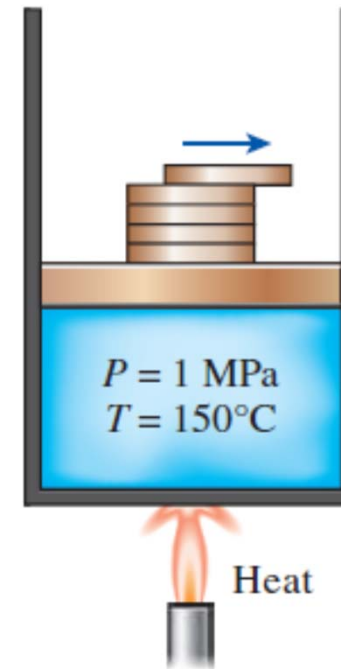
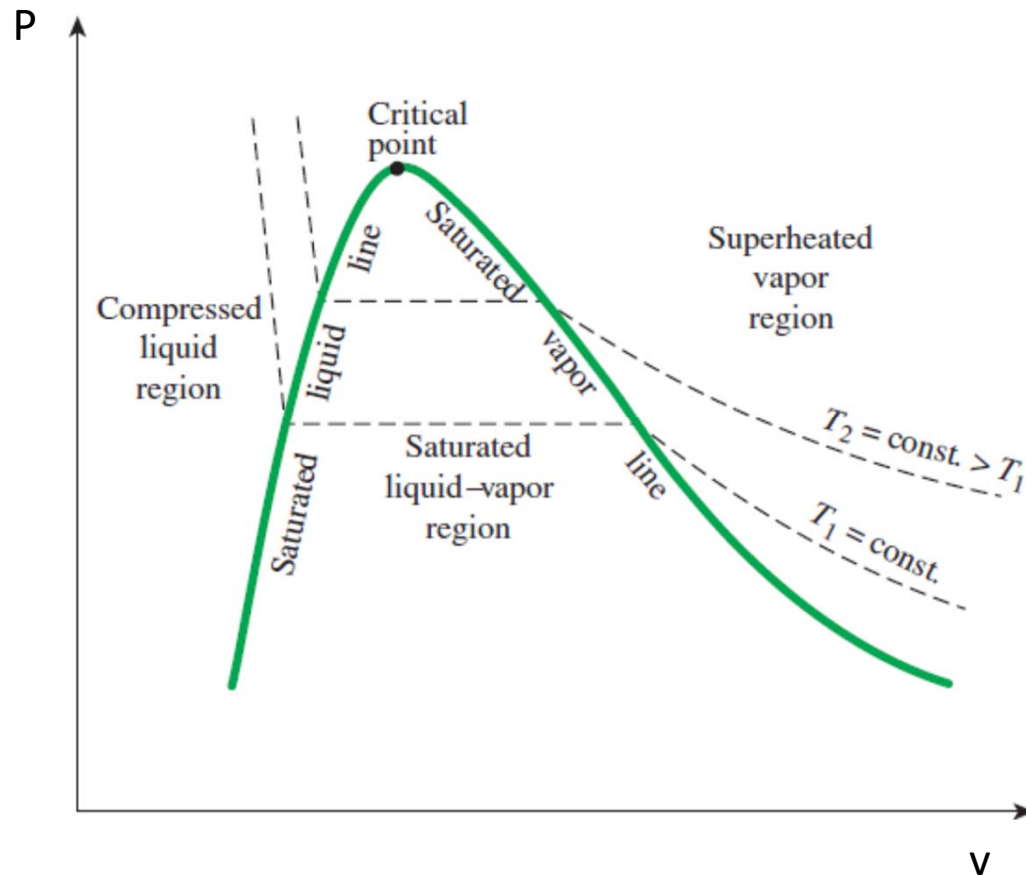


## P-v diagram :



Decompression at constant temperature of  $150^\circ\text{C}$  in 3 stages as described below

**Stage 1** : As P decreases starting from compressed liquid state, v increases slightly until saturated liquid state is achieved (P decreases from 1 MPa to 0.4762 MPa)

**Stage 2** : As saturated water is heated at constant P, vaporization occurs and v increases. Until all of liquid is vaporized and saturated vapor state is achieved (P is constant at 0.4762 MPa)

**Stage 3** : Reduction in P below the saturation value leads to expansion of the vapor from Saturated state to superheated vapor (P decreases below 0.4762 MPa)

## Vapor-solid equilibrium:



**Sublimation** involves direction transition between vapor and solid phase

Sublimation occurs (upon heating) if the pressure is below that at the **triple point** (to be discussed in later slides).



Dry ice (solid CO<sub>2</sub>)

CO<sub>2</sub> does not have a liquid state at Atmospheric pressure.

