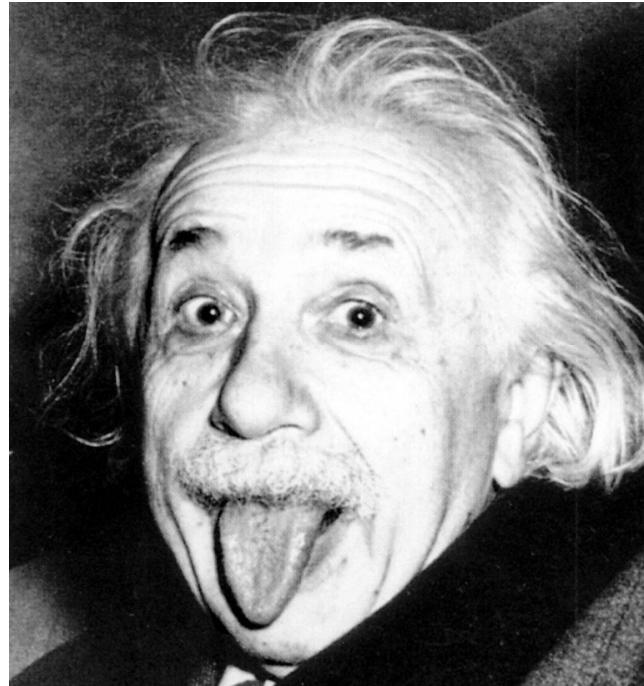


*Thermodynamics*  
*Why, What & How*

Raj Pala,  
[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme  
Indian Institute of Technology, Kanpur.

# *Thermodynamics (TD) in Social Media*



“ Thermodynamics is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.”

# *First course handout...*

- Posted on Mookit
- Very many relevant information...but will not be repeated here

# $\mathcal{T}\mathcal{D}$ : Why & what?

- **Mechanics:** Particles, forces and energy, stress & strain, viscosity, modulus, relativity...Gravitational constant- $G$
- **Electrostatics and electrodynamics:** Fields, electric and magnetic field, scalar and vector potential...Speed of light- $C$
- **Quantum mechanics:** Wave function, Unobservable & measurement, ...Planck's constant- $h$
- **Thermodynamics:** “Macroscopic” variable “Temperature-T”

# *Macroscopic & Microscopic*

- Relative, Absolute & Useful...
- Relative: Cosmology to elementary particles...
- Absolute: Planck length scale =  $\sqrt{\frac{Gh}{c^3}} \sim 10^{-35} \text{ m}$
- Useful: Macroscopic scale~ human length & time scale accessible to human senses/experience, “macro” equipment (measuring cylinder, thermometer, manometer...)
- Macroscale can be “reasoned” from microscopic...but the strength of macroscopics/thermodynamic is in reproducible measurements!  $PV=nRT$ ,  $\Delta E=mC \Delta T$ ...**Phenomenological**

# *Macroscopic & Microscopic: Obvious?*

- Familiarity brings in “pseudo-triviality”, take it for granted...
- At the level of atom T, P & V are undefined...
- Macro-description ~  **$10^{23}$  atoms**
- Averages from microscopic can be related to macroscopics
- Equipartition theorem: T & average kinetic energy

# *Macroscopics: Economy in description*

- Growth rate of a country...
- Tabulate the income of all people and keep track of it year to year...Present this data



- Present the data on the Per-Capita Income
- **Averages** provides an **economy in description**...also indicative of certain features of income distribution
- **Macroscopic thermodynamic properties** are averages over **microscopic properties**
- What kind of average? Weighted average...? Questions of **statistical** thermodynamics (ST)/**statistical** mechanics (SM)...

# *Microscopics: Power and limitations...*

- Mechanism behind physical properties and phenomenon
- Mother of Big Data- **$10^{23}$  atoms!**
- Propagate the equation of motion for large number of atoms (~  $10^{23}!$ ) in time to get averages... “sampling energies of different configuration” provide the *weight* for averages-ST/SM
- What & how to measure vs. What & how to compute...

# *Macroscopics & Human experience*

- Thermal “equilibrium” and sense of hotness-**Temperature**
- Something for nothing is impossible- **Energy conservation**
- Directionality of “natural process”- **Entropy increase**

# *Thermodynamics: Two viewpoints*

- Energy transformation (Greek: Therme-heat & dynamics-power; Lord Kelvin-1854 to emphasis “heat” as motion & not as a fluid!); Unification of “heat” & mechanics
- Theory underlying macroscopic measurements involving T; Arrow of time...

