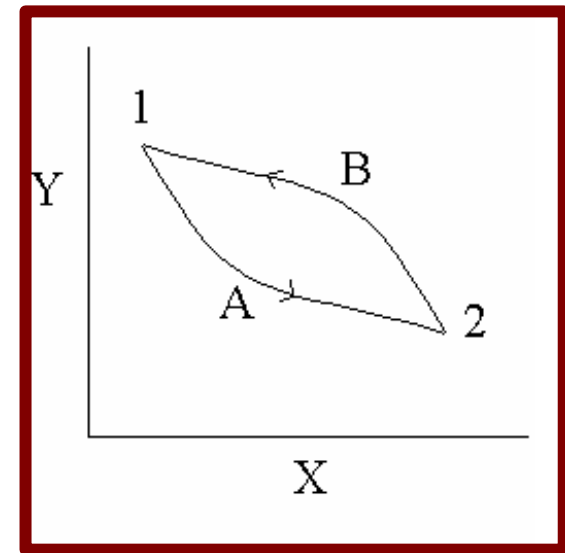
- The cyclic integral is to remind us that II Law holds only for a cycle.
- Note: Equality holds when the cycle is reversible.
- sign will be the most probable one for real cycles.
- Just as we had  $dW = p dV$
- Can we guess that there is something emerging to define Q?

# **MODULE III**

# **PURE SUBSTANCE**

# THE CONCEPT OF ENTROPY

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



# THE CONCEPT OF ENTROPY

- $Q/T) = Q/T \text{ along } 1A2 + Q/T \text{ along } 2B1 = 0$
- If A and B are reversible and  $<0$  if they are not.
- $Q/T \text{ along } 1A2 = -Q/T \text{ along } 2B1$
- $Q/T \text{ along } 1A2 = Q/T \text{ along } 1B2$

# THE CONCEPT OF ENTROPY

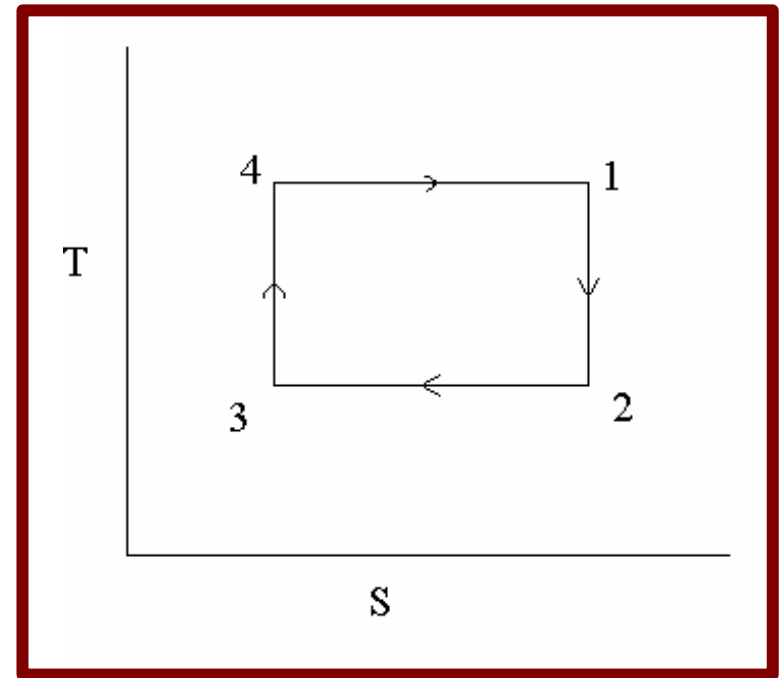
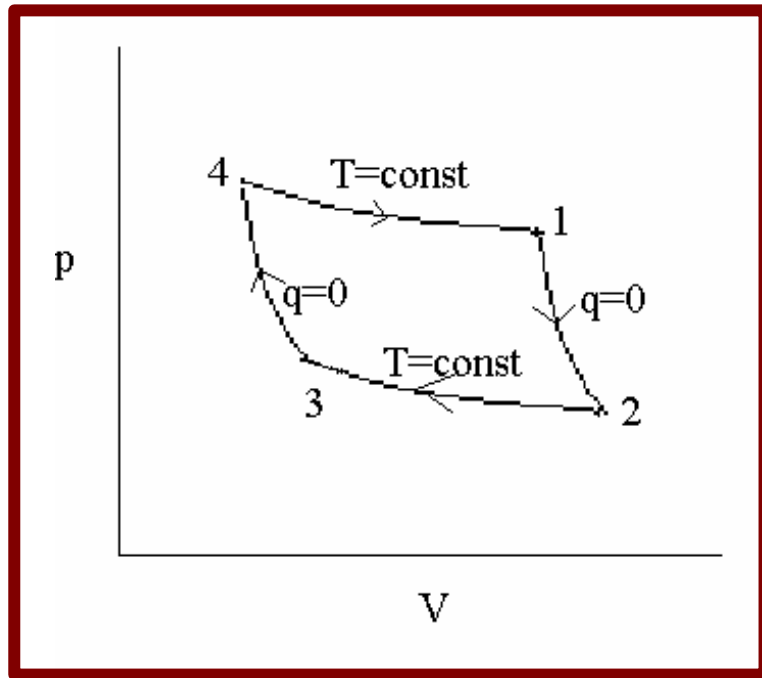
- ❖ In other words the integral remains the same no matter what the path is. It can be simply written as  $S_2 - S_1$ . The value depends only on the end states and not on the path followed. So it is a state function or a property.
- ❖ Like energy entropy ( $s$ ) is also an extensive property. It will 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

## ❖ Lesson learnt.

- Just as we can represent work interactions on P-V plane.
- we can represent heat interactions on T-S plane.
- Naturally, T will be the ordinate and S will be the abscissa.
- All constant temperature lines will be horizontal and constant entropy lines vertical. So Carnot cycle will be just a rectangle.
- ${}^1\int_2 \delta Q / T = S_2 - S_1$  or  ${}^1\int_2 \delta q / T = s_2 - s_1$        $\angle \delta q / T = \delta s$  or  $\delta q = T \delta s$

# The Concept Of Entropy



- ❖ Integrals under P-V plane give work interaction
- ❖ Integrals under T-S plane give heat interactions



# THE CONCEPT OF ENTROPY

- Let us invoke the I law for a process namely  $q=w+du$
- Substitute for  $q=Tds$  and  $w = p dv$   $Tds = pdv +du$
- For a constant volume process we have  $Tds = du... (1)$
- We have by definition
- Differentiating

# THE CONCEPT OF ENTROPY

❖ For a perfect gas  $du = cvdT$  and  $dh = cpdT$

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

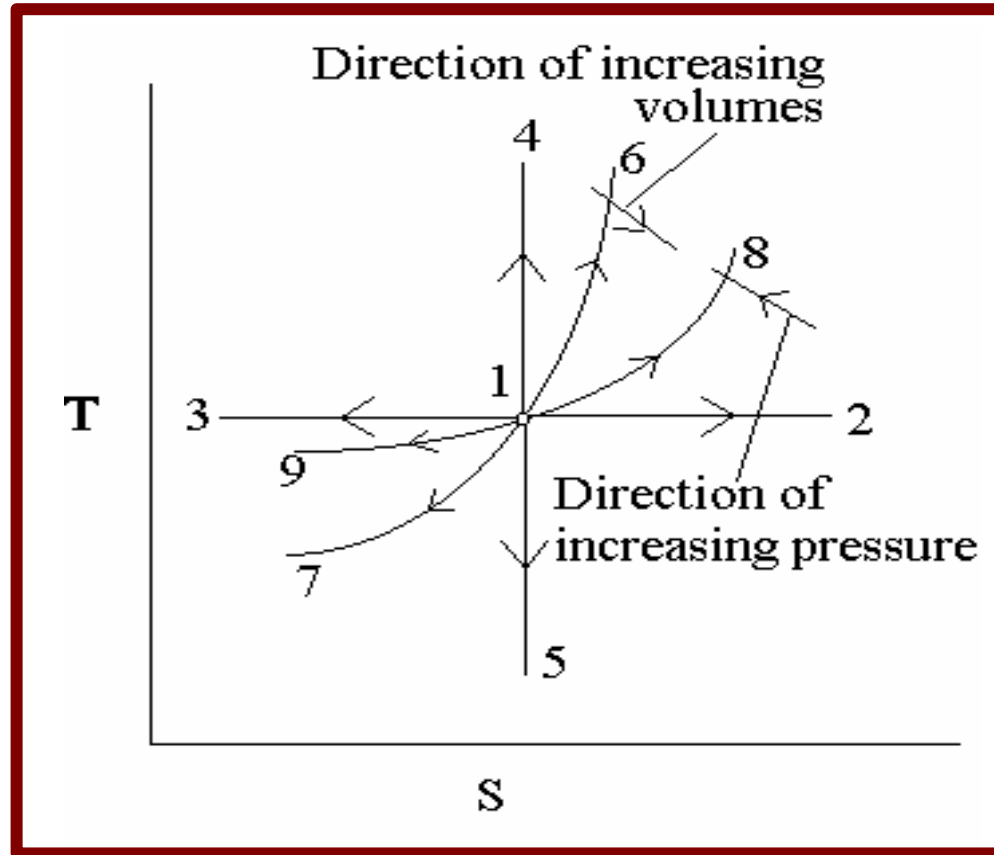
for  $v = \text{const}$   $Tds = cvdT$   $dT/ds|_{v=\text{const}} = T / cv$