Solid CO<sub>2</sub> (also known as dry ice) sublimates at 194.7 K (−78.5 °C; −109.2 °F)

## Liquid-solid equilibrium:



water ice equilibrium

Water expands upon cooling below  $4^{\circ}\text{C}$  at 1 atm.

Ice has a larger volume than water

Ice floats on water !!



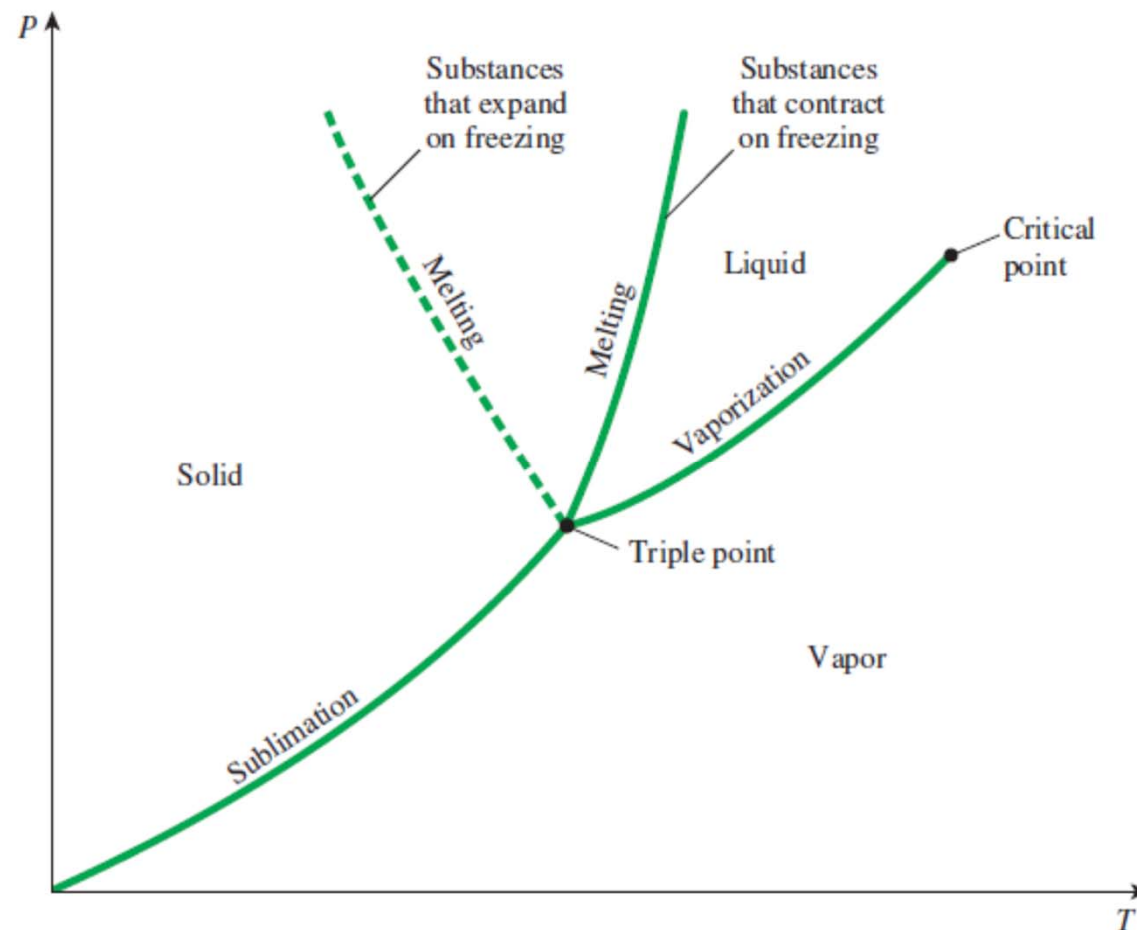
Antarctic ice sheets

## Triple point :



At pressure and temperature corresponding to **triple point**, three phases : vapor, liquid, and solid are in equilibrium

This is a unique point, i.e., it is a single point in the P-T diagram.



