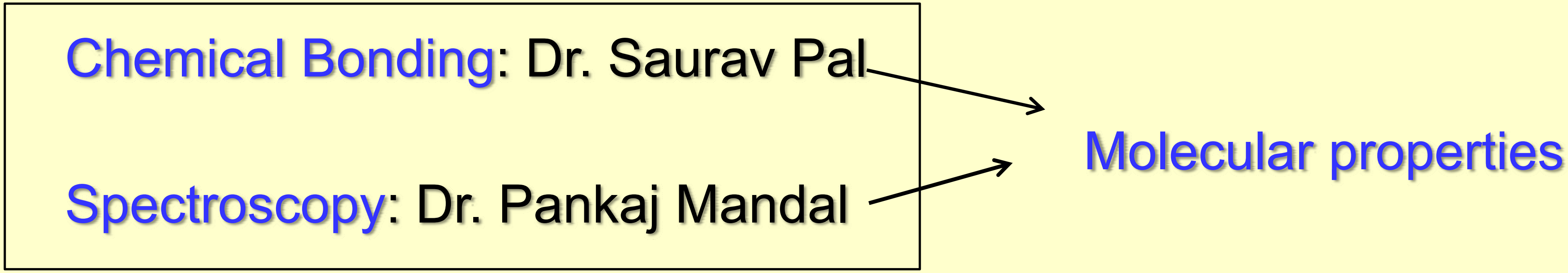
Classical Thermodynamics

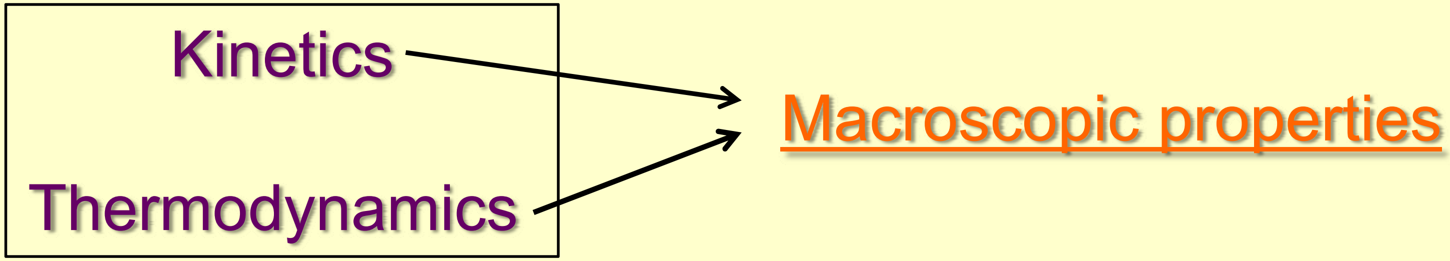
CHM102



Chemical Bonding: Dr. Saurav Pal

Spectroscopy: Dr. Pankaj Mandal

Molecular properties



Kinetics

Thermodynamics

Macroscopic properties

Thermodynamics: “Heat” + “Study of motion” ⟹ Heat Transfer

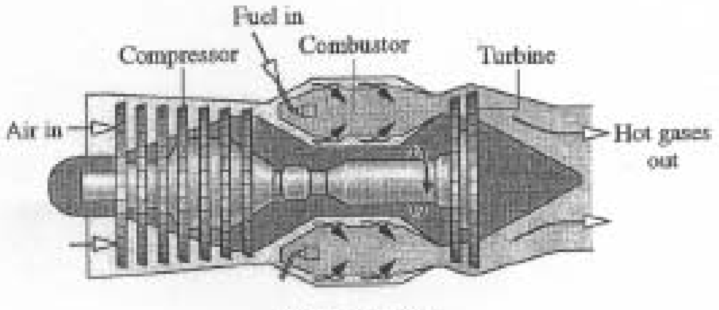
✵ Themodynamics: Heat, work, energy

Wide Applications:

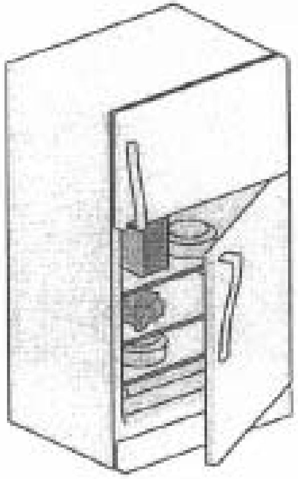
1. Energy change associated to all chemical and physical processes.
2. Mutual transformation of different kinds of energy.
3. To predict the direction and extent of chemical reaction.

Birth:

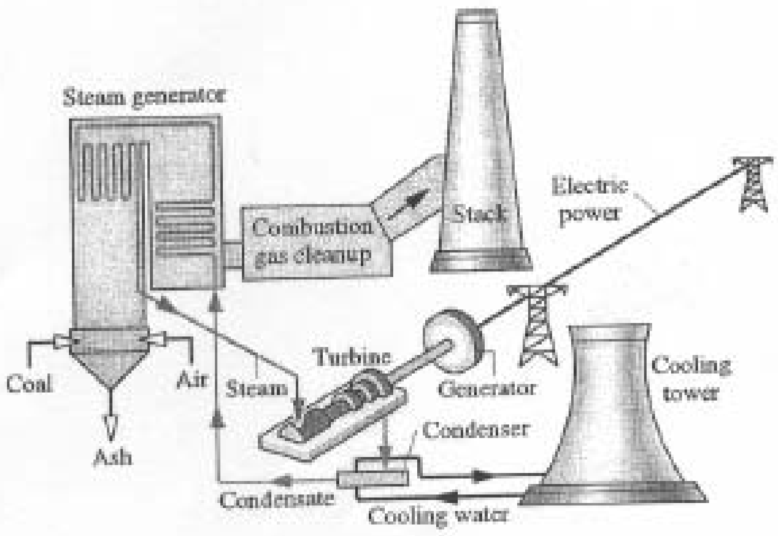
Industrial revolution (late 18th, early 19th century)



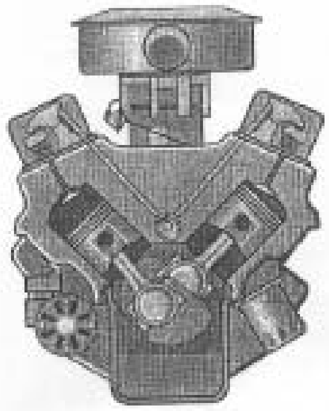
Turbojet engine



Refrigerator



Electrical power plant



Automobile engine

Thermodynamics

✸Basically is based on four laws.

✸These laws are not formulated, rather these are generalization deduced from our long experience in nature.

> *Classical thermodynamics… is the only physical theory of universal content which I am convinced that, within the applicability of its basic concepts, will never be overthrown.”*
>
> Albert Einstein

Classical Thermodynamics:

➔Describes macroscopic properties of the systems.

➔Entirely Empirical

➔ Based on 4 Laws:

0th Law ⇒ Defines Temperature (T)

1st Law ⇒ Law of conservation of energy. It tells that system may exchange energy with its surroundings strictly by heat flow or work. Defines Internal Energy (U)

2nd Law ⇒ Defines Entropy (S)

3rd Law ⇒ Gives Numerical Value to Entropy

Systems

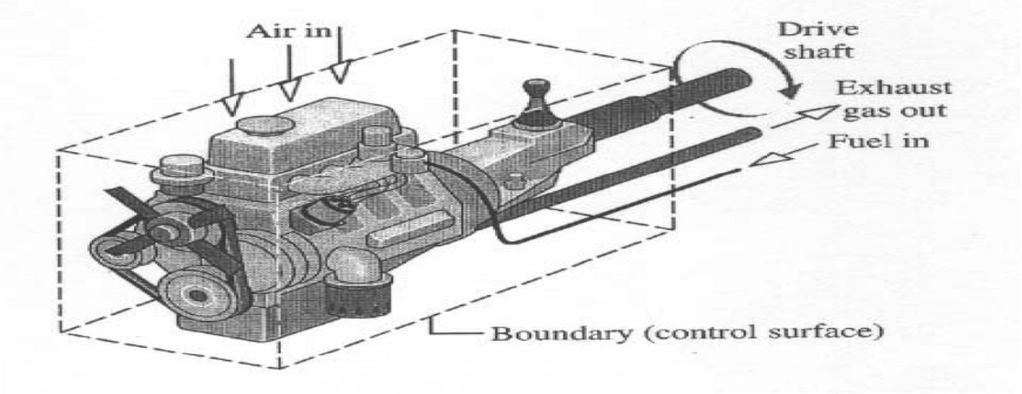
- A ***system*** is part of the universe chosen for observation, separately from the rest of the universe.
- The system plus surroundings comprise a ***universe***.
- The boundary between a system and its surroundings is the ***system wall***.
- If heat cannot pass through the system wall, it is termed an ***adiabatic wall***, and the system is said to be ***thermally isolated*** or ***thermally insulated***.
- If heat can pass through the wall, it is termed a ***diathermal wall***.
- Two systems connected by a diathermal wall are said to be in ***thermal contact.***