for  $p = \text{const}$   $Tds = cpdT$   $dT/ds|_{p=\text{const}} = T / cp$

1. Since  $cp > cv$  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

# THE CONCEPT OF ENTROPY



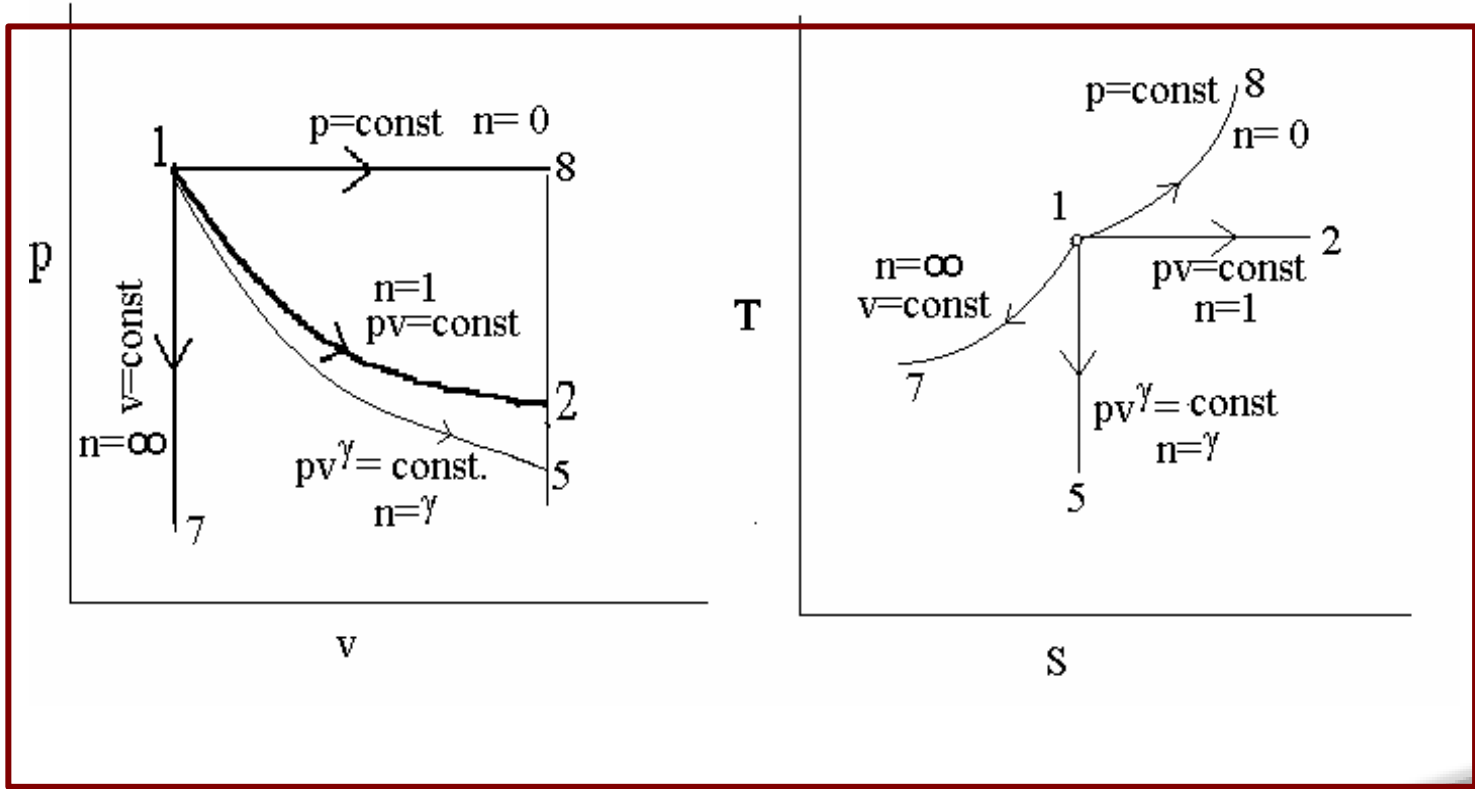
7-1-6 Const V line

9-1-8 Const. p line

# The Concept Of Entropy

	s	T	p	v
<b>1-2 Isothermal expansion</b>	↑	↓	↓	↑
<b>1-3 Isothermal compression</b>	↓	↓	↑	↓
<b>1.4 Isentropic compression</b>	↓	↑	↑	↓
<b>1-5 Isentropic expansion</b>	↓	↓	↓	↑
<b>1-6 Isochoric heating</b>	↑	↑	↑	↓
<b>1-7 Isochoric cooling</b>	↓	↓	↓	↓
<b>1-8 Isobaric heating/expansion</b>	↑	↑	↓	↑
<b>1-9 Isobaric cooling/compression</b>	↓	↓	↓	↓

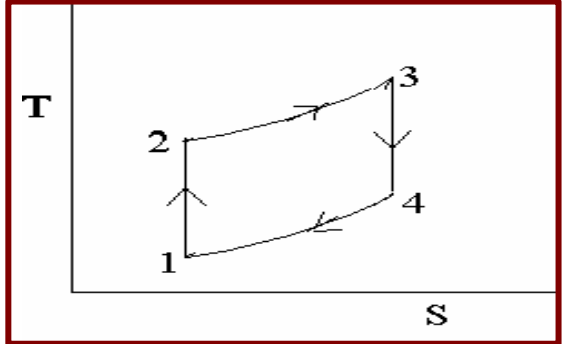
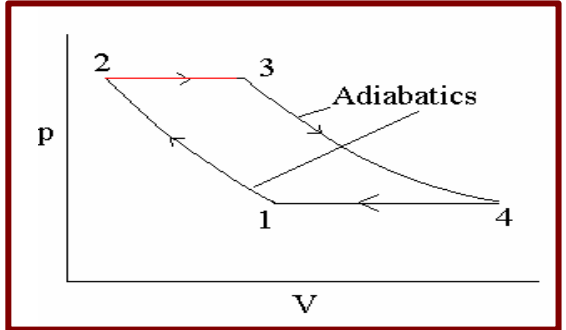
# COMPARISON BETWEEN P-V AND T-S



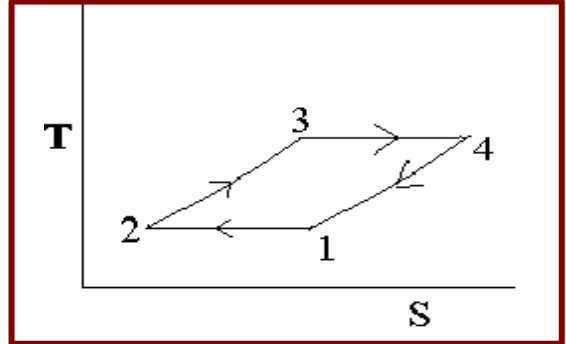
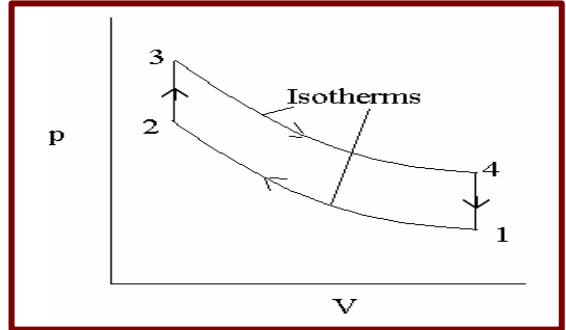
- **A similar comparison can be made for processes going in the other direction as well.**
- **Note that  $n$  refers to general index in  $pvn=\text{const}$ . Note:**
- **For  $1 < n < g$  the end point will lie between 2 and 5**
- **For  $n > g$  the end point will lie between 5 and 7**

# COMPARISON BETWEEN P-V AND T-S PLANES (CONTD...)

## Brayton cycle



## Stirling cycle



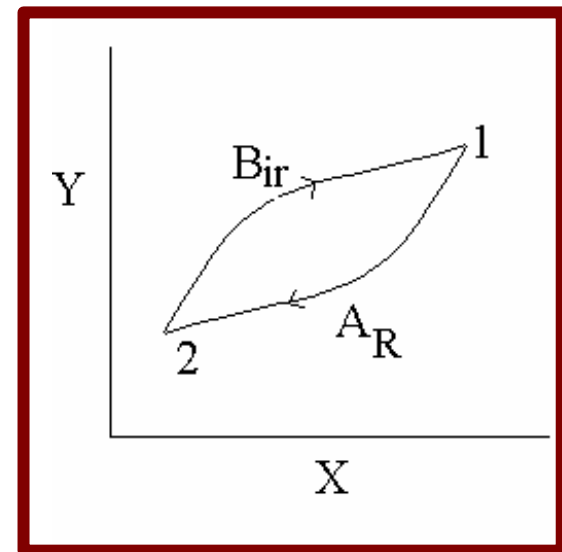
**Note: All work producing cycles will have a clockwise direction even on the T-s plane**

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

Consider the Clausius inequality

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

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





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

## ❖ Applying Clausius inequality

$Q / T_{\text{along } 1A2} + Q / T_{\text{along } 2B1} < 0$  (because the cycle is irreversible < sign applies)

Since A is reversible  $Q / T_{\text{along } 1A2} = S_2 - S_1$   $S_2 - S_1 + Q / T_{\text{along } 2B1} < 0$

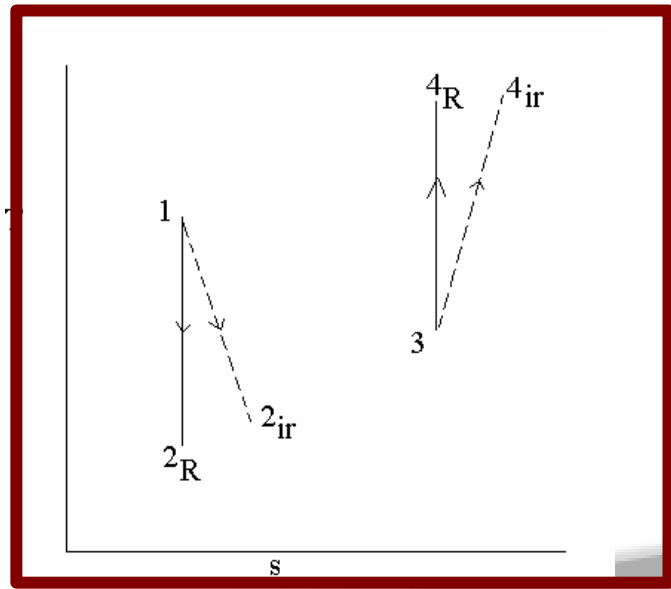
- Implying that  $Q / T_{\text{along } 2B1} < S_1 - S_2$
- Or  $S_1 - S_2 > Q / T_{\text{along } 2B1}$
- Had B also been reversible  $Q / T_{\text{along } 2B1}$  would have been equal to  $S_1 - S_2$

# COMPARISON BETWEEN P-V AND T-S PLANES (CONTD...)

## Moral 1

**(S1-S2) irreversible (S1-S2)reversible**

**An irreversible process generates more entropy than a reversible process.**



# COMPARISON BETWEEN P-V AND T-S PLANES (CONTD...)

- An irreversible engine can't produce more work than a reversible one.
- 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
- 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			$q-w=du$
Rewritten as			$Tds=pdv+cvdT$
1. Constant volume process	$dv=0$		$ds=cvdT/T$
which on integration yields			$s_2-s_1=$
			$cv\ln(T_2/T_1)$
2. For constant pressure process			$ds=$
which on integration yields			$cpdT/T$
			$s_2-s_1=$
			$cpln(T_2/T_1)$
3. Constant temperature process			$Tds=pdv$
( $dT=0$ ) But $p=RT/v$			$ds=Rdv/v$
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



**Starting point of equation**

$$q - w = du$$

**Rewritten as**

$$Tds = pdv + cvdT$$

**1. Constant volume process  $dv=0$**

$$ds = cvdT/T$$

**which on integration yields**

$$s_2 -$$

$$s_1 = cv \ln(T_2/T_1)$$

$$ds = cpdT/T$$

**2. For constant pressure**

**process which on**

$$s_2 - s_1 =$$

**integration yields**

$$cp \ln(T_2/T_1)$$

## 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  $W$**

**useful =  $W_{rev} - I$**

# IRREVERSIBILITY (contd...)

- **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.**

# 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**
- **$TdS = \Delta u + W$**
- **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.**



# GIBBS FREE ENERGY

- **Gibbs free energy is a measure of chemical energy**
- **All chemical systems tend naturally toward states of minimum**

## **Gibbs free energy**

- **$G = H - TS$**
- **Where:**
- **$G$  = Gibbs Free Energy**
- **$H$  = Enthalpy (heat content)**
- **$T$  = Temperature in Kelvins**
- **$S$  = Entropy (can think of as randomness)**