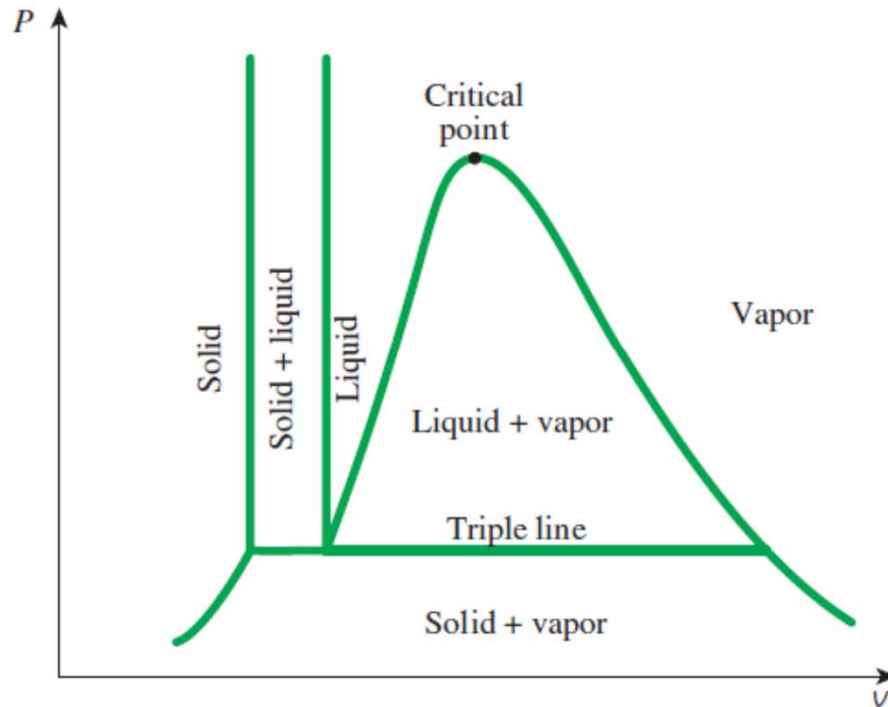
## Triple point :

**TABLE 3-3**

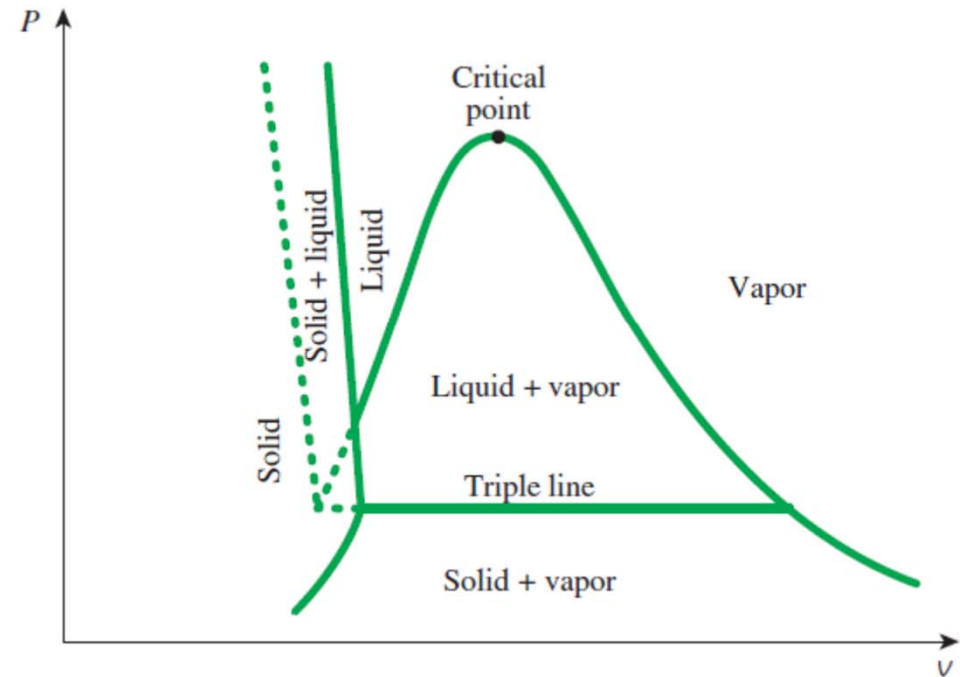
Triple-point temperatures and pressures of various substances

Substance	Formula	$T_{tp}$ , K	$P_{tp}$ , kPa
Acetylene	$C_2H_2$	192.4	120
Ammonia	$NH_3$	195.40	6.076
Argon	A	83.81	68.9
Carbon (graphite)	C	3900	10,100
Carbon dioxide	$CO_2$	216.55	517
Carbon monoxide	CO	68.10	15.37
Deuterium	$D_2$	18.63	17.1
Ethane	$C_2H_6$	89.89	$8 \times 10^{-4}$
Ethylene	$C_2H_4$	104.0	0.12
Helium 4 ( $\lambda$ point)	He	2.19	5.1
Hydrogen	$H_2$	13.84	7.04
Hydrogen chloride	HCl	158.96	13.9
Mercury	Hg	234.2	$1.65 \times 10^{-7}$
Methane	$CH_4$	90.68	11.7
Neon	Ne	24.57	43.2
Nitric oxide	NO	109.50	21.92
Nitrogen	$N_2$	63.18	12.6
Nitrous oxide	$N_2O$	182.34	87.85
Oxygen	$O_2$	54.36	0.152
Palladium	Pd	1825	$3.5 \times 10^{-3}$
Platinum	Pt	2045	$2.0 \times 10^{-4}$
Sulfur dioxide	$SO_2$	197.69	1.67
Titanium	Ti	1941	$5.3 \times 10^{-3}$
Uranium hexafluoride	$UF_6$	337.17	151.7
Water	$H_2O$	273.16	0.61
Xenon	Xe	161.3	81.5
Zinc	Zn	692.65	0.065