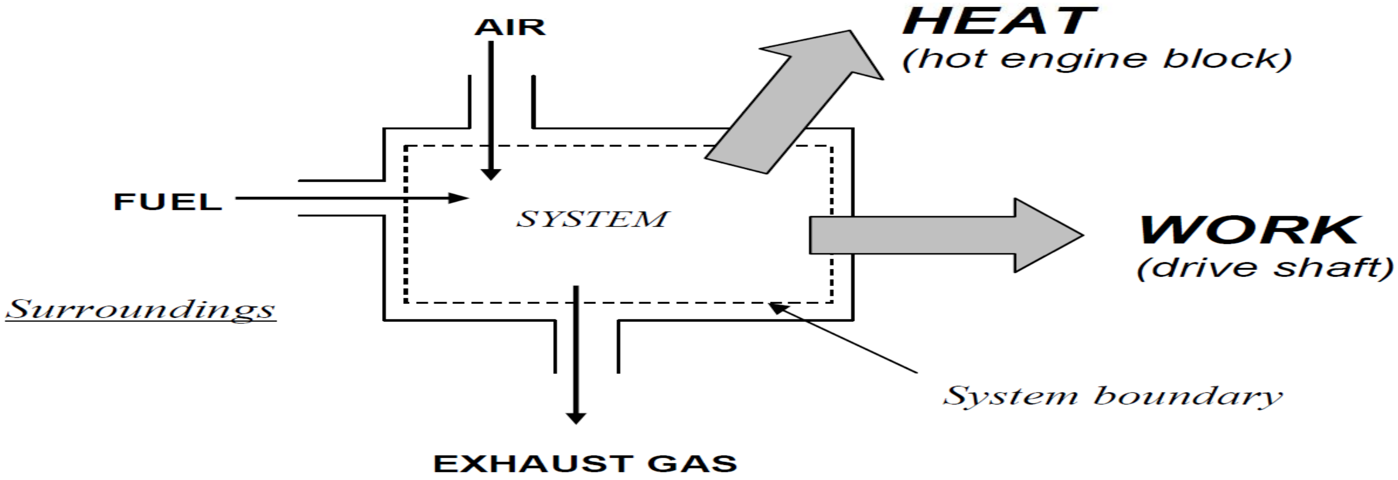
Isolated, Closed and Open Systems

- An ***isolated system*** cannot exchange mass or energy with its surroundings.
- The wall of an isolated system must be adiabatic.
- A ***closed system*** can exchange energy, but not mass, with its surroundings.
- The energy exchange may be mechanical (associated with a volume change) or thermal (associated with heat transfer through a diathermal wall).
- An ***open system*** can exchange both mass and energy with its surroundings.

Open System

As an example, consider an Internal Combustion (IC) Engine





AIR

HEAT
(hot engine block)

FUEL

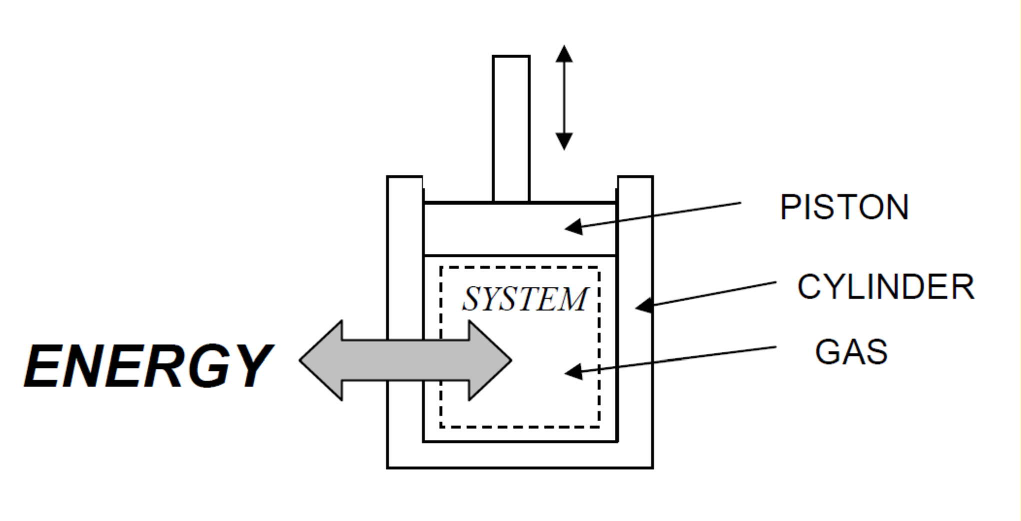
SYSTEM

WORK
(drive shaft)