# *What we won't cover in this course...*

- This course is about thermo**statics**-Systems under equilibrium
- Transformations occur via “**quasi-static**” processes
- Linear non-equilibrium TD: Fluxes because of forces (e.g. heat flux and temperature difference driving force)
- Entropy generation & Onsager’s reciprocal relationship
- Non-linear TD: Order due to long-range coherence giving raise to dissipative structures (multiple ordered structures)
- Implications to biology (Prigogine)

*Books*  
*Read, heard & downloaded*

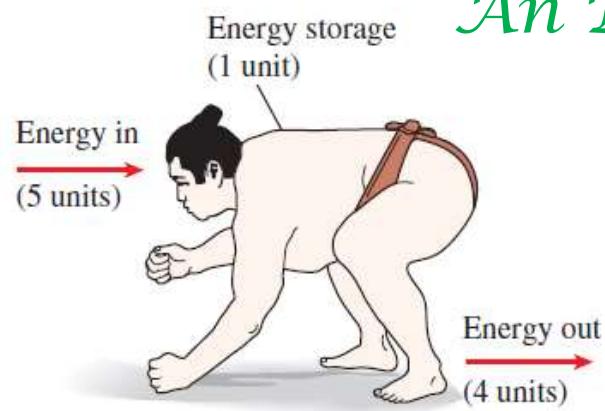
Raj Pala,  
[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme  
Indian Institute of Technology, Kanpur.

*Textbook: Cengel and Boles, Thermodynamics  
An Engineering Approach  
9th Edition (2017)-e-book access by IIT-K*

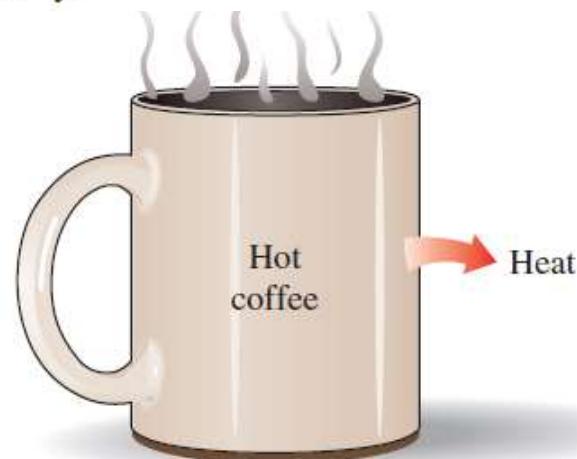


# Textbook: Cengel and Boles, Thermodynamics An Engineering Approach 9th Edition (2017)



**FIGURE 1–2**

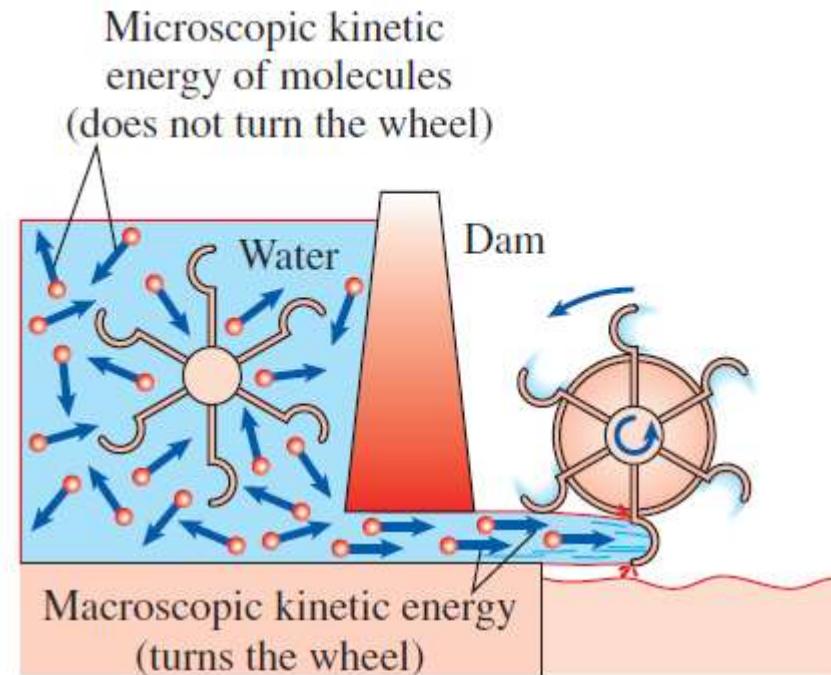
Conservation of energy principle for the human body.