## P-v diagrams involving all three phases :



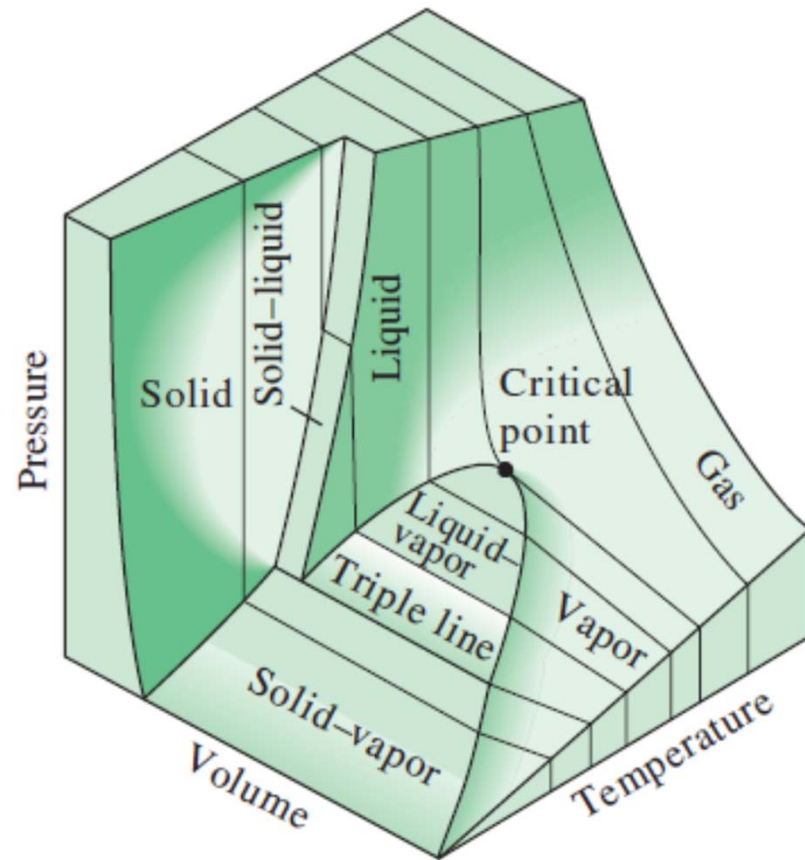
For substances which contract on freezing