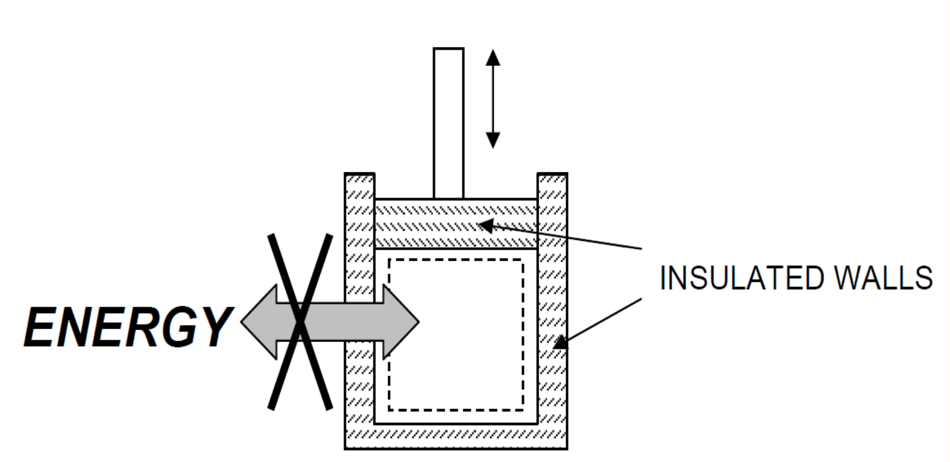
Surroundings

System boundary

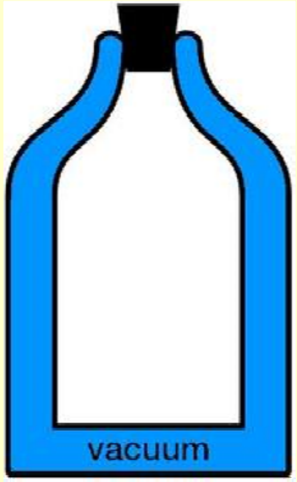
EXHAUST GAS



Closed System

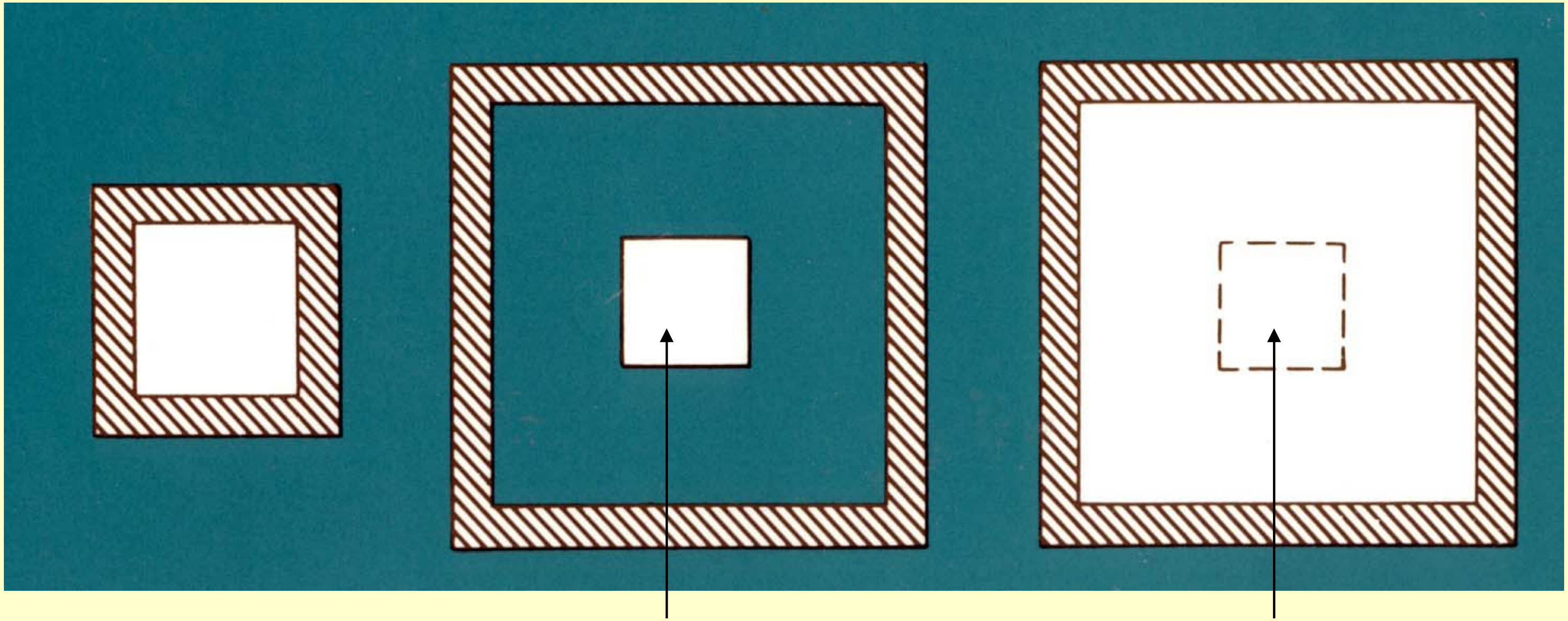


Isolated System



Isolated System

Isolated, Closed and Open Systems



Isolated System

Neither energy nor mass can be exchanged.

Closed System

Energy, but not mass can be exchanged.

Open System

Both energy and mass can be exchanged.

Properties of a System

Thermodynamic variables which are experimentally measurable. Such variables are macroscopic properties such as P, V, T, m, composition, viscosity etc.

Thermodynamic variables

Intensive variables

T, P, density, specific gravity, surface tension,
specific heat capacity, dielectric constant.

Does not depend upon mass of the system

extensive variables

Volume, energy, enthalpy,
Entropy, free energy, mass

Depends on the mass of the system.

States of a system

How do we define a State of a System?

Macroscopic state of a system can be specified by thermodynamic variables which are experimentally measurable

- Composition – mass of each chemical species that is present in the system.

- pressure (p or P), volume (V), Temperature (T), density, etc.

- field strength, if magnetic/electrical field act on the system

- gravitational field

Equilibrium States

1. Composition remains fixed and definite.

2. Temp. at all parts of the system is the same.

3. No unbalanced forces between different parts
of the system or between system and surroundings.

System at equilibrium must have definite P, T, and composition

Processes

A ***process*** refers to the change of a system from one equilibrium state to another.

Isothermal (T)

Adiabatic (no heat exchange between system and surroundings).

Isobaric (p),

Isochoric (V)

Cyclic

Reversible Process:

- Change must occur in ***successive stages of infinitesimal quantities***
- ***Infinite duration***
- Changes of the thermodynamic quantities in the different stages will be the ***same as in the forward direction but opposite in sign wrt forward direction***

Irreversible Process:

- **Real / Spontaneous**
- Occurs suddenly or *spontaneously* ***without the restriction of occurring in successive stages of infinitesimal quantities.***
- **Not remain in the *virtual equilibrium during the transition.***
- The work (w) in the ***forward and backward processes would be unequal.***

State function: Those thermodynamic properties depends on the state of the system, not on the path through which it has been brought in that state. Potential energy, Internal energy, entropy, enthalpy.

Path function: **Those thermodynamic properties depends on the path through which it has been brought in that state**.

(Heat, work).

Mathematical formulation of State function (TUTORIAL 1):

1. If any thermodynamic property or function, z = f(x,y) depends on the initial and final values of thermodynamic variables, then the change of z, i.e., dz is a perfect differential,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

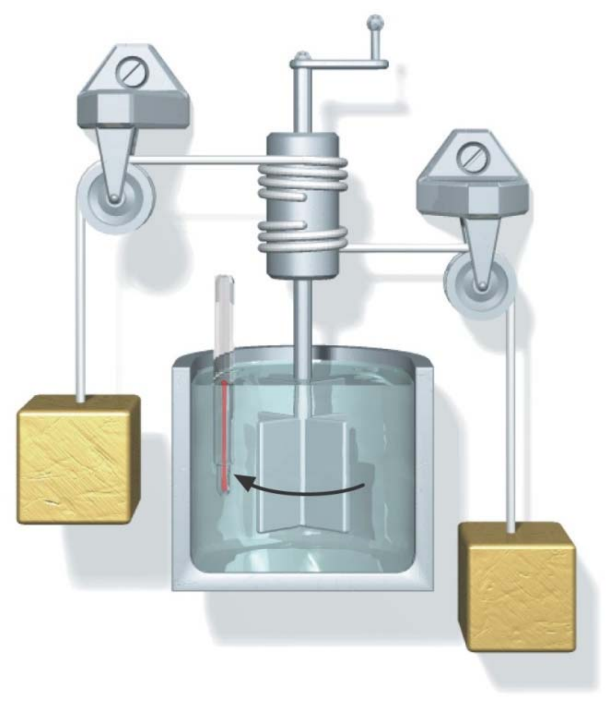
2. In case Z is state function, it will follow the following mathematical relationship,

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y$$

3. If Z = f(x,y) depends on the initial and final values of thermodynamic variables, then also $\oint dz = 0$

Concept of Heat and work

Joule's experiment



$W = JQ$

W = work expended in the production of heat or obtained from heat

Heat ⇔ Work

1 calorie = 4.184 Joules

✷Both heat and work represents energy in transit.

✷Work involved in a process , heat change involved during a process depend on the path of transformation.

✷ **Work and heat are the two methods by which energy is exchanged between system and surroundings.**

Sign Convention of heat and work:

Work:

✶The work done by the system is defined to be nagative (-).

✶ The work done on the system – the ***external work*** of mechanics – is positive (+).

Heat:

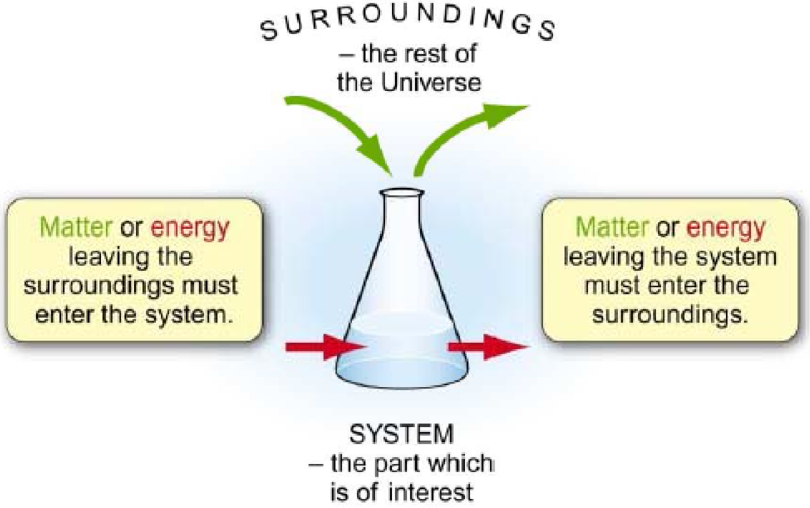
✶The heat absorbed by the system is defined to be positive (+).

✶ The given out by the system is negative (-).

Internal Energy

Units: Joules J

Internal Energy (U) : total kinetic & potential energy of system.
e.g. Gas in container with (n,P,V,T). Gas molecules translate, rotate & vibrate so $U = E_{trans} + E_{rot} + E_{vib}$



Matter or energy leaving the surroundings must enter the system.