# GIBBS FREE ENERGY

- Products and reactants are in equilibrium when their Gibbs free energies are equal

- A chemical reaction will proceed in the direction of lower Gibbs free energy (i.e.,  $\Delta G_r < 0$ )....so the reaction won't proceed if the reaction produces an increase in Gibbs free energy

$\Delta G^\circ_r > 0$ , backwards reaction with deficient energy

$\Delta G^\circ_r < 0$ , forwards reaction with excess energy

$\Delta G^\circ_r = 0$ , reaction is in equilibrium

$\Delta G^\circ_r$  is a measure of the driving force

# GIBBS FREE ENERGY

**For a phase we can determine  $V$ ,  $T$ ,  $P$ , etc., but not  $G$  or  $H$**

**We can only determine changes in  $G$  or  $H$  as we change some other parameters of the system**

**Example: measure  $\Delta H$  for a reaction by calorimetry - the heat given off or absorbed as a reaction proceeds Arbitrary reference state and assign an equally arbitrary value of  $H$  to it: Choose 298.15 K/25°C and 0.1 MPa/1 atm/1 bar (lab conditions)**

**...and assign  $H = 0$  for pure elements (in their natural state - gas, liquid, solid) at that reference**

# GIBBS FREE ENERGY

In our calorimeter we can then determine  $\Delta H$  for the reaction:



= molar enthalpy of formation of quartz (at 25°C, 1 atm)

It serves quite well for a standard value of  $H$  for the phase

Entropy has a more universal reference state:

entropy of every substance = 0 at 0K, so we use that

(and adjust for temperature)

Then we can use  $G = H - TS$  to determine  $G$  for

quartz = -856,288 J/mol

# GIBBS FREE ENERGY

$$\Delta G_R^o = -RT \ln K$$

K=equilibrium constant at standard T

T in kelvin 298.18K

R=gas constant=1.987 cal/mol<sup>o</sup>

$$K = 10^{\frac{-\Delta G_R^o}{1.364}}$$

$$\Delta G_R^o = -1.364 \log K$$

# GIBBS FREE ENERGY



Example: What is the DGoR of calcite dissociation?

Use data in appendix B for DGof

$$\text{DGoR} = [(-132.3) + (-126.17)] - [(-269.9)] = +11.43 \text{ kcal}$$

(+) means that the reaction goes from right to left

so K must be small

What is the value of K?

$$K = 10^{-\Delta G_R^o / 1.364}$$

$$K = 10(-11.43/1.364) = 10^{-8.3798} = 4.171 \times 10^{-9}$$

# GIBBS FREE ENERGY

What if  $T \neq 25^{\circ}\text{C}$ ?  $\Rightarrow$  Use the Van't Hoff Equation

We can derive:

$$\ln K_T - \ln K_T^{\circ} = (-\Delta H^{\circ}_R/R)(1/T - 1/T^{\circ})$$

$$\log K_T = \log K_T^{\circ} - \frac{\Delta H^{\circ}_R}{2.3025R} \left( \frac{1}{T} - \frac{1}{298.15} \right)$$

$\Delta H^{\circ}_R$  Enthalpy of reaction

$R=1.987 \text{ cal/mol}^{\circ}$

T in Kelvin

# GIBBS FREE ENERGY

**Example: What is  $K_T$  of calcite dissociation at  $T=38^\circ\text{C}$ ?**

$$\log K_T = \log K_T^\circ - \frac{\Delta H_R^\circ}{2.3025R} \left( \frac{1}{T} - \frac{1}{298.15} \right)$$

$$\Delta H_R^\circ = [(-129.74) + (-161.8)] - [(-288.46)] = -3.08$$

$$\log K_T = \log(4.71 \times 10^{-9}) - \frac{-3.08}{2.3025(1.987)} \left( \frac{1}{311} - \frac{1}{298.15} \right) = -9.0532$$

( $K_{T^\circ} = 4.71 \times 10^{-9}$ )

$$K_T = 8.85 \times 10^{-10}$$

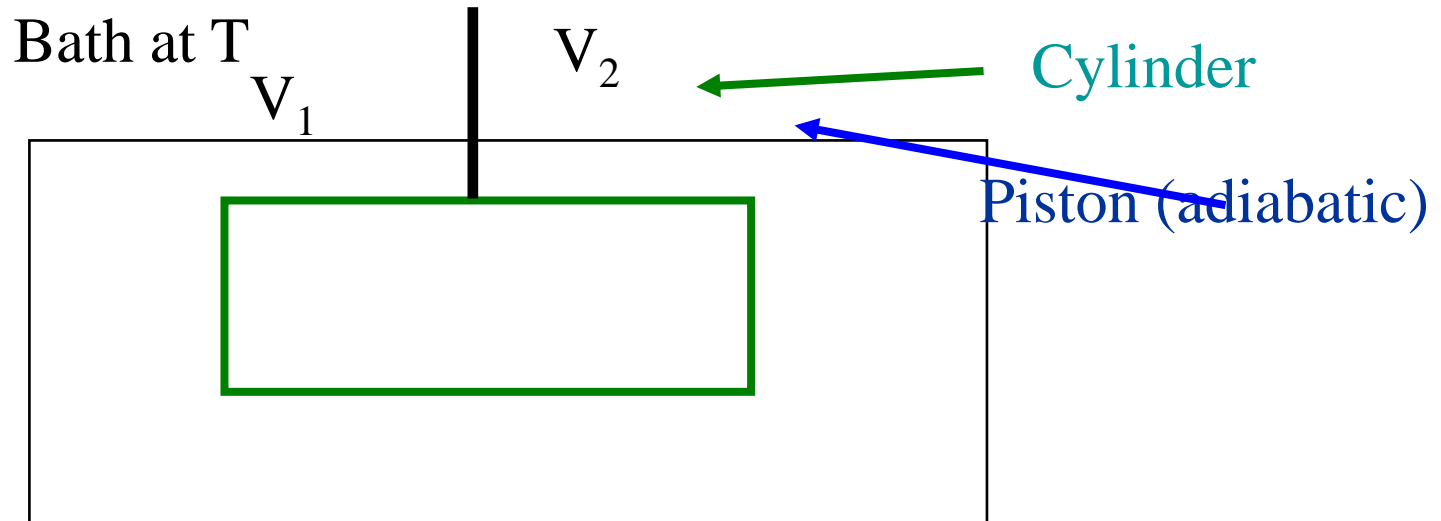
**When  $T$  increases,  $K$  decreases**



# HELMHOLTZ FUNCTION

- In statistical mechanics the quantity that is usually calculated is the Helmholtz Function. Other thermodynamic properties are then calculated from this. Before pursuing a general discussion of this function,
- let us consider an example to show how  $U$  and  $F$  differ by means of a simple example. We consider a closed cylinder in which there is a piston which separates two gases which are not initially at the same pressure. The situation is shown on the next slide.

# HELMHOLTZ FUNCTION



(a) Suppose that the wall of the cylinder is adiabatic.

$$\dagger Q = dU + PdV \quad \dagger Q = 0 \quad dU = -PdV \quad dU = dU_1 + dU_2 = -P_1 dV_1 - P_2 dV_2$$

Since the pressures are now the same and obviously  $dV_2 = -dV_1$

we have  $dU=0$ . At equilibrium the internal energy has its minimum value.

# HELMHOLTZ FUNCTION

**(b) Suppose that the wall of the cylinder is diathermal.**

$$dF = -SdT - PdV \quad dT = 0 \quad dF = -PdV \quad dF = dF_1 + dF_2 = -P_1dV_1 - P_2dV_2$$

Since the pressures are now the same and  $dV_2 = -dV_1$

we have  $dF=0$ . In this situation, it is  $F$ , not  $U$  that is a minimum at equilibrium.

( $U$  is not minimized in this case because the total entropy of the system and the reservoir must be maximized and the Helmholtz Function takes this into account.)

In continuing our discussion of the Helmholtz Potential, we consider isothermal processes.

{As an aside we have (slide 11)

$$\left( \frac{\partial F}{\partial V} \right)_T = -P$$

# HELMHOLTZ FUNCTION

Recall that if we have a system in contact with a reservoir then  $\Delta S$  (system) +  $\Delta S$  (reservoir)  $\geq 0$ .

If an amount of heat  $\Delta Q$  is transferred from the reservoir to the system, then  $\frac{\Delta Q}{T} \geq 0$  giving

$$\Delta Q \leq T (\Delta S) \text{ (system)}$$

The equality sign holds only for a reversible process. We have

$F = U - ST$  (This is just the Legendre Transformation.)

At constant temperature:  $\Delta F = \Delta U - T\Delta S$  or

$$\Delta F = \Delta Q - \Delta W - T\Delta S$$

# HELMHOLTZ FUNCTION

If no new entropy is created in a process (reversible process) then  $\Delta Q = T\Delta S$  and  $\Delta F = -\Delta W$  or  $\overline{(F_f - F_i)} = -\Delta W$  (constant T)

$$\Delta Q = T\Delta S \text{ and } \Delta F = -\Delta W \text{ or } \overline{(F_f - F_i)} = -\Delta W$$

The change in the Helmholtz function is then equal to the work done.

If new entropy is created in a process (irreversible) then  $\Delta Q < T\Delta S$

and  $\Delta F < -\Delta W$  or  $\overline{(F_f - F_i)} < -\Delta W$

The work is all the work on or by the system, including any done by the system's surroundings.

Conclusion:.

# HELMHOLTZ FUNCTION

## Conclusion:

The change in  $F$  in an isothermal reversible process is the work done on or by the system. In an isothermal process, the maximum amount of work that can be done by a system is the decrease in the Helmholtz function.

$$\Delta W = F_i - F_f \quad (\text{constant } T)$$

One can also say that the decrease in  $F$  gives the maximum amount of energy that can be fixed in an isothermal process and made available for work. (The symbol  $A$  is often used for the Helmholtz function. Arbeit is German for work). For this reason  $F$  is often called the Helmholtz free energy.

So  $F$  is intimately associated with work in an isothermal process.  
(See slide 22 for an example.)

# HELMHOLTZ FUNCTION

**EXAMPLE (Problem 8.5):** The Helmholtz function for a certain gas is:

**Obtain an expression for the pressure of the gas.**

**We have the reciprocity relation**

$$F(V, T) = -\frac{n^2 a}{V} - nRT \ln(V - nb) + J(T)$$

$$\left(\frac{\partial F}{\partial V}\right)_T = -P$$

$$-P = \frac{n^2 a}{V^2} - nRT \left(\frac{1}{V - nb}\right)$$

$$P = -\frac{n^2 a}{V^2} + \frac{nRT}{V - nb}$$

$$P + \frac{n^2 a}{V^2} = nRT \left(\frac{1}{V - nb}\right)$$

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

**Placing in a form using the specific volume:**

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

**(The reciprocity relationship has led to the equation of state.)**

**Van der Waals gas**

# HELMHOLTZ FUNCTION

**EXAMPLE:** A van der Waals gas undergoes an isothermal expansion from some initial specific volume to a final specific volume. Calculate the change in the specific Helmholtz function.