**FIGURE 6–1**

A cup of hot coffee does not get hotter in a cooler room.

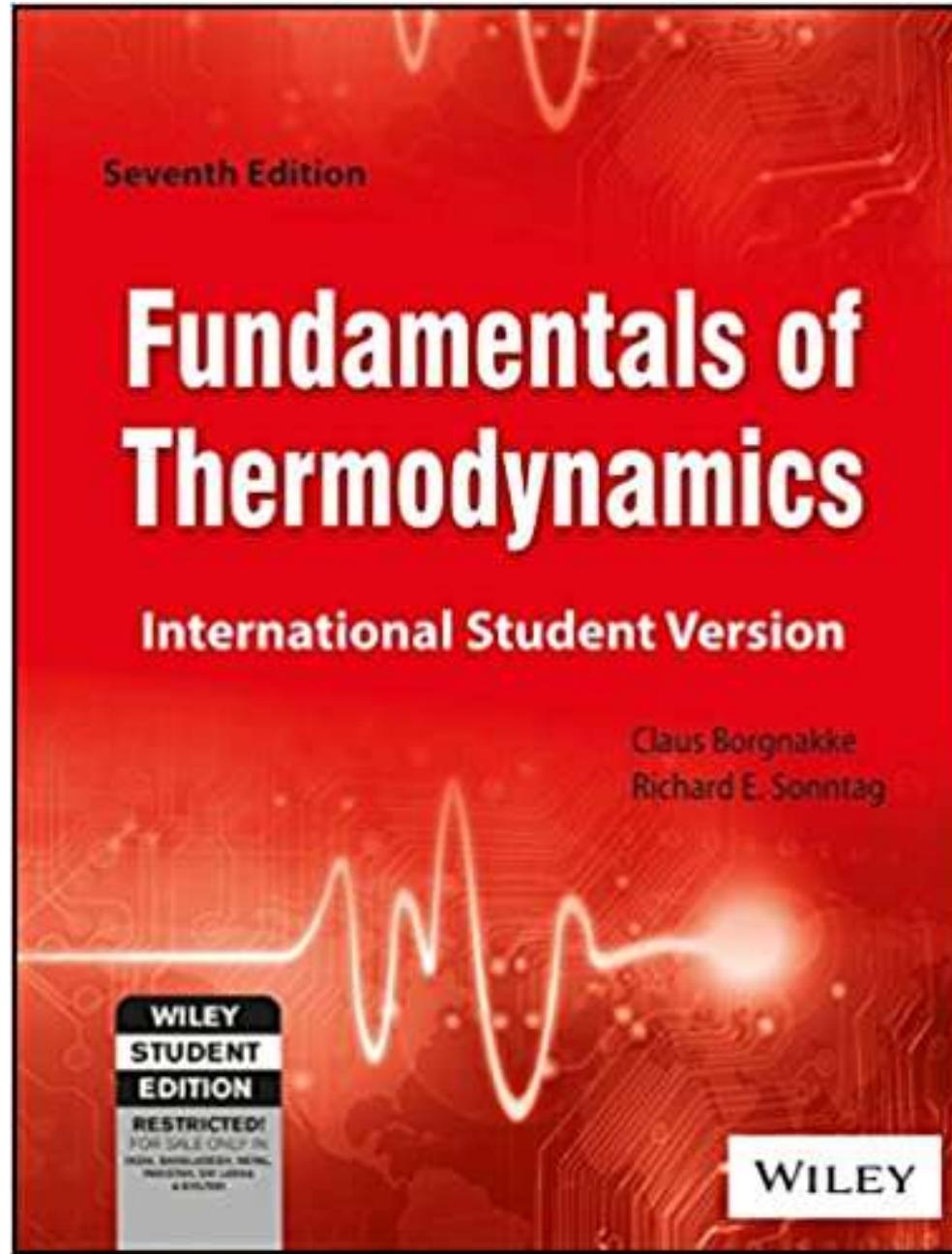
- Clear and simple explanations with many applications