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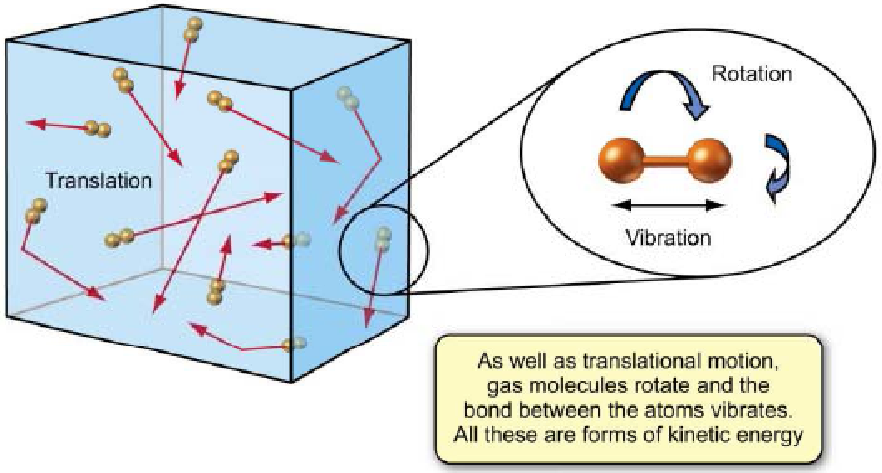


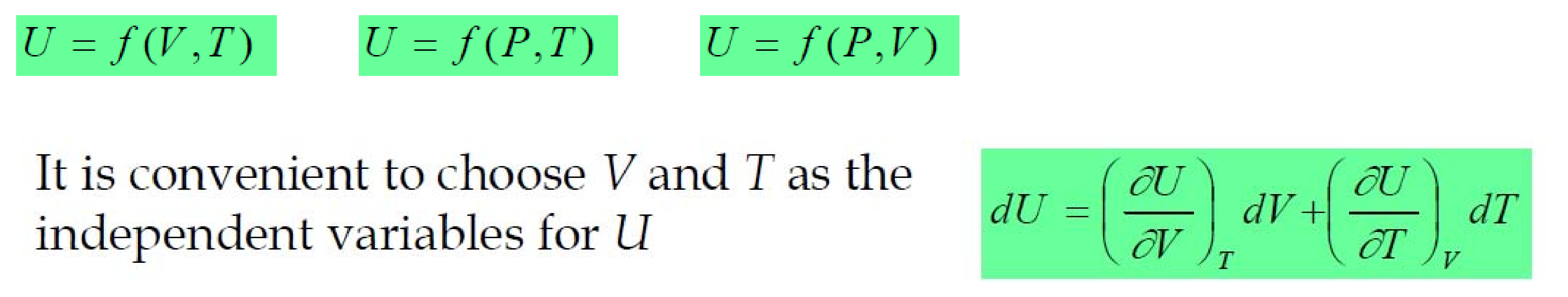
As well as translational motion, gas molecules rotate and the bond between the atoms vibrates. All these are forms of kinetic energy

$\Delta U = U_f - U_i$ → Measurable

(TUTORIAL-1)
Concept of Internal energy:

Internal Energy, U. is the total energy within a system.

U is the internal energy of the body (due to molecular motions and intermolecular interactions)



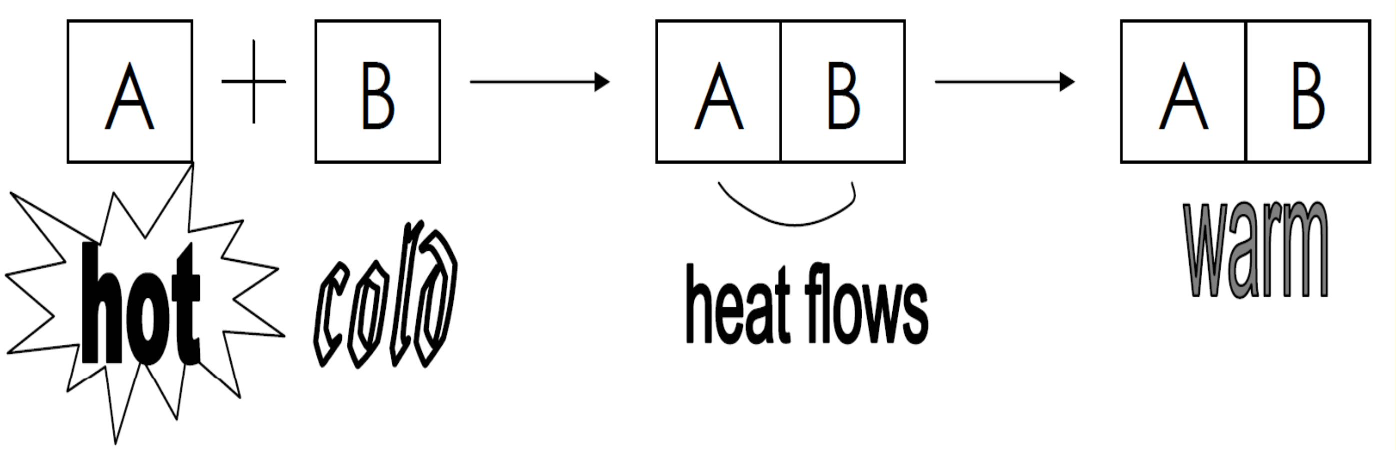
$U = f(V,T)$ $U = f(P,T)$ $U = f(P,V)$

It is convenient to choose V and T as the independent variables for U

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

- Extensive property.
- State function, independent of path.
- For cyclic process, $\oint dU = 0$
- dU is a perfect or exact differential

Thermal Equilibrium and Zero'th Law of Thermodynamics



====== ZERO'th LAW of Thermodynamics ======

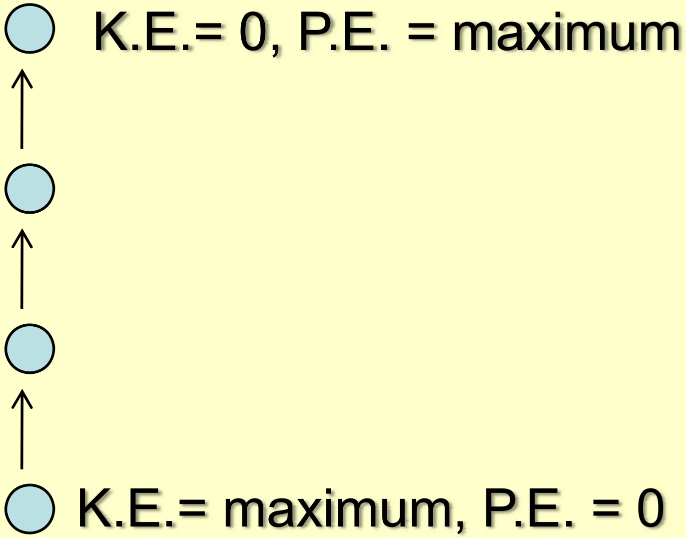
If A and B are in thermal equilibrium and
B and C are in thermal equilibrium,
then A and C are in thermal equilibrium.

Consequence of the zero'th law:

B acts like a thermometer, and A , B , and C are all at the same "temperature".

First Law of Thermodynamics:

Energy cannot be destroyed, it can be transformed to one form to another. (Law of conservation of energy).