We have

$$dF = -PdV - SdT = -PdV \quad df = -Pdv$$

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

$$\Delta f = -\int_{v_1}^{v_2} \left[ \left( \frac{RT}{v - b} \right) - \frac{a}{v^2} \right] dv$$

$$\Delta f = -RT \ln \left( \frac{v_2 - b}{v_1 - b} \right) - a \left( \frac{1}{v_2} - \frac{1}{v_1} \right)$$

(Again the Helmholtz thermodynamic potential is closely associated with the work done in an isothermal process.)



# HELMHOLTZ FUNCTION

Considering a process which is both isothermal and isobaric  $\Delta G = \Delta U - T\Delta S + P\Delta V$  and since  $\Delta U = Q - W$ , then

$$\Delta G = Q - W - T\Delta S + P\Delta V$$

In general, besides any mechanical work, we can have some other work, such as electrical work.

$$\begin{aligned}\Delta W &= P\Delta V + W(\text{other}) \\ \Delta G &= Q - T\Delta S - W(\text{other})\end{aligned}$$

Suppose  $W(\text{other}) = 0$

As before  $Q \leq T\Delta S$  and so  $\Delta G \leq 0$  for constant T, P.

Again, in an evolving process, equilibrium will be established when G reaches its minimum value.

# HELMHOLTZ FUNCTION

Suppose  $W(\text{other}) \neq 0$

If we have a reversible process  $Q = T\Delta S$  and  
 $\Delta G = -W(\text{other})$ , so

$$G_f - G_i = -W(\text{other}) \quad \text{or}$$

The change in the Gibbs function gives the maximum energy that can be freed in an isothermal, isobaric process and made available for non-mechanical work. For this reason one often speaks of the Gibbs free energy. This can be confusing as we have the Helmholtz free energy also. It is best to avoid using free in both cases.

**N.B.** The state variables  $T$  and  $P$  need not be fixed throughout the process, but must have the same initial and final values.

# Maxwell's relations

Let us apply the condition for an exact differential to the differential forms of the potentials.

$$dU = TdS - PdV$$

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

$$dH = TdS + VdP$$

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

$$dF = -SdT - PdV$$

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

$$dG = -SdT + VdP$$

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

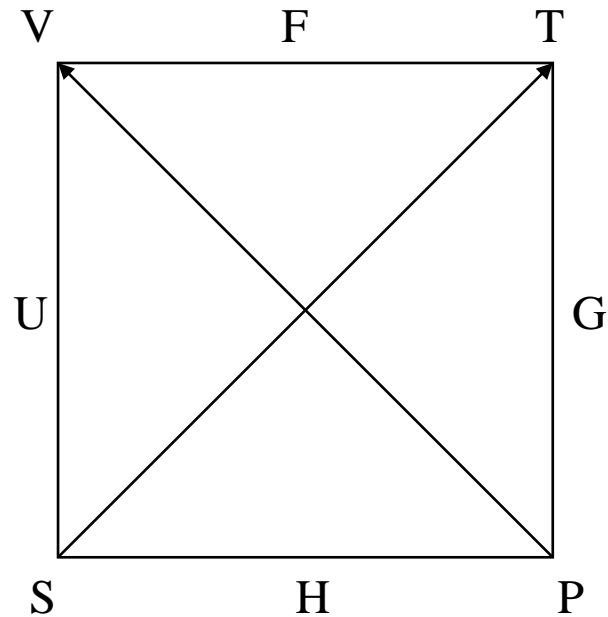
# Maxwell's relations

- The relationships among the partials are Maxwell's relations. These relations are enormously useful. Each partial involves a state variable that can be integrated along any convenient reversible path between two states to obtain the difference in the value of a state variable between two equilibrium states.
- They can be used to obtain values, or differences between values, for quantities not easily measured from more easily measured quantities, such as  $P$ ,  $V$  or  $T$ . They are often used to replace a partial, which cannot be evaluated, by another partial which can be determined

# Maxwell's relations

The VFT-VUS diagram is a device for remembering the differential forms of the potentials. Notice the direction of the arrows. If you go in a direction opposite to an arrow, the quantity is negative. The potentials are at the sides. They are functions of the state variables at the corresponding corners. The corresponding conjugate coordinate to the variable is obtained by following the diagonal arrow.

# Maxwell's relations



Consider the Gibbs function,  $dG$  will consist of a  $dT$  and a  $dP$ . The coefficient of  $dT$  will be  $-S$  and the coefficient of  $dP$  will be  $V$ .

$$dG = -SdT + VdP$$

# **MODULE-IV**

## **MIXTURE OF PERFECT GASES**

# IDEAL-GAS MIXTURES

The discussions in this chapter are restricted to non reactive ideal-gas mixtures. Those interested in real-gas mixtures are encouraged to study carefully.

$$PV = mRT \quad \text{or} \quad PV = NR_u T$$

Many thermodynamic applications involve mixtures of ideal gases. That is, each of the gases in the mixture individually behaves as an ideal gas. In this section, we assume that the gases in the mixture do not react with one another to any significant degree.



# MOLE FRACTION

## Definitions

Consider a container having a volume  $V$  that is filled with a mixture of  $k$  different gases at a pressure  $P$  and a temperature  $T$ .

A mixture of two or more gases of fixed chemical composition is called a *nonreacting gas mixture*. Consider  $k$  gases in a rigid container as shown here. The properties of the mixture may be based on the mass of each component, called gravimetric analysis, or on the moles of each component, called molar analysis.

# MOLE FRACTION

The composition of a gas mixture is described by specifying either the mass fraction  $m_i$  or the mole fraction  $y_i$  of each component  $i$ .

Note that 
$$\sum_{i=1}^k m_i = 1 \quad \text{and} \quad \sum_{i=1}^k y_i = 1$$

The mass and mole number for a given component are related through the molar mass (or molecular weight).

$$m_i = N_i M_i$$

To find the average molar mass for the mixture  $M_m = \frac{m_m}{N_m}$ , note  $m_m = \sum_{i=1}^k N_i M_i = N_m M_m$

Solving for the average or apparent molar mass  $M_m$

$$M_m = \frac{m_m}{N_m} = \sum_{i=1}^k \frac{N_i}{N_m} M_i = \sum_{i=1}^k y_i M_i \quad (\text{kg / kmol})$$

# MOLE FRACTION

The apparent (or average) gas constant of a mixture is expressed as

$$R_m = \frac{R_u}{M_m} \quad (kJ / kg \cdot K)$$

Can you show that  $R_m$  is given as

$$R_m = \sum_{i=1}^k mf_i R_i$$

To change from a mole fraction analysis to a mass fraction analysis, we can show that

$$mf_i = \frac{y_i M_i}{\sum_{i=1}^k y_i M_i}$$

To change from a mass fraction analysis to a mole fraction analysis, we can show that

$$y_i = \frac{mf_i / M_i}{\sum_{i=1}^k mf_i / M_i}$$

# VOLUME FRACTION ( AMAGAT MODEL)

Divide the container into  $k$  subcontainers, such that each subcontainer has only one of the gases in the mixture at the original mixture temperature and pressure.

Amagat's law of additive volumes states that the volume of a gas mixture is equal to the sum of the volumes each gas would occupy if it existed alone at the mixture temperature and pressure.

Amagat's law:

$$V_m = \sum_{i=1}^k V_i(T_m, P_m)$$

The volume fraction of the  $v_{fi}$  of any component is

and

$$v_{fi} = \frac{V_i(T_m, P_m)}{V_m}$$

$$\sum_{i=1}^k v_{fi} = 1$$

# VOLUME FRACTION (AMAGAT MODEL)

For an ideal gas mixture

$$V_i = \frac{N_i R_u T_m}{P_m} \quad \text{and} \quad V_m = \frac{N_m R_u T_m}{P_m}$$

Taking the ratio of these two equations gives

$$vf_i = \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i$$

The volume fraction and the mole fraction of a component in an ideal gas mixture are the same.

**Partial pressure (Dalton model)**

The partial pressure of component  $i$  is defined as the product of the mole fraction and the mixture pressure according to Dalton's law.

For the component  $i$

$$P_m = \sum_{i=1}^k P_i(T_m, V_m) \quad \text{Dalton's law:}$$

# VOLUME FRACTION (AMAGAT MODEL)

Now, consider placing each of the  $k$  gases in a separate container having the volume of the mixture at the temperature of the mixture. The pressure that results is called the component pressure,  $P_i'$ .

$$P_i' = \frac{N_i R_u T_m}{V_m} \quad \text{and} \quad P_m = \frac{N_m R_u T_m}{V_m}$$

Note that the ratio of  $P_i'$  to  $P_m$  is

$$\frac{P_i'}{P_m} = \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i$$

For ideal-gas mixtures, the partial pressure and the component pressure are the same and are equal to the product of the mole fraction and the mixture pressure.

# PROPERTIES OF IDEAL-GAS MIXTURES

## Other properties of ideal-gas mixtures

The *extensive properties* of a gas mixture, in general, can be determined by summing the contributions of each component of the mixture. The evaluation of *intensive properties* of a gas mixture, however, involves averaging in terms of mass or mole fractions:

$$U_m = \sum_{i=1}^k U_i = \sum_{i=1}^k m_i u_i = \sum_{i=1}^k N_i \bar{u}_i \quad (\text{kJ})$$

$$H_m = \sum_{i=1}^k H_i = \sum_{i=1}^k m_i h_i = \sum_{i=1}^k N_i \bar{h}_i \quad (\text{kJ})$$

$$S_m = \sum_{i=1}^k S_i = \sum_{i=1}^k m_i s_i = \sum_{i=1}^k N_i \bar{s}_i \quad (\text{kJ / K})$$

# PROPERTIES OF IDEAL-GAS MIXTURES

and

$$u_m = \sum_{i=1}^k mf_i u_i \quad \text{and} \quad \bar{u}_m = \sum_{i=1}^k y_i \bar{u}_i \quad (\text{kJ / kg or kJ / kmol})$$

$$h_m = \sum_{i=1}^k mf_i h_i \quad \text{and} \quad \bar{h}_m = \sum_{i=1}^k y_i \bar{h}_i \quad (\text{kJ / kg or kJ / kmol})$$

$$s_m = \sum_{i=1}^k mf_i s_i \quad \text{and} \quad \bar{s}_m = \sum_{i=1}^k y_i \bar{s}_i \quad (\text{kJ / kg} \cdot \text{K or kJ / kmol} \cdot \text{K})$$

$$C_{v,m} = \sum_{i=1}^k mf_i C_{v,i} \quad \text{and} \quad \bar{C}_{v,m} = \sum_{i=1}^k y_i \bar{C}_{v,i}$$

$$C_{p,m} = \sum_{i=1}^k mf_i C_{p,i} \quad \text{and} \quad \bar{C}_{p,m} = \sum_{i=1}^k y_i \bar{C}_{p,i}$$



# ENTROPY OF A MIXTURE OF IDEAL GASES

These relations are applicable to both ideal- and real-gas mixtures. The properties or property changes of individual components can be determined by using ideal-gas or real-gas relations developed in earlier chapters.