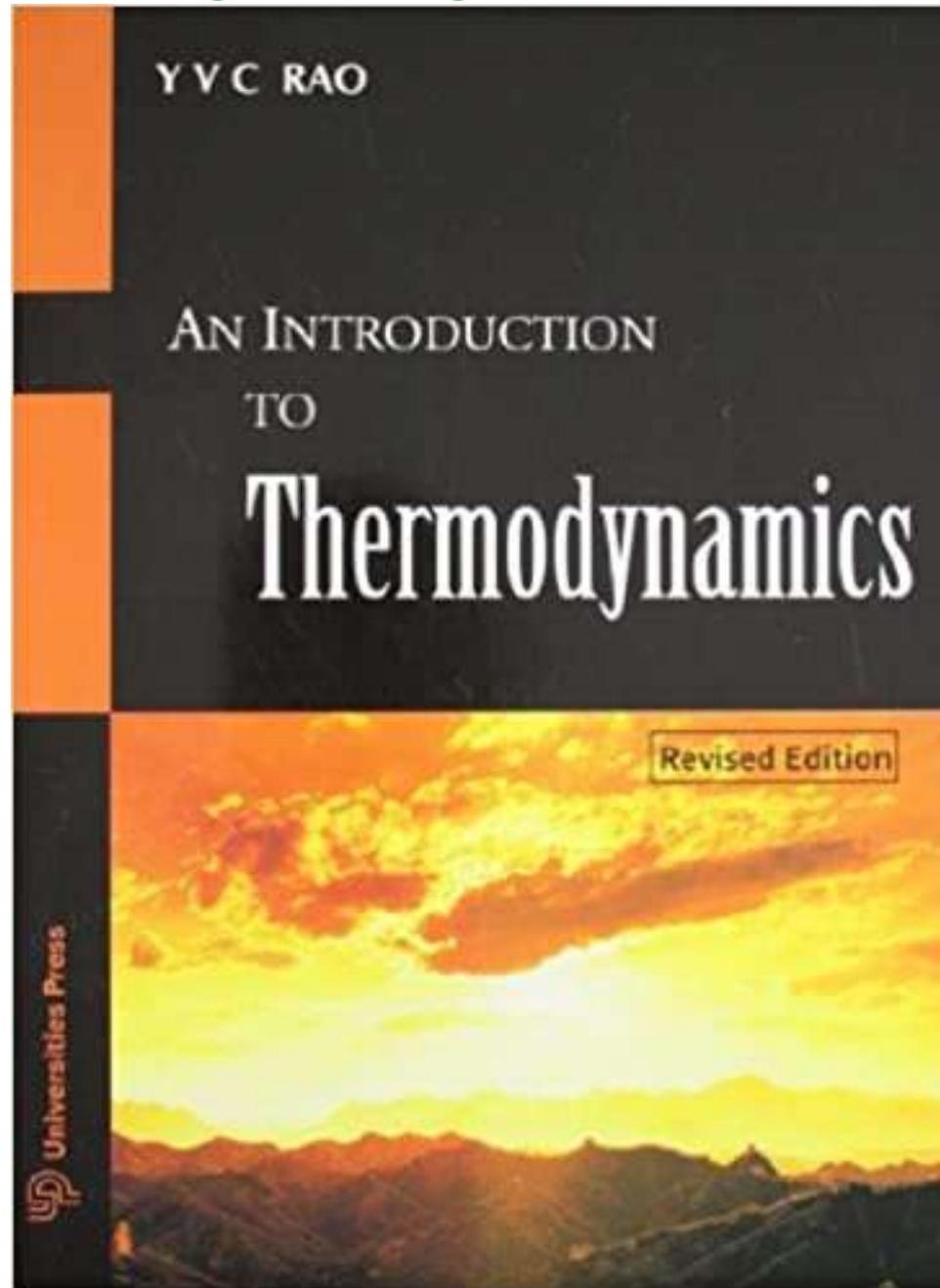
**FIGURE 2–8**

The *macroscopic* kinetic energy is an organized form of energy and is much more useful than the disorganized *microscopic* kinetic energies of the molecules.