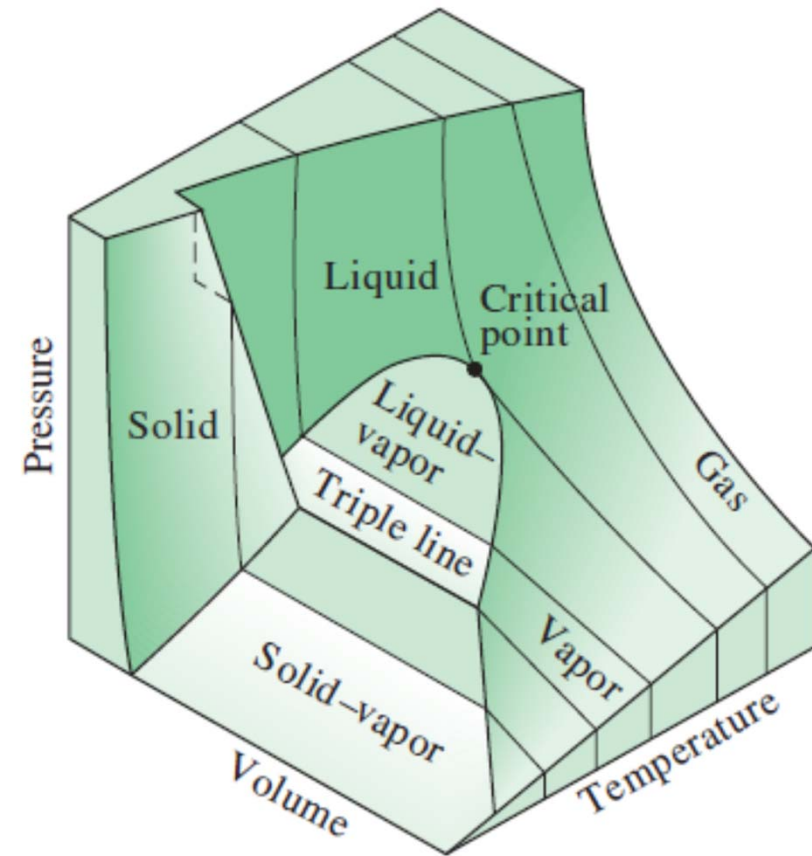
For substances which expand on freezing



## P-v-T surface :



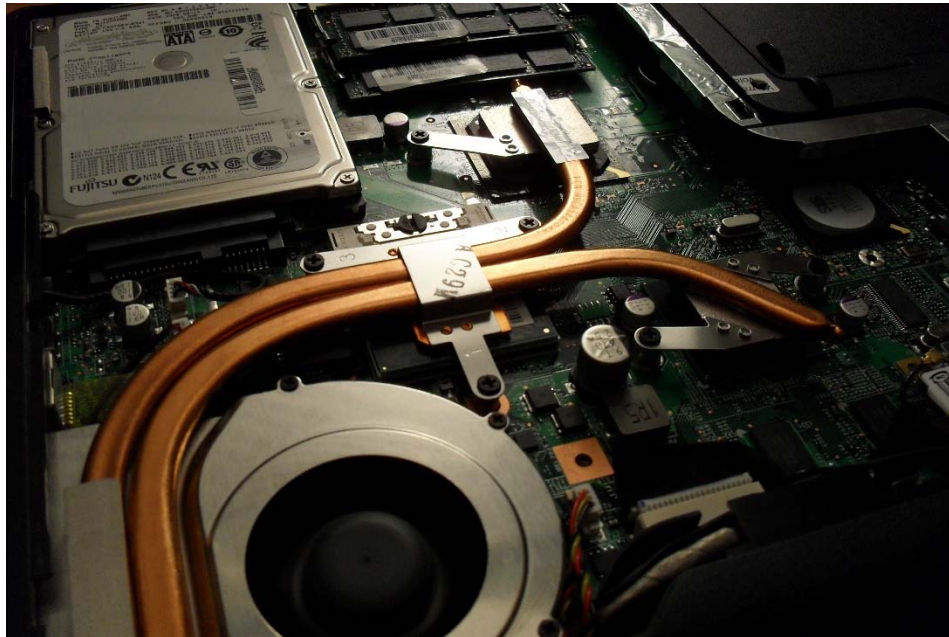
For substances which contract on freezing



For substances which expand on freezing

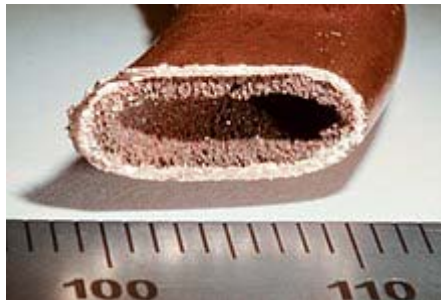
# Applications of phase change processes :

## Heat pipes



Heat pipes are used for cooling of electronic circuits

Heat pipes with copper envelop and water as the working fluid are commonly used for  $T$  from 20 to 150°C