Ratio of specific heats  $k$  is given as

$$k_m = \frac{C_{p,m}}{C_{v,m}} = \frac{\bar{C}_{p,m}}{\bar{C}_{v,m}}$$

The entropy of a mixture of ideal gases is equal to the sum of the entropies of the component gases as they exist in the mixture. We employ the Gibbs-Dalton law that says each gas behaves as if it alone occupies the volume of the system at the mixture temperature. That is, the pressure of each component is the partial pressure.

For constant specific heats,  $\Delta s_i = C_{p,i} \ln\left(\frac{T_2}{T_1}\right) - R_i \ln\left(\frac{P_{i,2}}{P_{i,1}}\right)$  ent is

# ENTROPY OF A MIXTURE OF IDEAL GASES

The entropy change of the mixture per mass of mixture is

$$\begin{aligned}\Delta s_m &= \frac{\Delta S_m}{m_m} = \sum_{i=1}^2 mf_i \Delta s_i \\ &= \sum_{i=1}^k mf_i \left( C_{p,i} \ln \left( \frac{T_2}{T_1} \right) - R_i \ln \left( \frac{P_{i,2}}{P_{i,1}} \right) \right)\end{aligned}$$

The entropy change of the mixture per mole of mixture is

$$\begin{aligned}\Delta \bar{s}_m &= \frac{\Delta S_m}{N_m} = \sum_{i=1}^2 y_i \Delta \bar{s}_i \\ &= \sum_{i=1}^k y_i \left( \bar{C}_{p,i} \ln \left( \frac{T_2}{T_1} \right) - R_u \ln \left( \frac{P_{i,2}}{P_{i,1}} \right) \right)\end{aligned}$$

# ENTROPY OF A MIXTURE OF IDEAL GASES

In these last two equations, recall that

$$P_{i,1} = y_{i,1} P_{m,1}$$

Example

$$P_{i,2} = y_{i,2} P_{m,2}$$

An ideal-gas mixture has the following volumetric analysis

Component	% by Volume
N <sub>2</sub>	60
CO <sub>2</sub>	40

(a) Find the analysis on a mass basis.

For ideal-gas mixtures, the  $y_i = vf_i$  percent by volume is the volume fraction. Recall

# ENTROPY OF A MIXTURE OF IDEAL GASES

Comp.	$y_i$	$M_i$ kg/kmol	$y_i M_i$ kg/kmol	$m_{fi} = y_i M_i / M_m$ kgi/kgm
N <sub>2</sub>	0.60	28	16.8	0.488
CO <sub>2</sub>	0.40	44	17.6	0.512
$M_m = \sum y_i M_i = 34.4$				

(b) What is the mass of 1 m<sup>3</sup> of this gas when P = 1.5 MPa and T = 30°C?

$$R_m = \frac{R_u}{M_m} \quad (kJ / kg \cdot K)$$

$$= \frac{8.314 \frac{kJ}{kmol \cdot K}}{34.4 \frac{kg}{kmol}} = 0.242 \frac{kJ}{kg \cdot K}$$

$$m_m = \frac{P_m V_m}{R_m T_m}$$

$$= \frac{1.5 MPa (1 m^3)}{(0.242 kJ / (kg \cdot K))(30 + 273) K} \frac{10^3 kJ}{m^3 MPa}$$

$$= 20.45 kg$$

# GAS-VAPOR MIXTURES AND AIR-CONDITIONING

We will be concerned with the mixture of dry air and water vapor. This mixture is often called atmospheric air.

The temperature of the atmospheric air in air-conditioning applications ranges from about  $-10$  to about  $50^{\circ}\text{C}$ . Under these conditions, we treat air as an ideal gas with constant specific heats. Taking  $C_{pa} = 1.005 \text{ kJ/kg}\cdot\text{K}$ , the enthalpy of the dry air is given by (assuming the reference state to be  $0^{\circ}\text{C}$  where the reference enthalpy is taken to be 0

$$h_a = C_{pa} T \left( \frac{\text{kJ}}{\text{kg}_a} \right) \quad T \text{ in } ^{\circ}\text{C}$$

$$= \left[ 1.005 \frac{\text{kJ}}{\text{kg}\cdot^{\circ}\text{C}} \right] T \quad \frac{\text{kJ}}{\text{kg}_a}$$

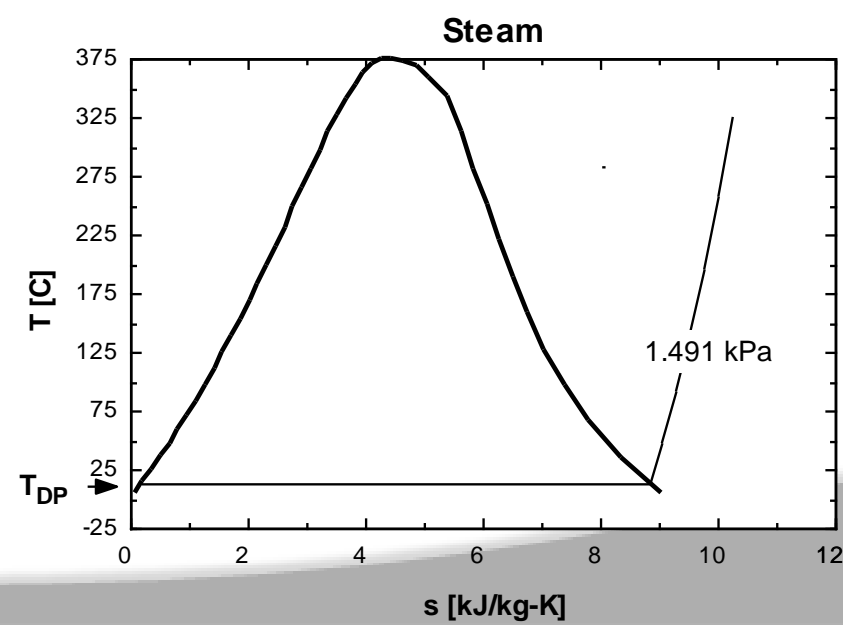
The assumption that the water vapor is an ideal gas is valid when the mixture temperature is below  $50^{\circ}\text{C}$ . This means that the saturation pressure of the water vapor in the air-vapor mixture is below  $12.3 \text{ kPa}$ . For these conditions, the enthalpy of the water vapor is approximated by  $h_v(T) = hg$  at mixture temperature  $T$ . The following  $T$ - $s$  diagram for water illustrates the ideal-gas behavior at low vapor pressures. See Figure A-9 for the actual  $T$ - $s$  diagram.

# Dew Point, $T_{dp}$

The dew point is the temperature at which vapor condenses or solidifies when cooled at constant pressure.

Consider cooling an air-water vapor mixture while the mixture total pressure is held constant. When the mixture is cooled to a temperature equal to the saturation temperature for the water-vapor partial pressure, condensation begins.

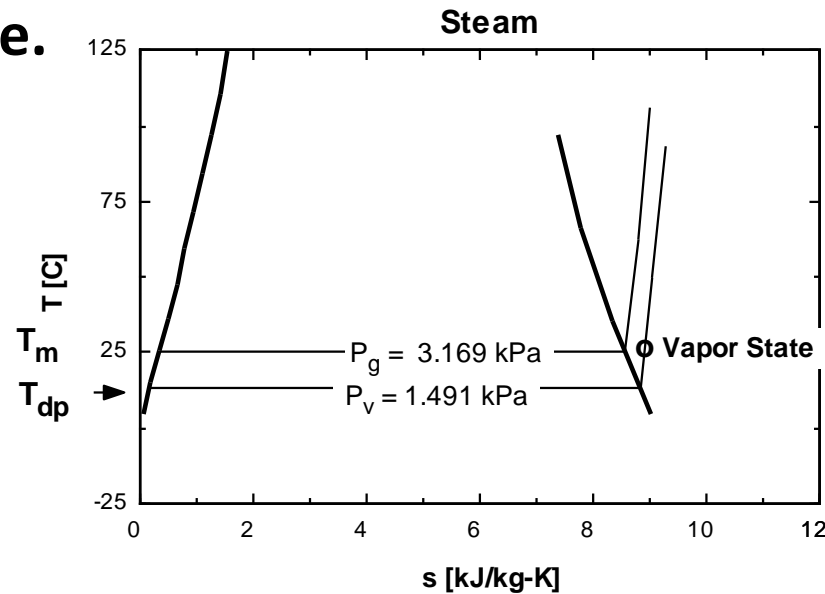
When an atmospheric air-vapor mixture is cooled at constant pressure such that the partial pressure of the water vapor is 1.491 kPa, then the dew point temperature of that mixture is 12.95°C.



# Dew Point, $T_{dp}$

## Relative Humidity, $\phi$

$P_v$  and  $P_g$  are shown on the following  $T$ - $s$  diagram for the water-vapor alone.



Since

$$P_g \geq P_v, \phi \leq 1 \text{ or } 100\%, \phi = \frac{P_v}{P_g} = \frac{1.491 \text{ kPa}}{3.169 \text{ kPa}} = 0.47$$

# Dew Point, $T_{dp}$

**Absolute humidity or specific humidity  
(sometimes called humidity ratio) ,  $\omega$**

**Using the definition of the specific humidity, the relative humidity may be expressed as**

$$\phi = \frac{\omega P}{(0.622 + \omega) P_g} \quad \text{and} \quad \omega = \frac{0.622 \phi P_g}{P - \phi P_g}$$

**Volume of mixture per mass of dry air,  $v$**

$$v = \frac{V}{m_a} = \frac{m_m R_m T_m / P_m}{m_a}$$

**After several steps, we can show (you should try this)**

$$v = \frac{V}{m_a} = v_a = \frac{R_a T_m}{P_a}$$



# MASS OF MIXTURE

$$m = m_a + m_v = m_a \left(1 + \frac{m_v}{m_a}\right) = m_a (1 + \omega)$$

$\dot{m}_a$

Mass flow rate of dry air,

**Based on the volume flow rate of mixture at a given state, the mass flow rate of dry air is**

$$\dot{m}_a = \frac{\dot{V}}{v} \quad \frac{m^3 / s}{m^3 / kg_a} = \frac{kg_a}{s}$$

**Enthalpy of mixture per mass dry air,  $h$**

$$\begin{aligned} h &= \frac{H_m}{m_a} = \frac{H_a + H_v}{m_a} = \frac{m_a h_a + m_v h_v}{m_a} \\ &= h_a + \omega h_v \end{aligned}$$

# Example

Atmospheric air at 30°C, 100 kPa, has a dew point of 21.3°C. Find the relative humidity, humidity ratio, and  $h$  of the mixture per mass of dry

T

Since  $T_{dp} = 21.3^\circ\text{C}$ ,  $P_v = 2.548 \text{ kPa}$

At  $T = 30^\circ\text{C}$ ,  $P_g = 4.247 \text{ kPa}$ .