K.E.= 0, P.E. = maximum

K.E.= maximum, P.E. = 0

✷ Energy is conserved

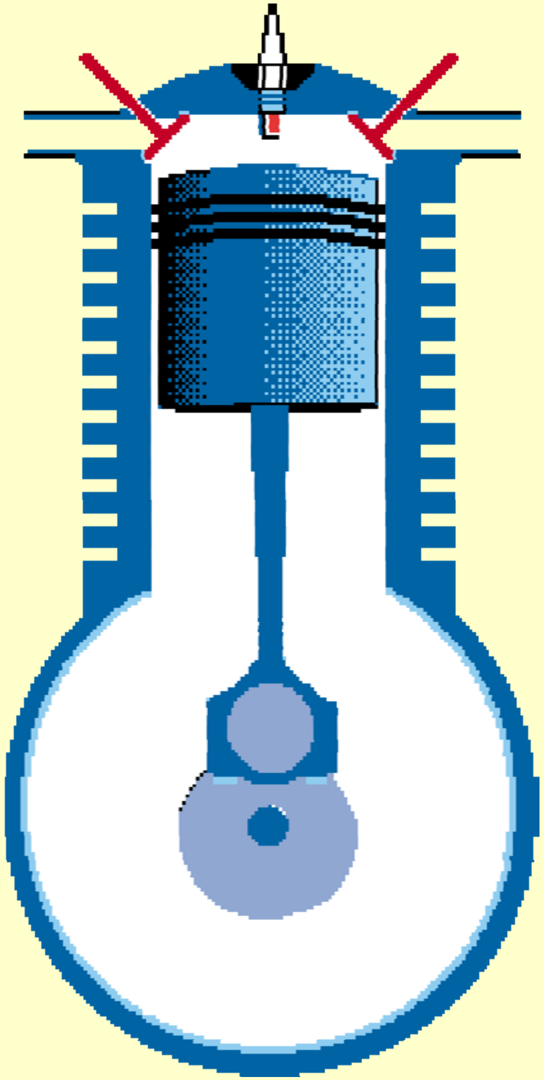
1st law of Thermodynamics

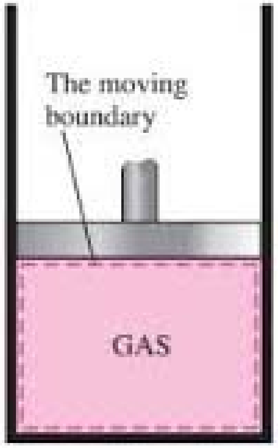
The first law for a closed system or a fixed mass may be expressed as:

net energy transfer to (or from)
the system as heat and work = net increase (or decrease) in the
total energy of the system

$$q + w = \Delta U$$

Moving Boundary Work

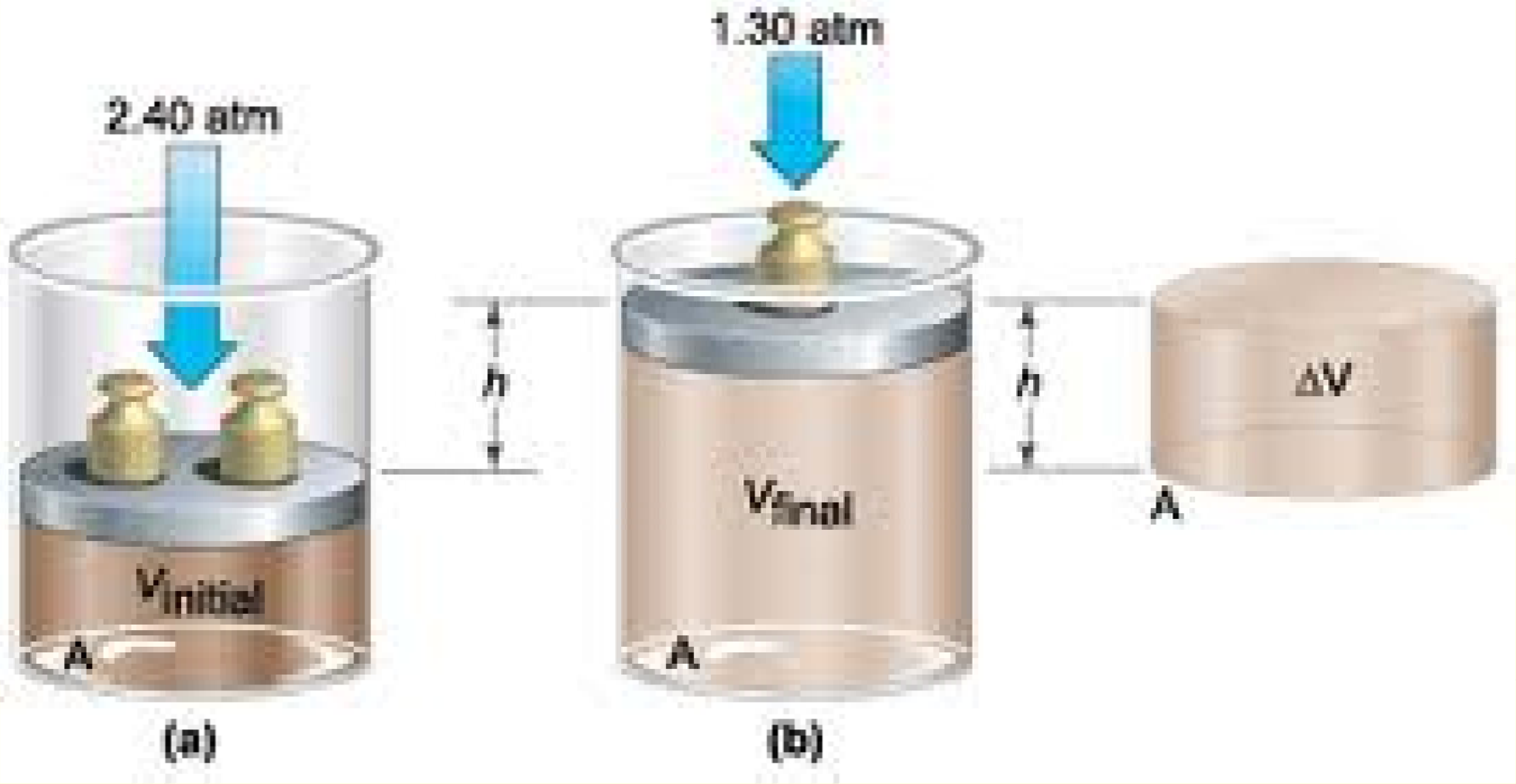




FIGURE

The work associated with a moving boundary is called *boundary work.*

How the expansion takes place in a piston-cylinder device

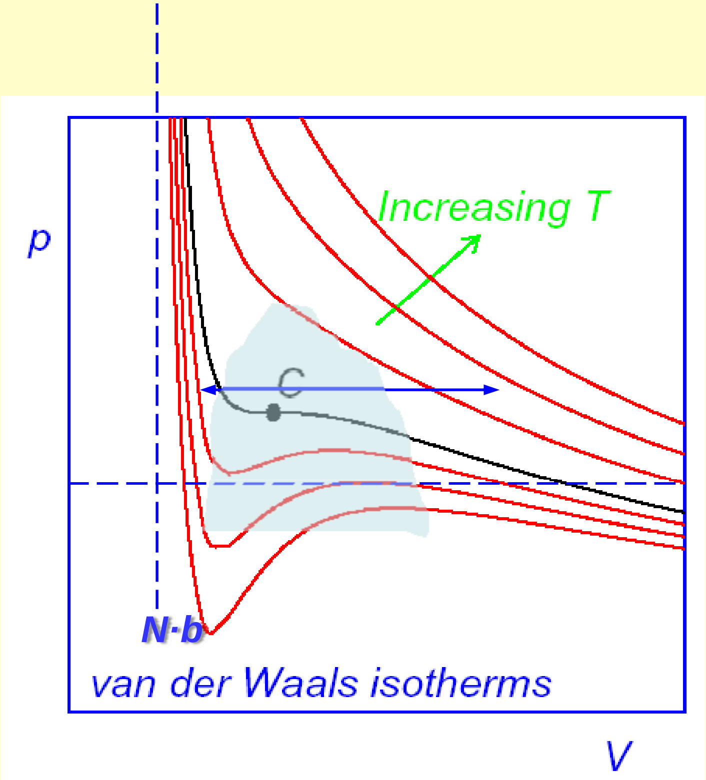


Equation of state for Ideal and Real gas

Ideal gas: $PV = nRT$

Real gas: van der Waal’s equation

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



TUTORIAL 2-3

Work and heat change associated in Isothermal Reversibl and irreversible expansion

Expansion Work:

(a) General expression of work (**reversible process**)

$$w_{rev} = \int_{1}^{2} PdV$$ closed syst., rev. process

(b) Irreversible process:

$$W_{irr} = P_{ext} (V_2 - V_1)$$

TUTORIAL 4

Adiabatic process in an Ideal Gas

- Since $dQ = 0$ for an adiabatic process,

$dU = -P\,dV$ and $dU = C_V\,dT$, so that $dT = -(P/C_V)\,dV$.

- For an ideal gas, $PV = nRT$,

so that $P\,dV + V\,dP = nR\,dT = -(nRP/C_V)\,dV$.

Hence $V\,dP + P\,(1 + nR/C_V)\,dV = 0$.

Thus, $C_V\,dP/P + (C_V + nR)\,dV/V = 0$.