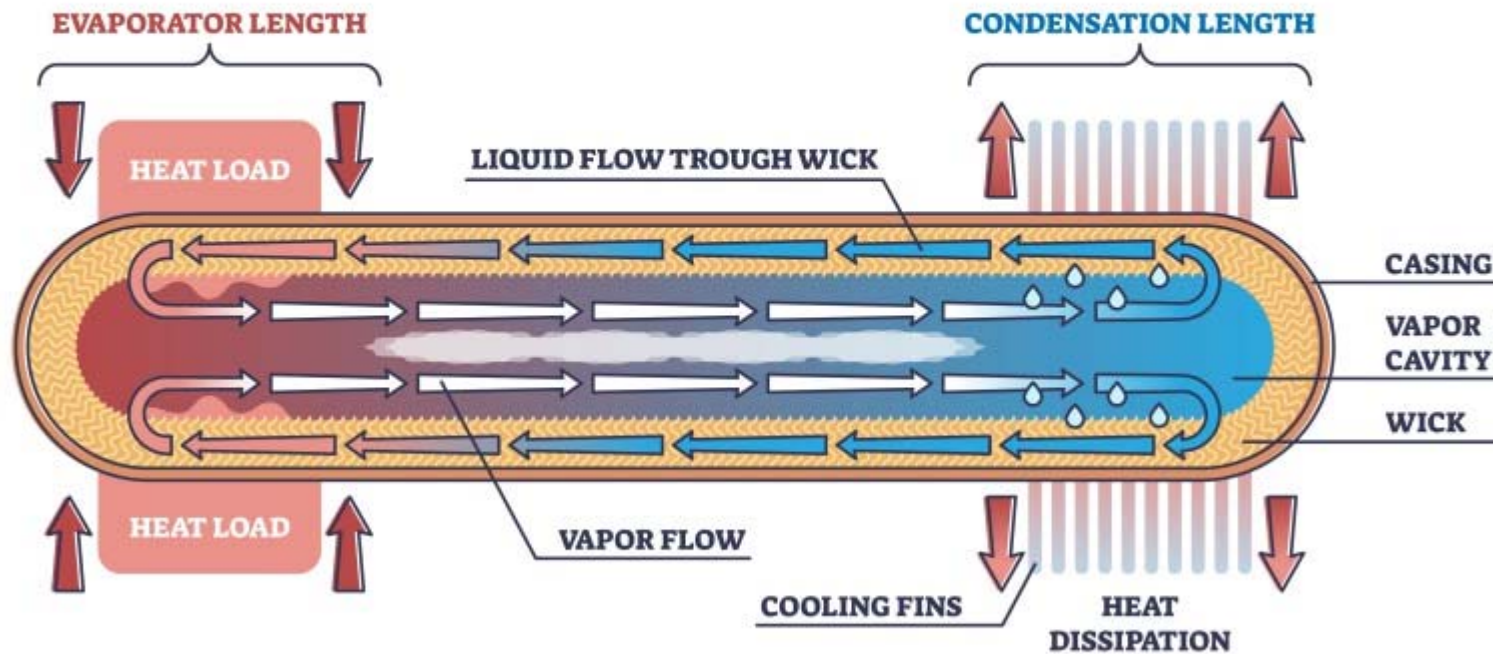


Cross section of a heat pipe  
(scale shown in mm)



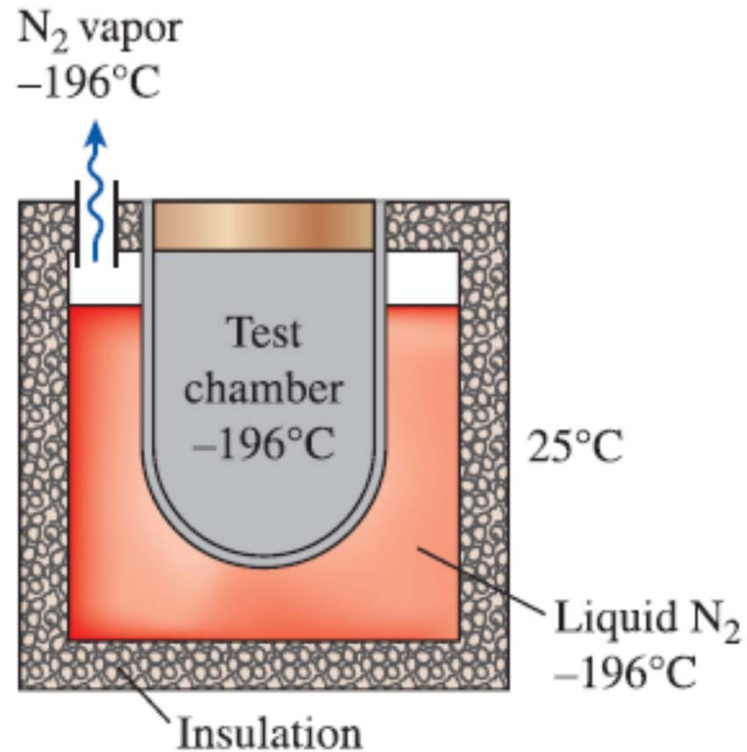
## Applications of phase change processes :

### HEAT PIPE



Effective thermal conductivity of heat pipes can be as large as  $100 \text{ kW}/(\text{m.K})$  which is **2500 times** as compared to copper  $0.4 \text{ kW}/(\text{m.k})$

## Applications of phase change processes :



Liquid nitrogen can be used to maintain very low temperatures  
In cryogenic applications

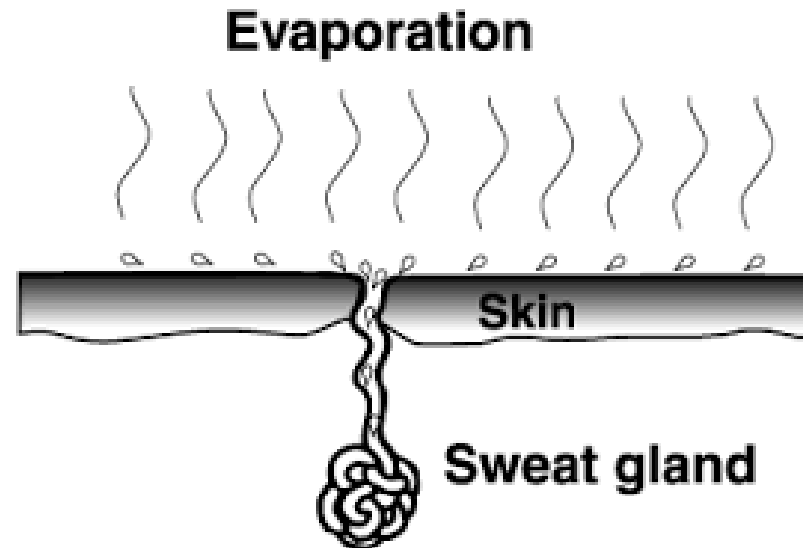
## Applications of phase change processes :



Latent heat of evaporation of water is used for cooling applications

# Applications of phase change processes :

## Sweating



A person's internal body temperature generally is maintained at around 98 degrees Fahrenheit.