Locate the  $T$ 's and  $P$ 's on the  $T$ - $s$  plot.



s

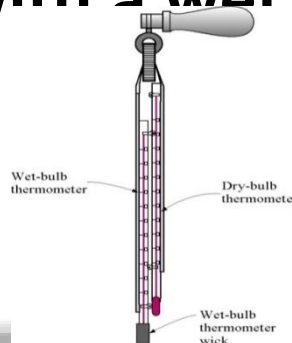
$$\phi = \frac{P_v}{P_g} = \frac{2.548 \text{ kPa}}{4.247 \text{ kPa}} = 0.6 \text{ or } 60\%$$

# **MODULE-V**

# **POWER CYCLES**

# Wet-Bulb and Dry-Bulb Temperatures

In normal practice, the state of atmospheric air is specified by determining the wet-bulb and dry-bulb temperatures. These temperatures are measured by using a device called a psychrometer. The psychrometer is composed of two thermometers mounted on a sling. One thermometer is fitted with a wet gauze and reads the wet-bulb temperature.

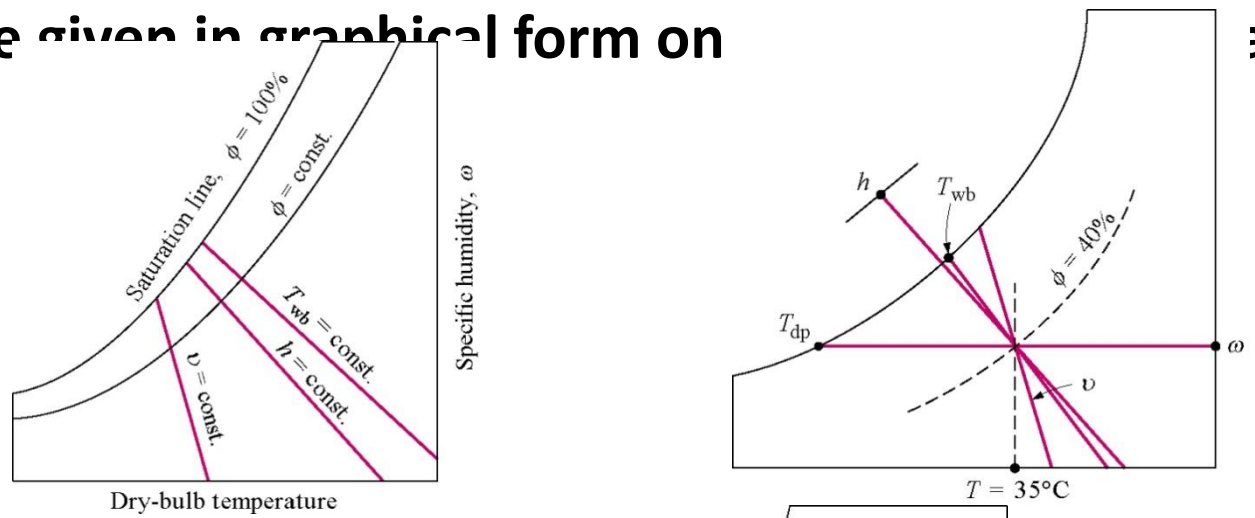


# Wet-Bulb and Dry-Bulb Temperatures

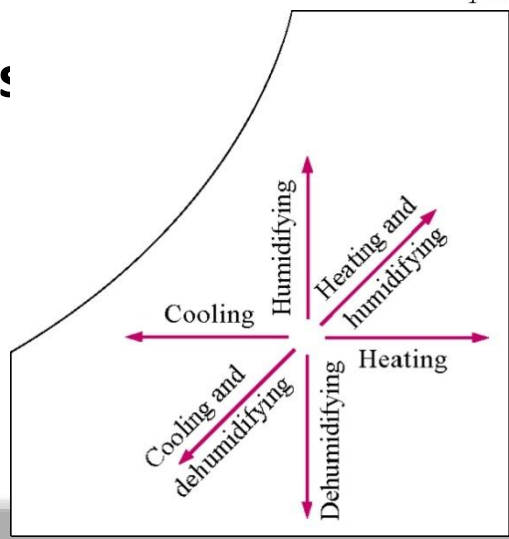
The other thermometer reads the dry-bulb, or ordinary, temperature. As the psychrometer is slung through the air, water vaporizes from the wet gauze, resulting in a lower temperature to be registered by the thermometer. The dryer the atmospheric air, the lower the wet-bulb temperature will be. When the relative humidity of the air is near 100 percent, there will be little difference between the wet-bulb and dry-bulb temperatures. The wet-bulb temperature is approximately equal to the adiabatic saturation temperature. The wet-bulb and dry-bulb temperatures and the atmospheric pressure uniquely determine the state of the atmospheric air.

# THE PSYCHROMETRIC CHART

For a given, fixed, total air-vapor pressure, the properties of the mixture are given in graphical form on a psychrometric chart.

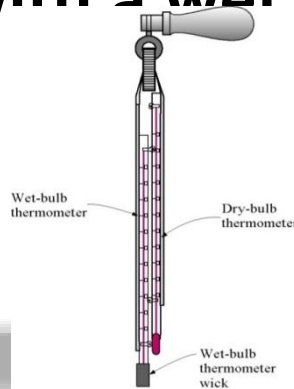


The air-conditioning processes



# Wet-Bulb and Dry-Bulb Temperatures

In normal practice, the state of atmospheric air is specified by determining the wet-bulb and dry-bulb temperatures. These temperatures are measured by using a device called a psychrometer. The psychrometer is composed of two thermometers mounted on a sling. One thermometer is fitted with a wet gauze and reads the wet-bulb temperature.

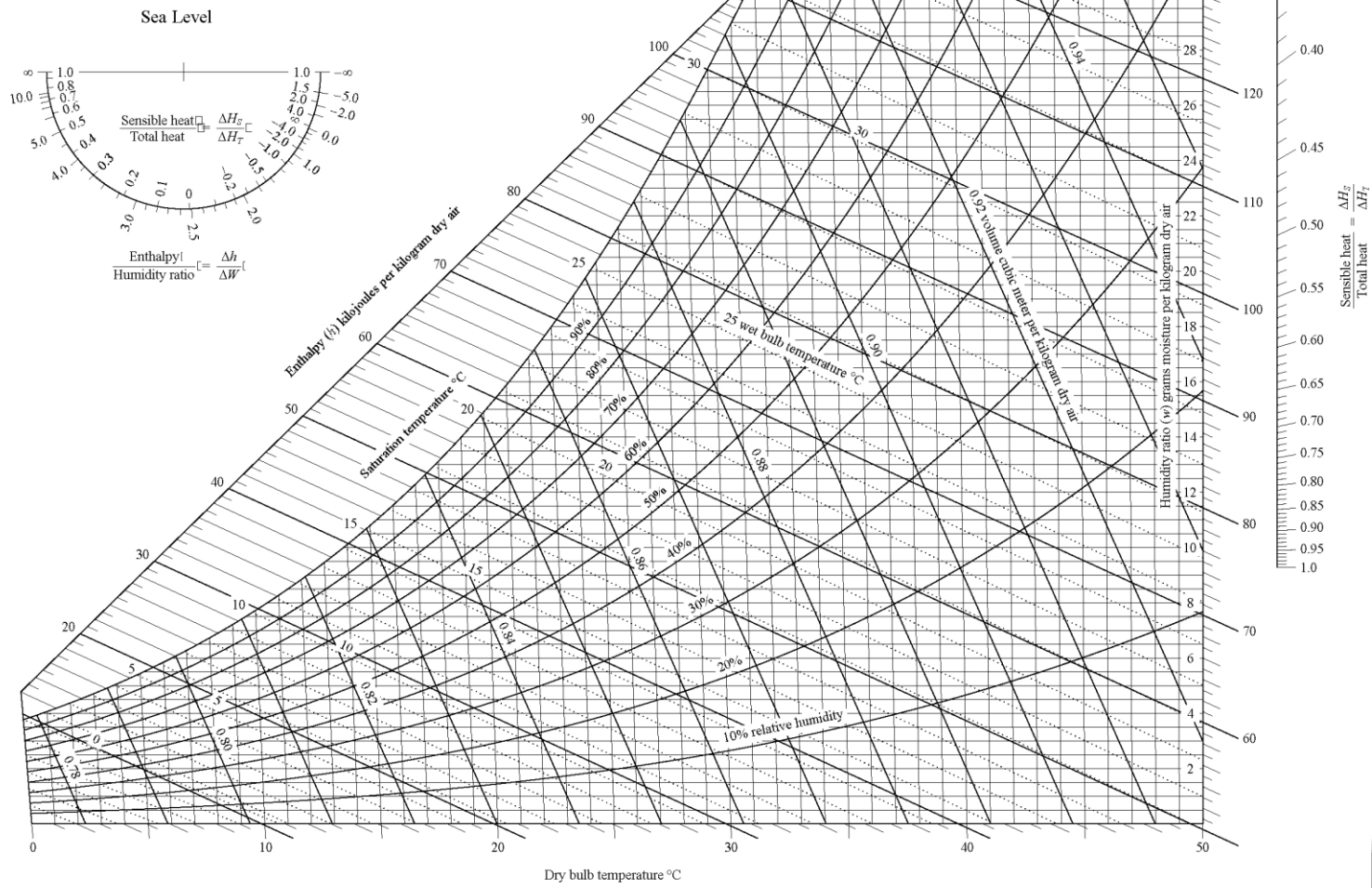


# THE PSYCHROMETRIC CHART

ASHRAE Psychrometric Chart No. 1  
Normal Temperature  
Barometric Pressure: 101.325 kPa



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Prepared by Center for Applied Thermodynamic Studies, University of Idaho



# THE PSYCHROMETRIC CHART

Determine the relative humidity, humidity ratio (specific humidity), enthalpy of the atmospheric air per mass of dry air, and the specific volume of the mixture per mass of dry air at a state where the dry-bulb temperature is 24°C, the wet-bulb temperature is 16°C, and atmospheric pressure is 100 kPa.

$$\phi = 44\%$$

From the psychrometric chart read

$$\omega = 8.0 \frac{g_v}{kg_a} = 0.008 \frac{kg_v}{kg_a}$$

$$h = 46 \frac{kJ}{kg_a}$$

$$v = 0.853 \frac{m^3}{kg_a}$$

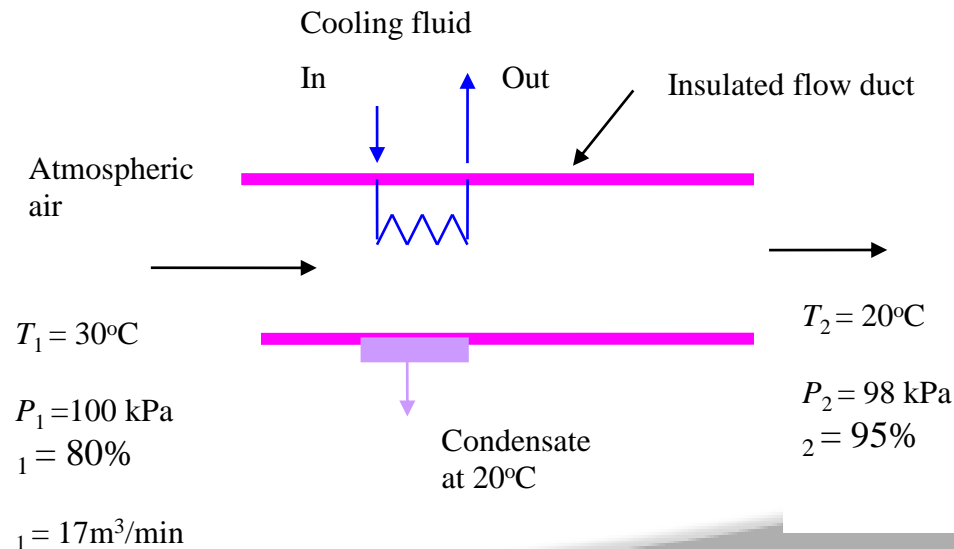
**NOTE: THE ENTHALPY READ FROM THE PSYCHROMETRIC CHART IS THE TOTAL ENTHALPY OF THE AIR-VAPOR MIXTURE PER UNIT MASS OF DRY AIR.**

$$h = H/m_a = h_a + \omega h_v$$

# EXAMPLE

Rework Example 14-3 neglecting the effect of atmospheric pressure and use the psychrometric diagram.