For an ideal gas, $C_P - C_V = nR$.

so that $C_V\,dP/P + C_P\,dV/V = 0$, or $dP/P + \gamma\,dV/V = 0$.

- Integration gives $\ln P + \gamma \ln V = \text{constant}$, so that

$$PV^{\gamma} = \text{constant.}$$

Adiabatic process in an Ideal Gas

- Work done in a **reversible** adiabatic process

For a reversible adiabatic process, $PV^{\gamma} = K$.

- Since the process is reversible, $W = -C_V \Delta T = C_v(T_1 - T_2)$,

For 1 mole of gas , $T = PV/R$

so that Wadi $= = Cv[P_1V_1/R - P_2V_2/R]$

$= Cv/R[P1V1-P2V2]$

$$\therefore \qquad W = 1/(\gamma - 1)\ [P_2V_2 - P_1V_1].$$

- For an monatomic gas, $\gamma = 5/3$, so that

$$W = -(3/2)]\ [P_2V_2 - P_1V_1].$$

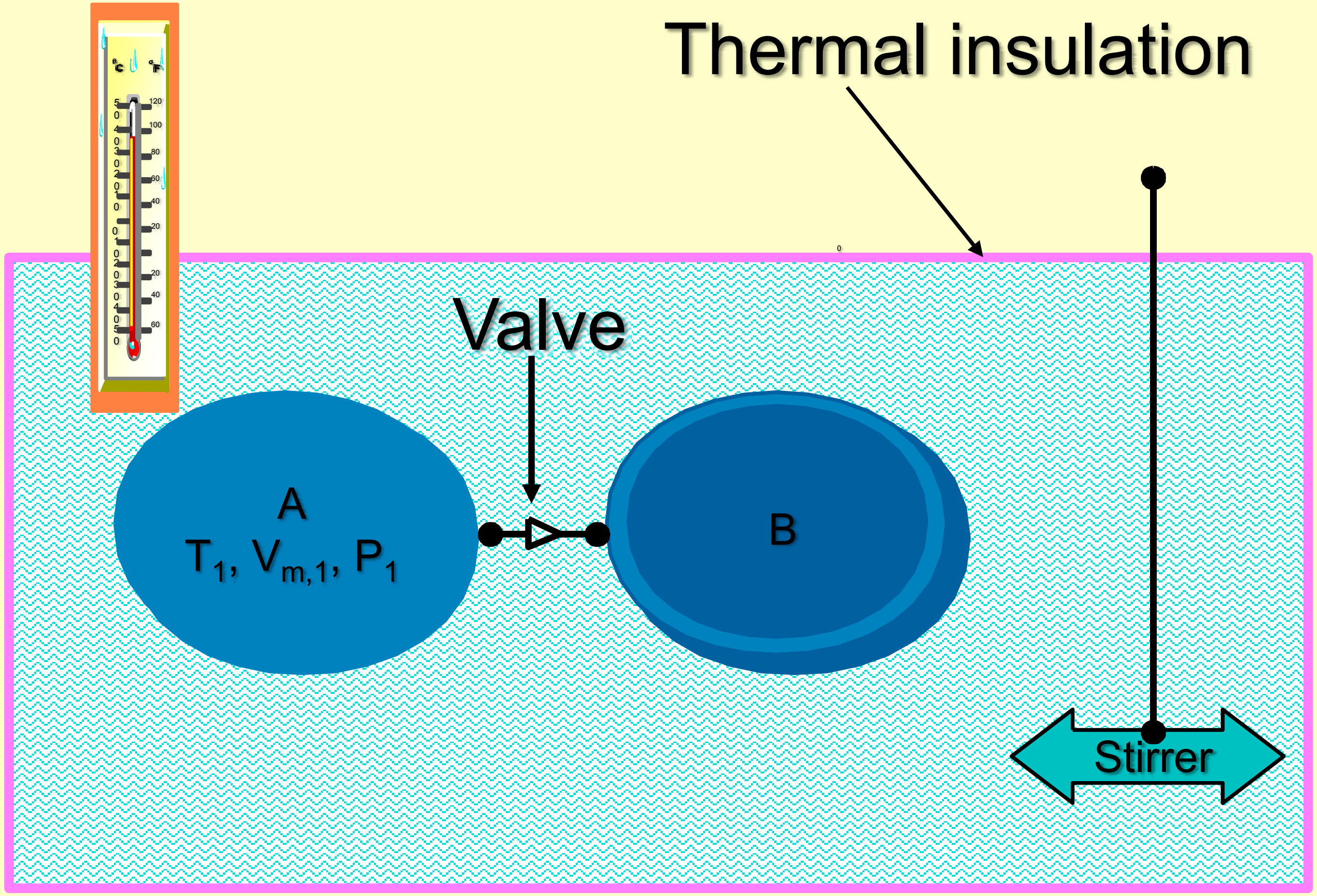
Reversible Processes for an Ideal Gas

Adiabatic process	Isothermal process	Isobaric process	Isochoric process
$PV^\gamma = K$ $\gamma = C_P/C_V$	T constant	P constant	V constant
$W = -[1/(\gamma - 1)] . [P_2V_2 - P_1V_1]$	$W = nRT \ln(V_2/V_1)$	$W = P \Delta V$	$W = 0$
$\Delta U = C_V \Delta T$	$\Delta U = 0$	$\Delta U = C_V \Delta T$	$\Delta U = C_V \Delta T$

$PV = nRT$, $U = nc_VT$, $c_P - c_V = R$, $\gamma = c_P/c_V$.

Monatomic ideal gas $c_V = (3/2)R$, $\gamma = 5/3$.

The Joule Experiment



Thermal insulation

Valve

A

T_1, $V_{m,1}$, P_1

B

Stirrer

1. No change in temperature was detected,

dq = 0

2. As expansion is taking place against **zero pressure**,

dw = 0,

As a result, dU = 0

U = f(V,T)

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial U}{\partial T}\right)_V$$

$$\left(\frac{\partial T}{\partial V}\right)_U = 0,$$

$$Hence \quad , \left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$ (VALID for ideal gas only)

$$\left(\frac{\partial U}{\partial V}\right)_T \neq 0 \quad \left(\frac{\partial U}{\partial V}\right)_T = a/v^2$$ (VALID for REAL gas only)

😐Actually the gas which had expanded into B was somewhat cooler and when thermal equilibrium was finally established the gas was at a slightly different temperature from that before the expansion.

😐😐 Because the system used by Joule had a very large heat capacity compared with the heat capacity of air, the small change of temperature that took place was not observed.