As soon as your body's internal temperature starts rising, your hypothalamus (a small region in your brain) tells eccrine sweat glands distributed all over your body that it's time to start cooling you down by producing sweat.

# Internal energy:

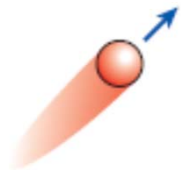
The energy transfer in the form of heat and work processes results in changes of internal energy  $U$ . Hence it is important to have a better understanding of changes in  $U$ .

$$U = \langle K. E. \rangle + \langle P. E. \rangle$$

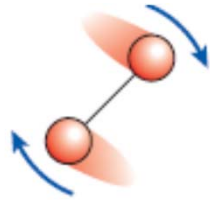
$\langle K. E. \rangle$  = Average kinetic energy of atoms and molecules and Subatomic particles

$\langle P. E. \rangle$  = Average potential energy of due to intermolecular, Intra-molecular and intra-atomic binding forces

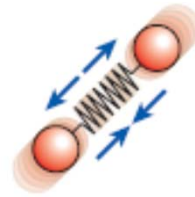
$$\langle \text{K. E.} \rangle = \langle \text{translational K.E.} + \text{rotational K.E.} + \text{vibrational K.E.} \rangle$$



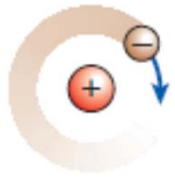
Molecular translation



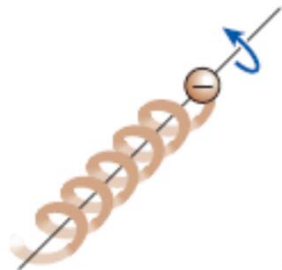
Molecular rotation



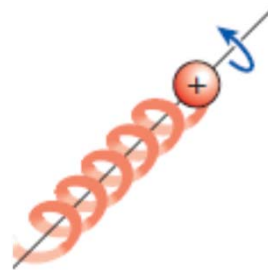
Molecular vibration



Rotation of electrons



Electron spin



Nuclear spin

$$\langle \text{K. E.} \rangle \propto T$$

Average (microscopic) kinetic energy is also known as **Sensible energy.**

For gases, changes in microscopic kinetic energy is mostly due to translation and rotation of molecules from room temperature to moderately high temperatures. **Vibrational motion becomes significant only at high temperatures.**