Given the inlet and exit conditions to an air conditioner shown below. What is the heat transfer to be removed per kg dry air flowing through the device? If the volume flow rate of the inlet atmospheric air is  $17 \text{ m}^3/\text{min}$ , determine the required rate of heat transfer.



# EXAMPLE

$$\dot{m}_{in} = \dot{m}_{out}$$

$$\text{dry air : } \dot{m}_{a1} = \dot{m}_{a2} = \dot{m}_a$$

$$\text{water vapor : } \dot{m}_{v1} = \dot{m}_{v2} + \dot{m}_{liq2}$$

$$\dot{m}_{liq2} = \dot{m}_a (\omega_1 - \omega_2)$$

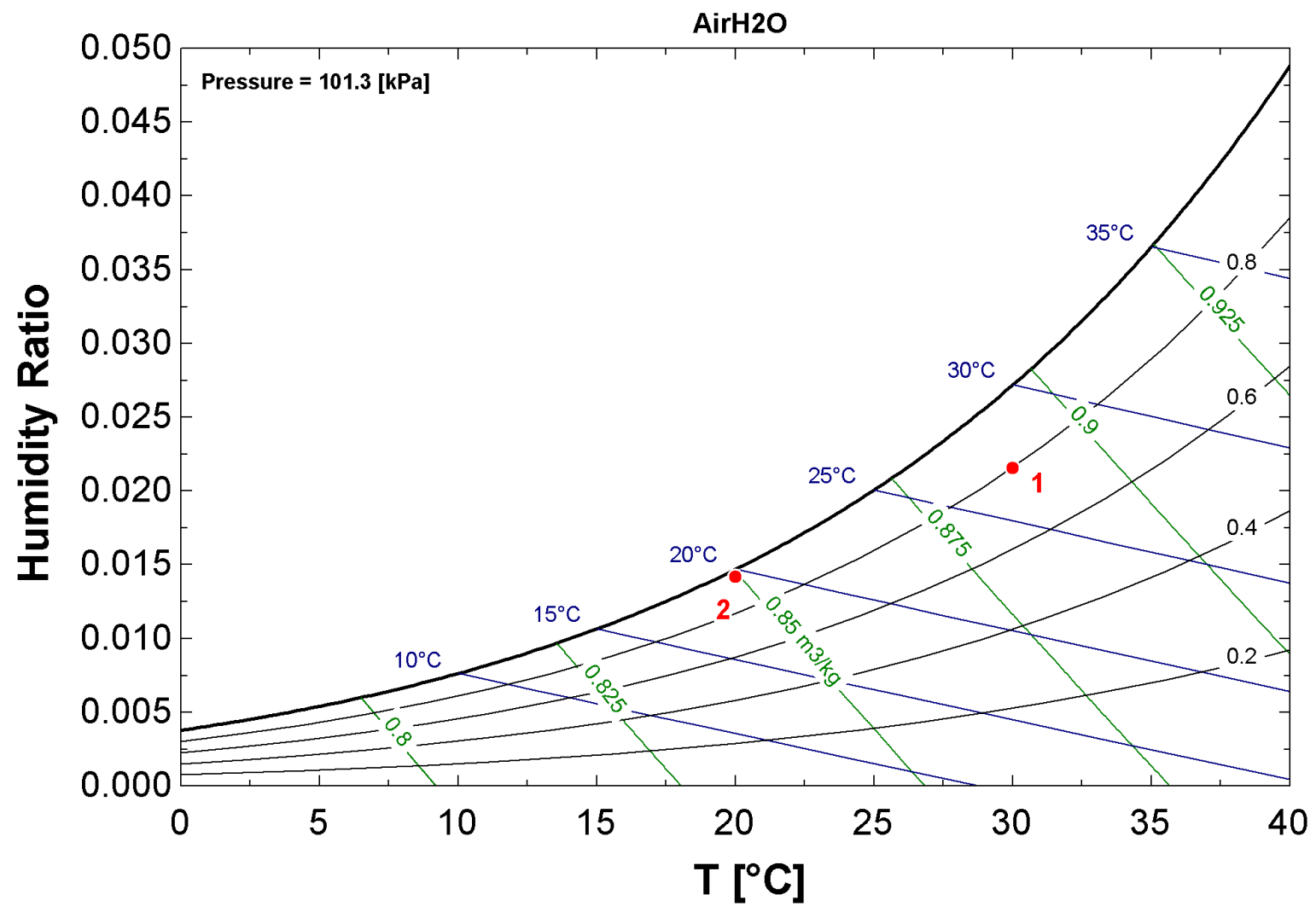
$$\dot{E}_{in} = \dot{E}_{out}$$

$$\dot{Q}_{net} + \dot{m}_a h_1 = \dot{m}_a h_2 + \dot{m}_{liq2} h_{liq2}$$

$$\dot{Q}_{net} = \dot{m}_a (h_2 + (\omega_1 - \omega_2) h_{liq2} - h_1)$$

# PSYCHROMETRIC CHART

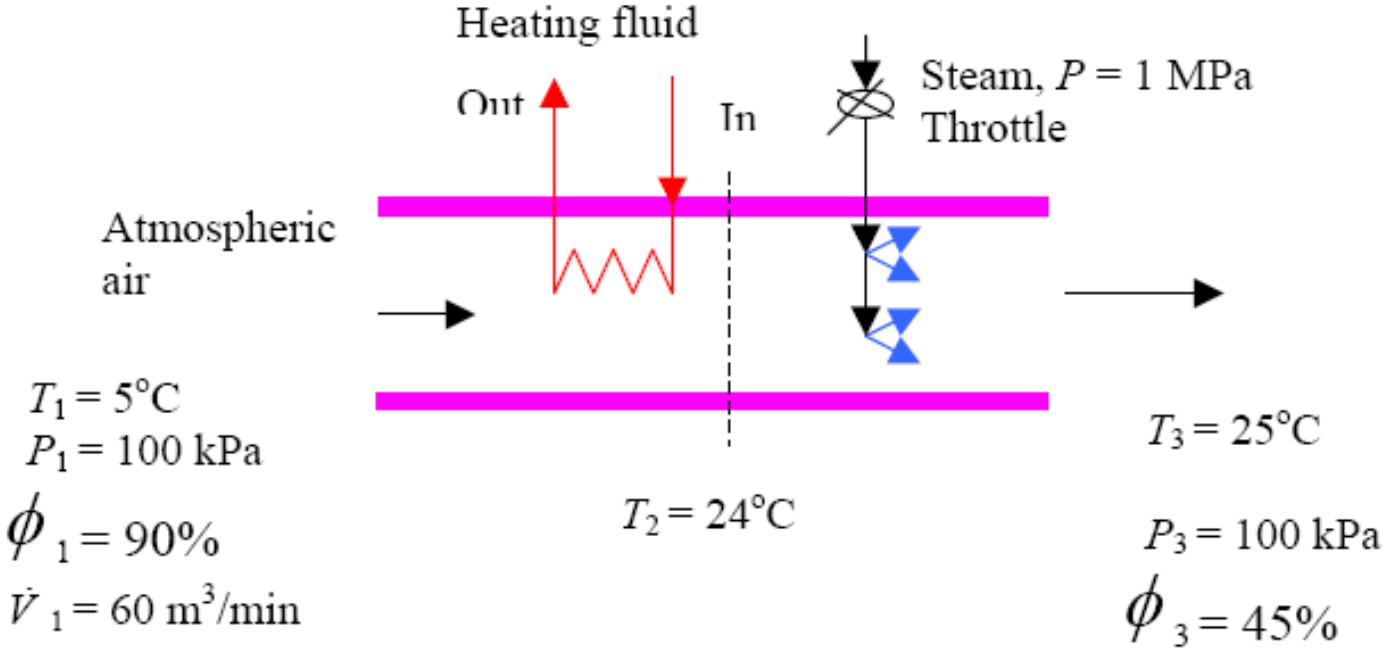
Now, use the psychrometric chart to find the mixture properties.



# Dew Point, $T_{dp}$

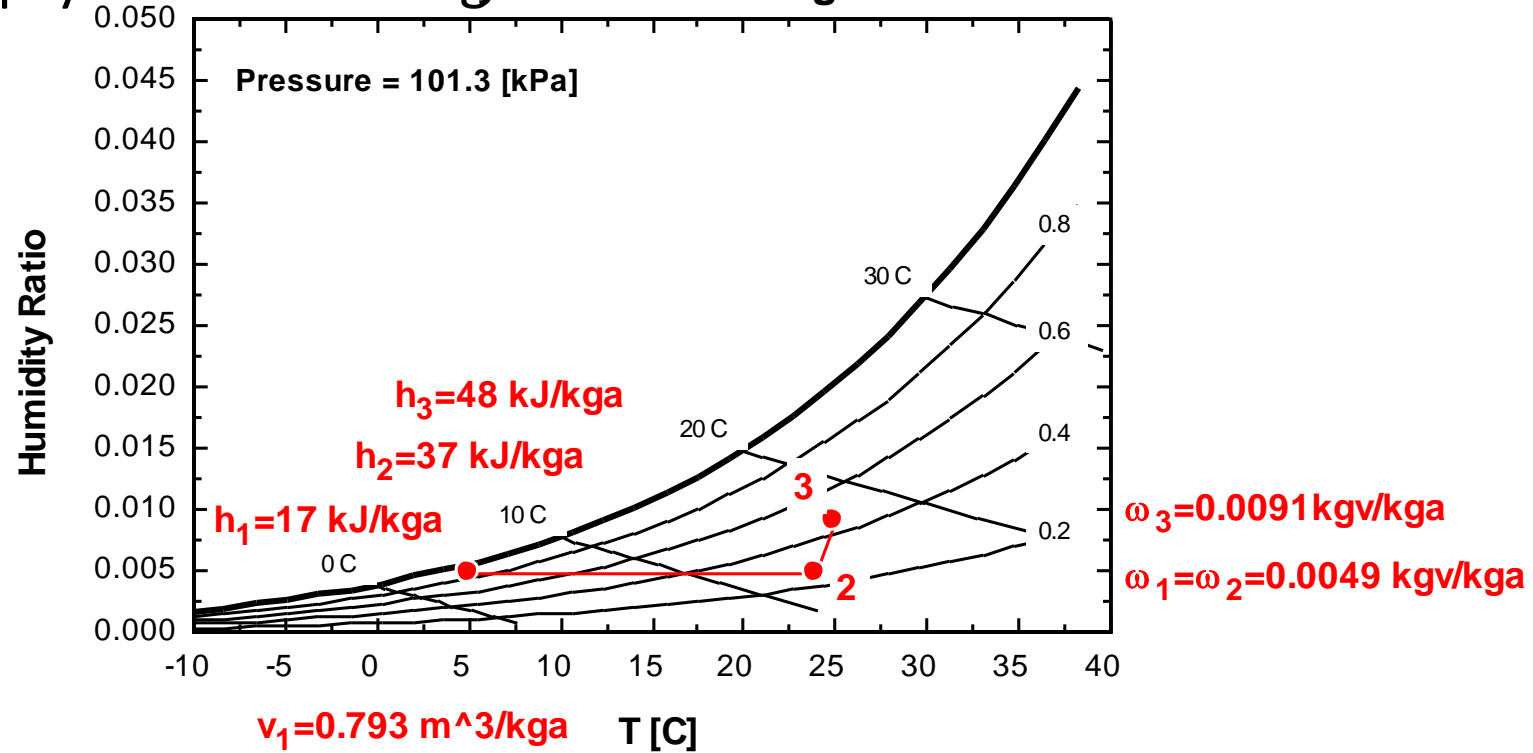
## Example

For the air-conditioning system shown below in which atmospheric air is first heated and then humidified with a steam spray, determine the required heat transfer rate in the heating section and the required steam temperature in the humidification section when the steam pressure is 1 MPa.