Concept of Enthalpy and heat Capacities

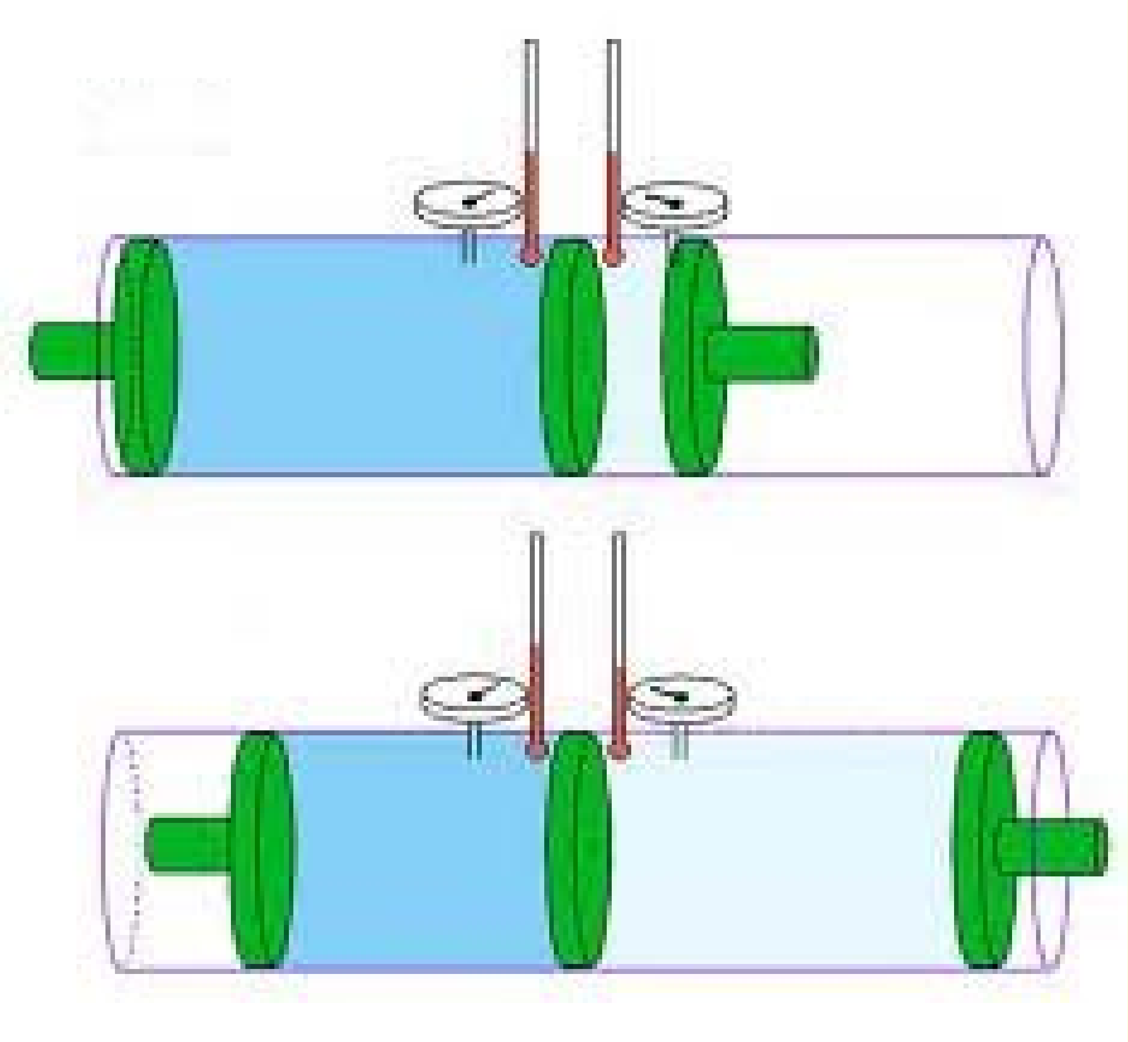
😐 Prove that, $\Delta H = \Delta q_P$

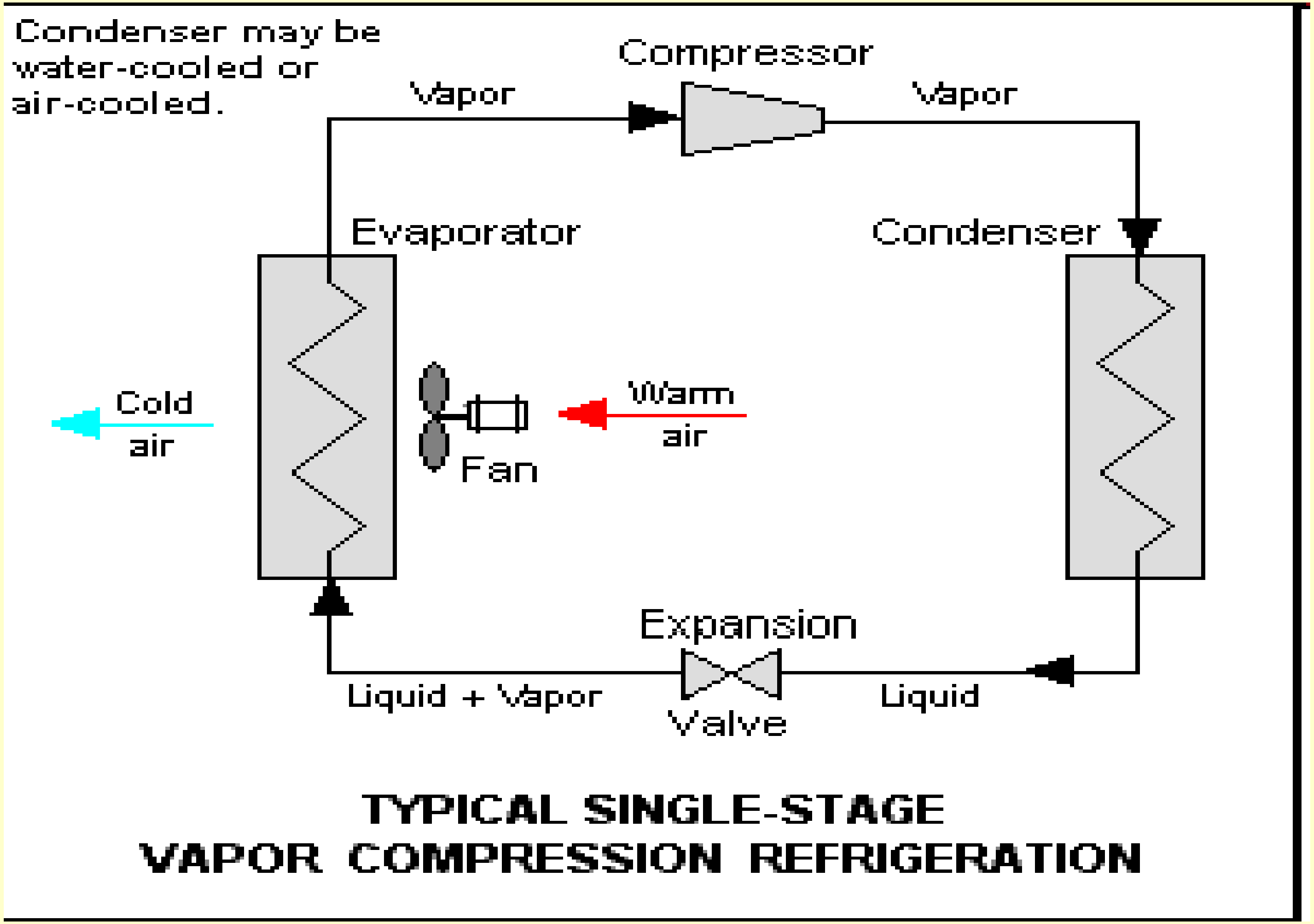
😐 Prove that, $C_P - C_V = R$ (for one mole of Ideal gas)

Joule-Thompson Effect

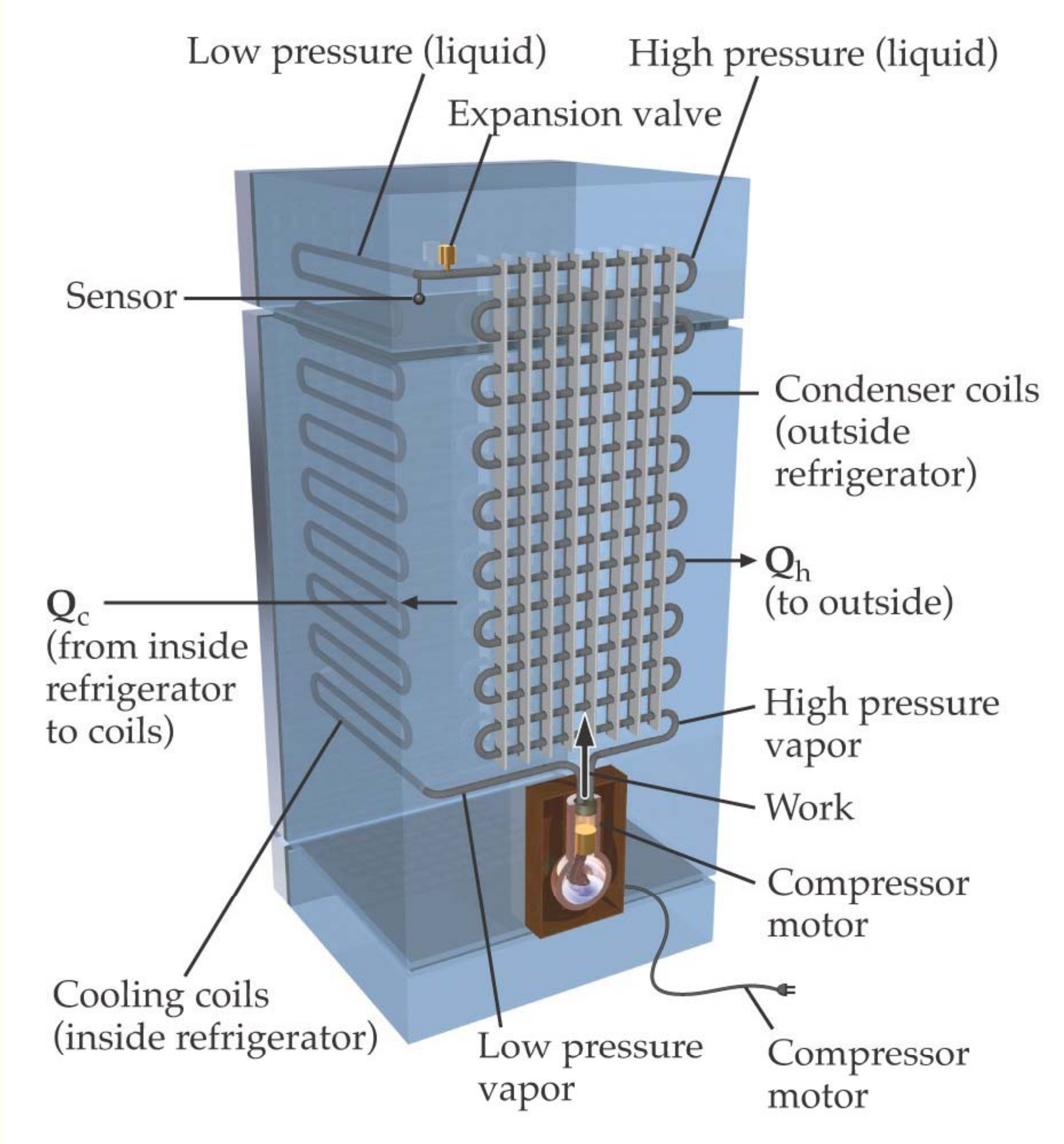
A gas passes through a POROUS PLUG from a region where it is at high pressure to a region where it is at lower pressure. The gas expands, and the temperature of the gas can be lowered. This is an important tool in low temperature physics.