# Heat capacity at constant volume $C_v$ :

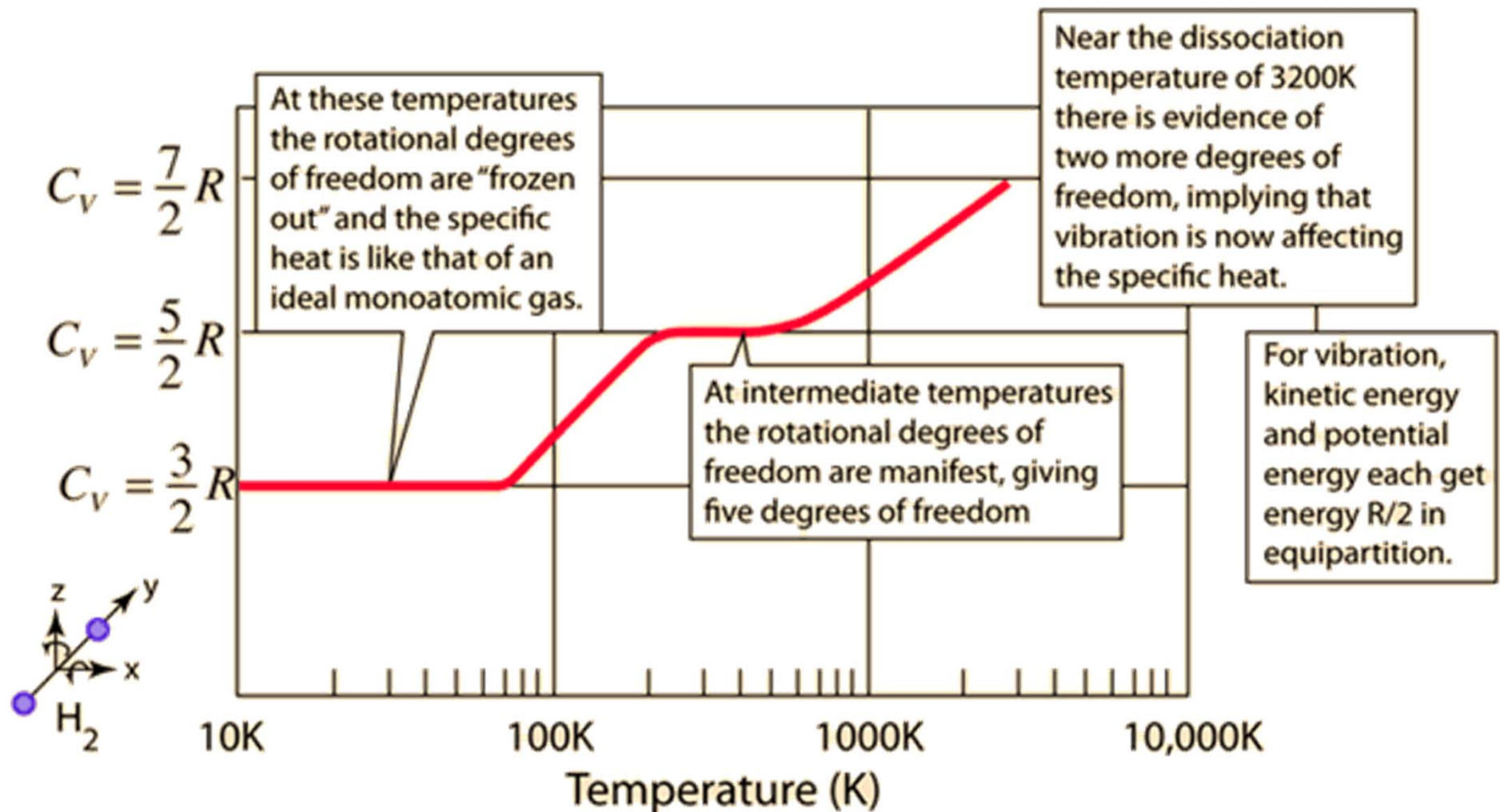
Processes involving changes of temperature are affected by changes in kinetic energies due to translation, rotation, and (intra-molecular) vibration of molecules

The amount of heat per kg or per mole of a substance required to increase the temperature by  $1^\circ\text{C}$  is known as specific heat .

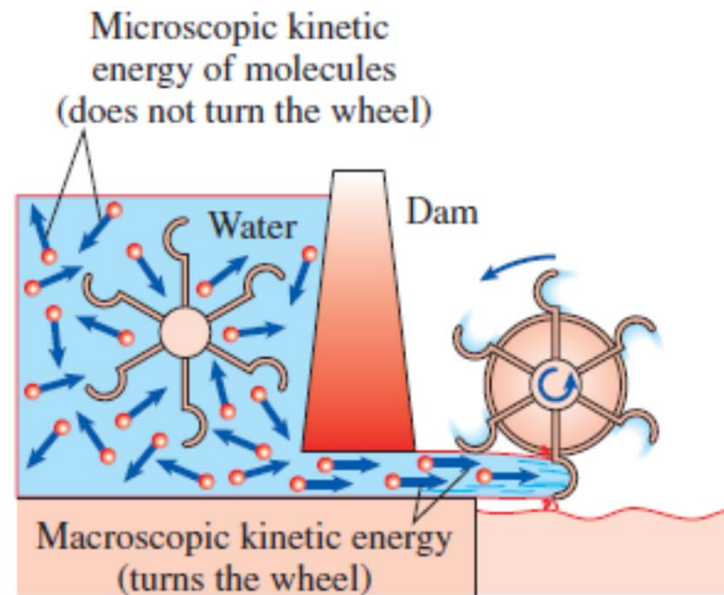
So, these microscopic kinetic energies directly affect specific heat.

Specific heat at constant volume ( $C_v$ ) refer to amount of heat absorbed per unit mass or per mole to increase temperature by  $1^\circ\text{C}$  at constant volume. Similarly specific heat at constant pressure ( $C_p$ ) is defined.

Hydrogen gas is composed of diatomic molecules of  $H_2$ . The following plot shows how specific heat at constant volume ( $C_v$ ) is affected by kinetic energies due to translation, rotation, and vibration of  $H_2$  molecules. Each degree of freedom contributes  $(1/2) R$  to  $C_v$



# Microscopic and macroscopic kinetic energy



Microscopic kinetic energy (due to random motion) contributes to temperature. These random motions occur on a very small time scale.

Macroscopic kinetic energy is due to overall motion of the system.