# Dew Point, $T_{dp}$

## The psychrometric diagram



Apply conservation of mass and conservation of energy for steady-flow to process

1-2.

$$\sum_{inlets} \dot{m}_i = \sum_{exits} \dot{m}_e$$

# DEW POINT, TDP

For the dry air

$$\dot{m}_{a1} = \dot{m}_{a2} = \dot{m}_a$$

For the water vapor (note: no water is added)

$$\dot{m}_{v1} = \dot{m}_{v2}$$

Thus,

$$\omega_2 = \omega_1$$

Neglecting the kinetic and potential energies and noting that the work is zero, and letting the enthalpy of the mixture per unit mass of air  $h$  be defined as we obtain

$$h = h_a + \omega h_v$$

$$\dot{E}_{in} = \dot{E}_{out}$$

$$\dot{Q}_{in} + \dot{m}_a h_1 = \dot{m}_a h_2$$

$$\dot{Q}_{in} = \dot{m}_a (h_2 - h_1)$$

# DEW POINT, TDP

Now to find the  $\dot{m}_a$  and  $h$ 's using the psychrometric chart.

At  $T_1 = 50^\circ\text{C}$ ,  $\phi_1 = 90\%$ , and  $T_2 = 24^\circ\text{C}$ :

$$\left. \begin{array}{l} \phi_1 = 90\% \\ T_1 = 5^\circ\text{C} \end{array} \right\} \begin{cases} h_1 = 17 \frac{\text{kJ}}{\text{kg}_a} \\ \omega_1 = 0.0049 \frac{\text{kg}_v}{\text{kg}_a} \\ v_1 = 0.793 \frac{\text{m}^3}{\text{kg}_a} \end{cases}$$

$$\left. \begin{array}{l} \omega_2 = \omega_1 = 0.0049 \frac{\text{kg}_v}{\text{kg}_a} \\ T_2 = 24^\circ\text{C} \end{array} \right\} \begin{cases} h_2 = 37 \frac{\text{kJ}}{\text{kg}_a} \end{cases}$$

The mass flow rate of dry air is given by

$$\dot{m}_a = \frac{\dot{V}_1}{v_1}$$



# DEW POINT, TDP

$$\dot{m}_{in} = \dot{m}_{out}$$

$$\text{dry air : } \dot{m}_{a1} = \dot{m}_{a2} = \dot{m}_a$$

$$\text{water vapor : } \dot{m}_{v1} = \dot{m}_{v2} + \dot{m}_{liq2}$$

$$\dot{m}_{liq2} = \dot{m}_a (\omega_1 - \omega_2)$$

$$\dot{E}_{in} = \dot{E}_{out}$$

$$\dot{Q}_{net} + \dot{m}_a h_1 = \dot{m}_a h_2 + \dot{m}_{liq2} h_{liq2}$$

$$\dot{Q}_{net} = \dot{m}_a (h_2 + (\omega_1 - \omega_2) h_{liq2} - h_1)$$

# DEW POINT, TDP

$$\dot{m}_a = \frac{60 \frac{m^3}{\min}}{0.793 \frac{m^3}{kg_a}} = 75.66 \frac{kg_a}{\min} \frac{1 \min}{60s} = 1.261 \frac{kg_a}{s}$$

The required heat transfer rate for the heating section is

$$\begin{aligned} \dot{Q}_{in} &= 1.261 \frac{kg_a}{s} (37 - 17) \frac{kJ}{kg_a} \frac{1kW_s}{kJ} \\ &= 25.22 kW \end{aligned}$$

This is the required heat transfer to the atmospheric air. List some ways in which this amount of heat can be supplied.

At the exit, state 3,  $T_3 = 25^\circ\text{C}$  and  $\phi_3 = 45\%$ . The psychrometric chart gives

$$\left. \begin{array}{l} \phi_3 = 45\% \\ T_3 = 25^\circ\text{C} \end{array} \right\} \begin{cases} h_3 = 48 \frac{kJ}{kg_a} \\ \omega_3 = 0.0089 \frac{kg_v}{kg_a} \\ v_3 = 0.858 \frac{m^3}{kg_a} \end{cases}$$

# DEW POINT, TDP

Apply conservation of mass and conservation of energy to process 2-3.

Conservation of mass for the steady-flow control volume is

For the dry air

$$\sum_{\text{inlets}} \dot{m}_i = \sum_{\text{exits}} \dot{m}_e$$

$$\dot{m}_{a2} = \dot{m}_{a3} = \dot{m}_a$$

For the water vapor (note: water is added during the humidification process)

$$\dot{m}_{v2} + \dot{m}_s = \dot{m}_{v3}$$

$$\dot{m}_s = \dot{m}_{v3} - \dot{m}_{v2}$$

$$\dot{m}_s = \dot{m}_a (\omega_3 - \omega_2)$$

$$= 1.261 \frac{\text{kg}_a}{\text{s}} (0.0089 - 0.0049) \frac{\text{kg}_v}{\text{kg}_a}$$

$$= 0.00504 \frac{\text{kg}_v}{\text{s}}$$

# Dew Point, $T_{dp}$

Neglecting the kinetic and potential energies and noting that the heat transfer and work are zero, the conservation of energy yields

$$\dot{E}_{in} = \dot{E}_{out}$$

$$\dot{m}_a h_2 + \dot{m}_s h_s = \dot{m}_a h_3$$

$$\dot{m}_s h_s = \dot{m}_a (h_3 - h_2)$$

Solving for the enthalpy of the steam,

$$\dot{m}_a (\omega_3 - \omega_2) h_s = \dot{m}_a (h_3 - h_2)$$

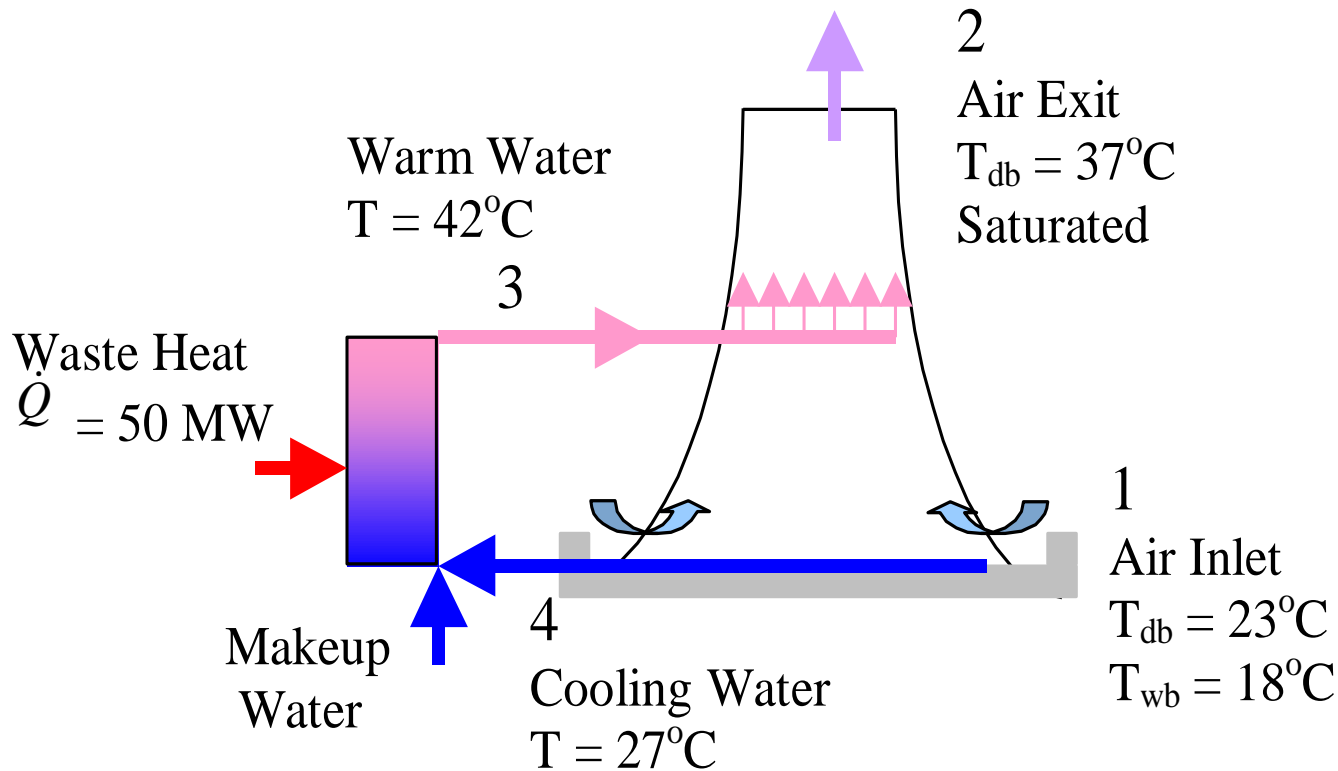
$$h_s = \frac{h_3 - h_2}{\omega_3 - \omega_2}$$

# EXAMPLE

**The natural-draft cooling tower shown below is to remove 50 MW of waste heat from the cooling water leaving the condenser of a steam power plant. The cooling water enters the tower at 42 °C and leaves at 27 °C. Atmospheric air enters the tower at 1 atm with dry- and wet-bulb temperatures of 23 and 18 °C, respectively, leaves saturated at 37 °C. Plot the effect of air inlet wet-bulb temperature (14 - 23°C) on the required air volume flow rate and the makeup water flow rate. All other input data were the stated values.**

# NATURAL-DRAFT COOLING

## Natural-Draft Cooling Tower



# NATURAL-DRAFT COOLING

Effect of  $T_{wb,1}$  on inlet volume flow rate and makeup water flow rate