Joule-Thompson Apparatus



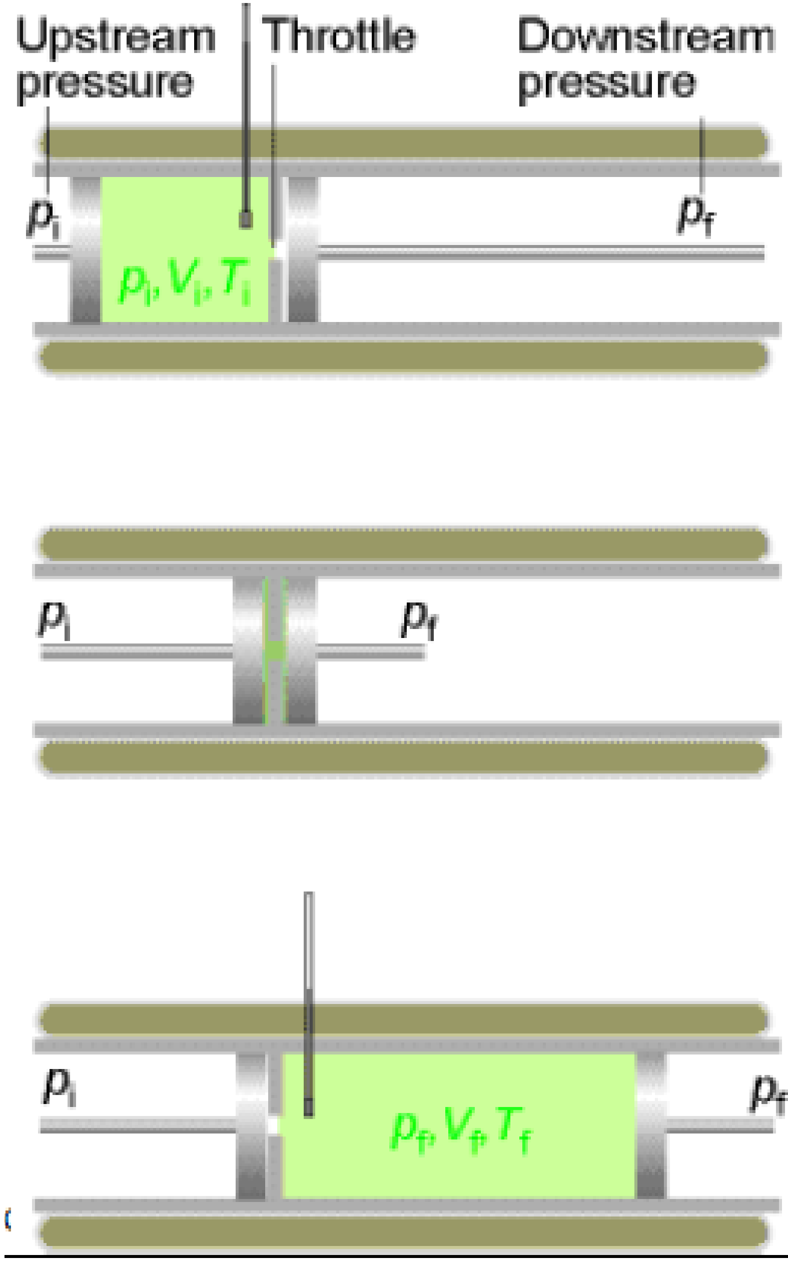


TYPICAL SINGLE-STAGE
VAPOR COMPRESSION REFRIGERATION


Low pressure (liquid)
High pressure (liquid)
Expansion valve
Sensor
Condenser coils (outside refrigerator)
Q_h (to outside)
Q_c (from inside refrigerator to coils)
High pressure vapor
Work
Compressor motor
Cooling coils (inside refrigerator)
Low pressure vapor
Compressor motor

THE JOULE-THOMPSON EXPERIMENT

A further test of intermolecular forces in real gases.



$$\Delta H = \left(\frac{\partial H}{\partial T}\right)_P \Delta T + \left(\frac{\partial H}{\partial P}\right)_T \Delta P = 0$$

Imagine a sample of gas pushed through a porous plug, in an isolated tube (adiabatic system). The temperature is measured on each side of the plug.

Analysis

$$w = p_i V_i - p_f V_f$$

Since $\Delta U = U_f - U_i = w$ (because $q = 0$),

$$U_f + p_f V_f = U_i + p_i V_i$$

$$H_f = H_i \text{ i.e. } \Delta H = 0$$

This is a constant enthalpy (isenthalpic) process.

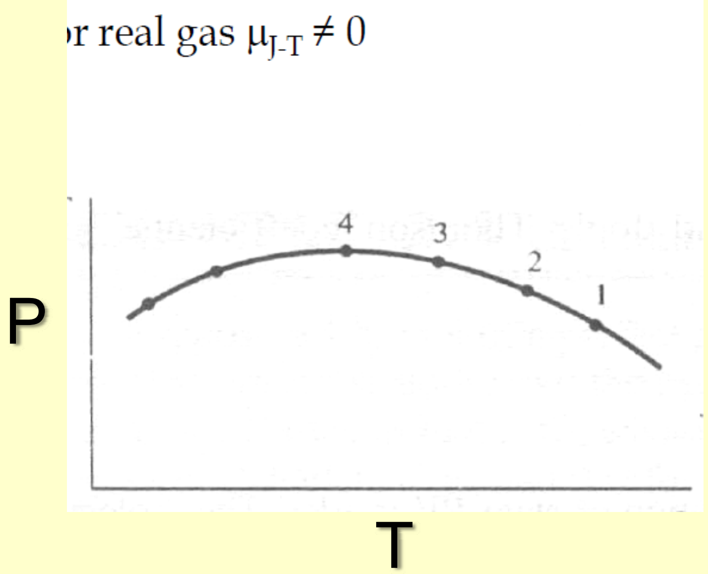
What is

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \qquad ??? = -\left(\frac{\partial H}{\partial P}\right)_T$$

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T = \mu_{JT}$$

Later we can show

$$\left(\frac{\partial T}{\partial P}\right)_H = \mu_{JT} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$



- In an adiabatic throttle process, the gas pressure is reduced ($P_2 < P_1$), and thus
- If $\mu_{J-T} = (\frac{\partial T}{\partial P})_H > 0$ the temperature of the gas is reduced, **T2<T1** , which produces a cooling effect;
- If $\mu_{J-T} = (\frac{\partial T}{\partial P})_H < 0$,the temperature of the gas is raised, **T2>T1**, which produces a heating effect;
- If $\mu_{J-T} = (\frac{\partial T}{\partial P})_H = 0$, the temperature of the gas has no change, i.e., **T2=T1**