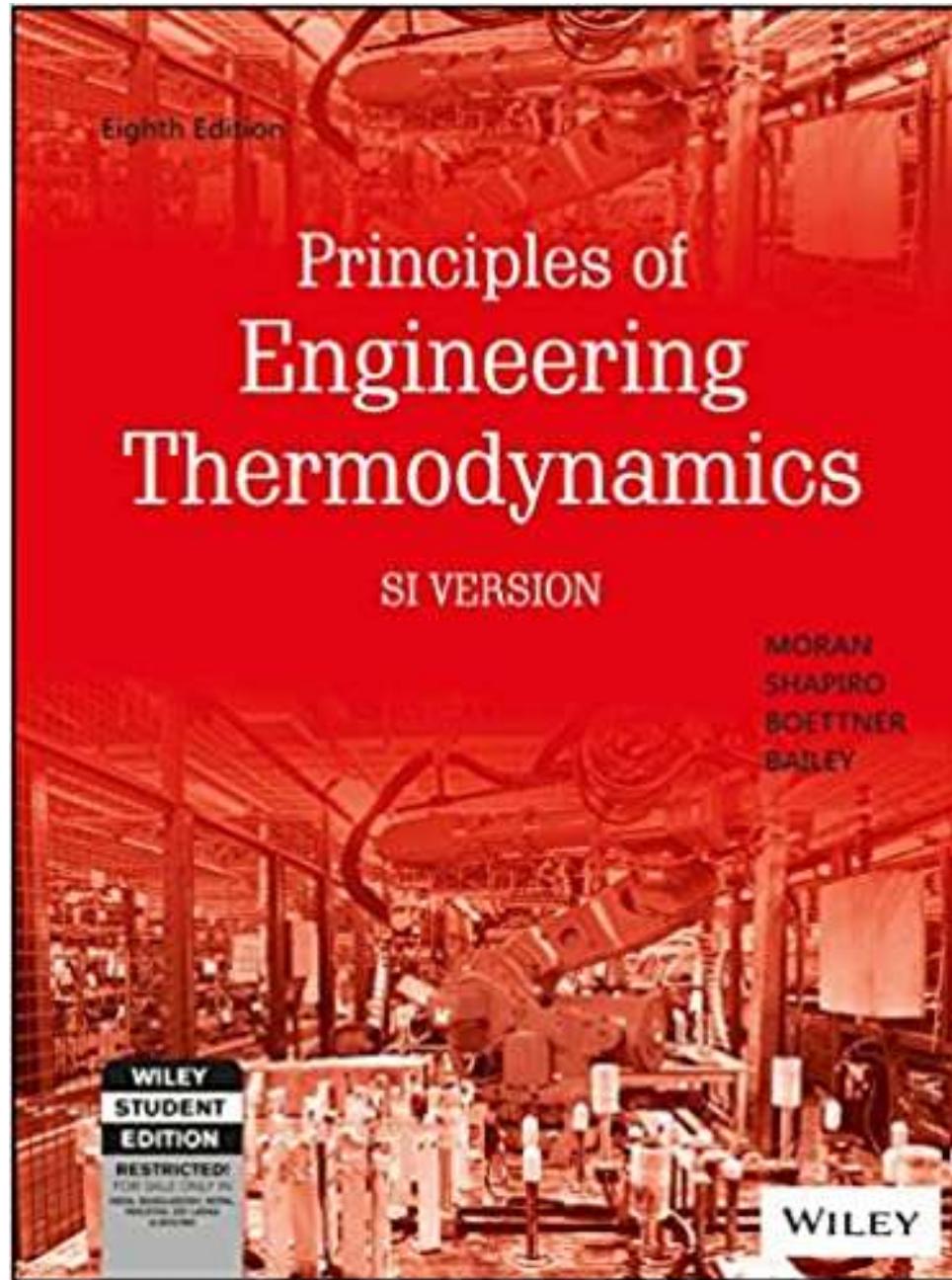
## *Useful references-1*



## *Useful references-2*



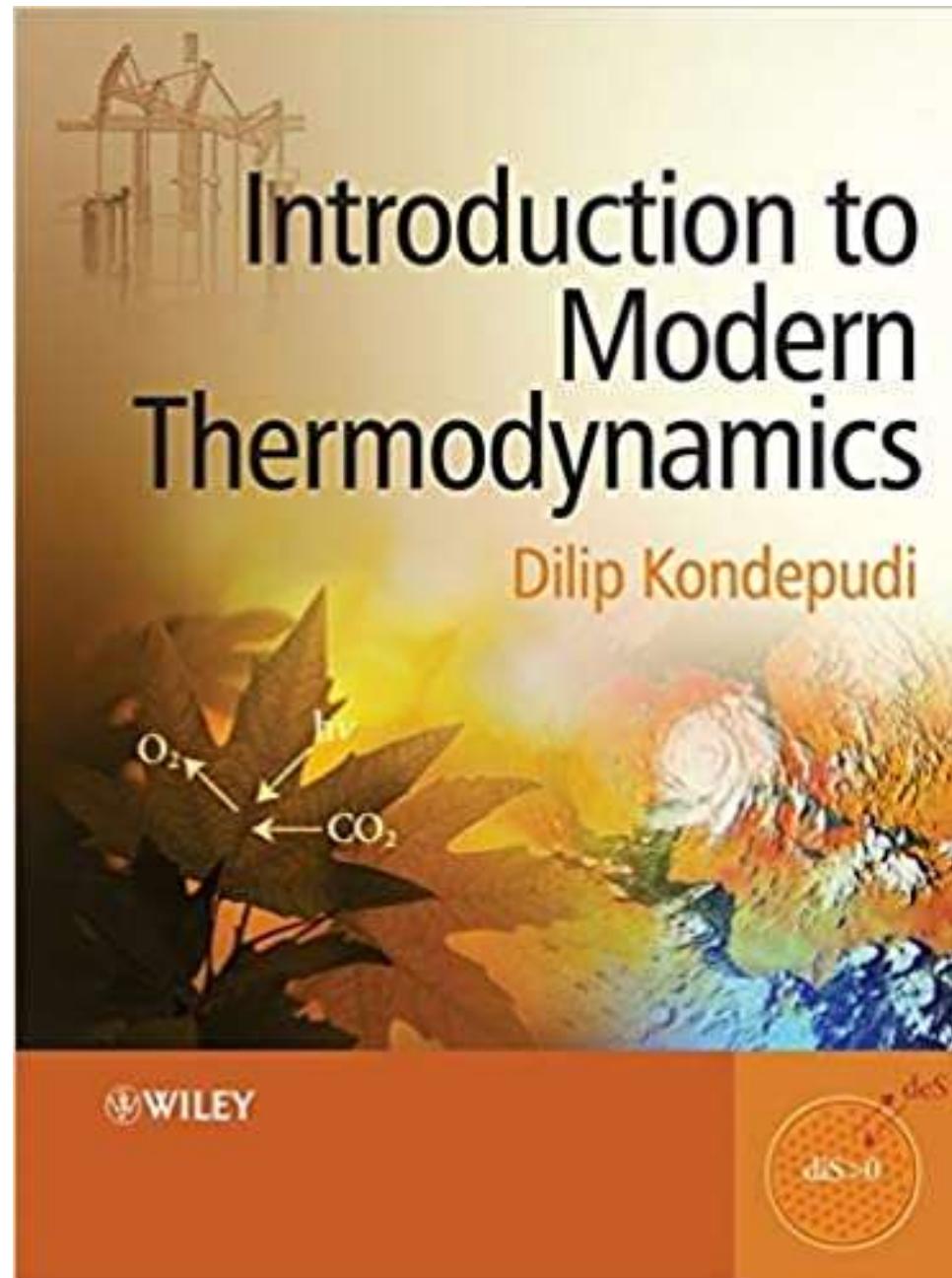
## *Useful references-3*



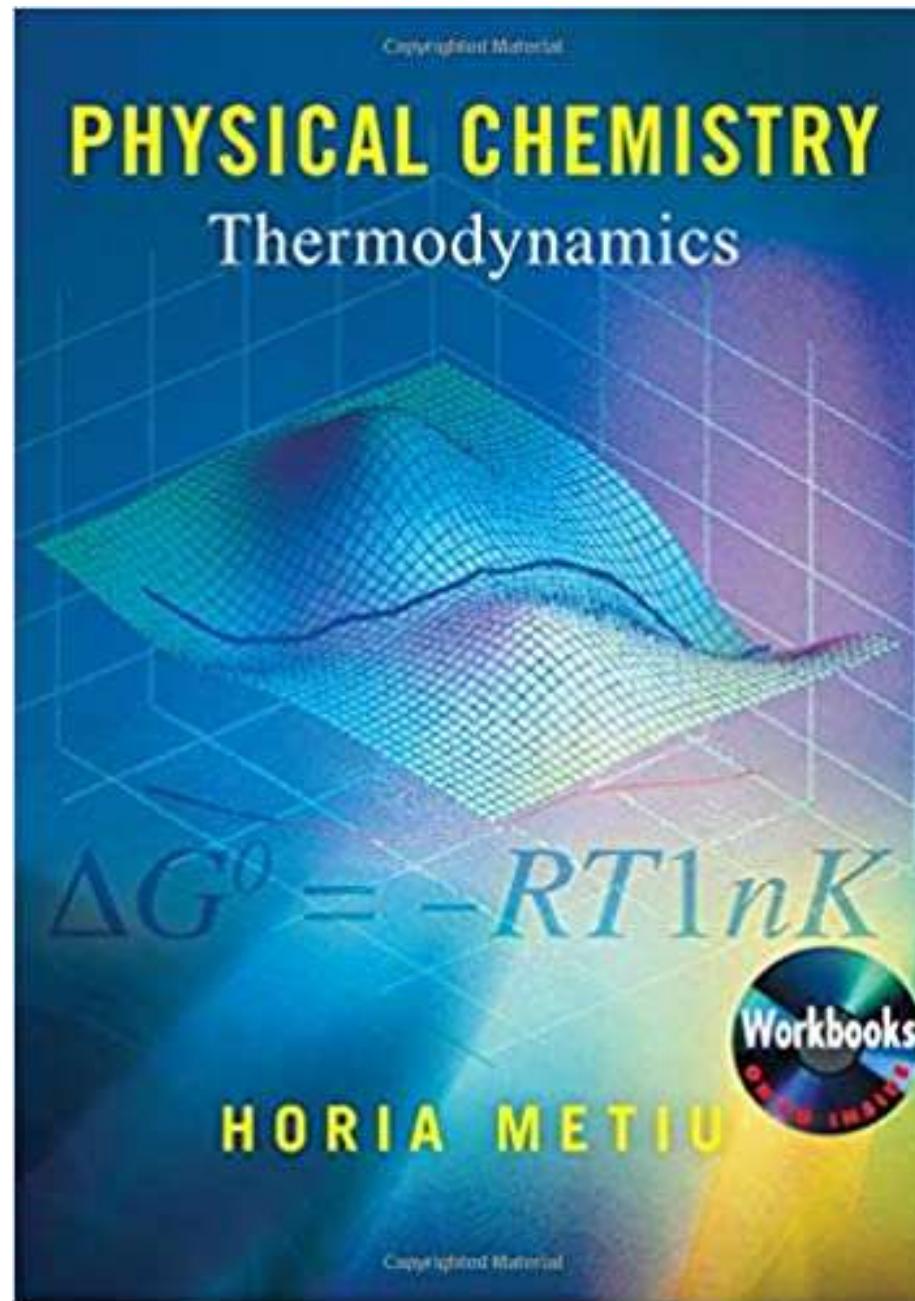
*Classic (~238 pages!)*



*UG book: Stepping stone to modern topics*



*UG book: Properties of matter perspective*



# *Thermodynamic state & variables*

Raj Pala,

[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

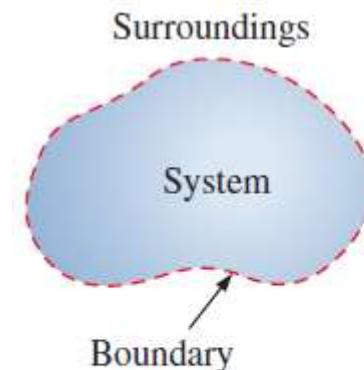
Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme  
Indian Institute of Technology, Kanpur.

## *Human motivations, constraints & semantics*

- Two viewpoints: Energy conversion vs. properties of matter
- What can be measured?
- TD is about equilibrium and “quasi-static” transformation
- Approximations (e.g. surface can be neglected) vs. Idealization (e.g. adiabatic boundary)
- Thermodynamic system?

# *Thermodynamic system*

- Thermodynamic variables: **T, P & V**
- **TD system** -Quantity of matter or a region in space containing energy converting devices where TD variables can be measured/well defined
- **Surrounding** -Rest of the “universe”
- **Boundary** -Surface that separates system and surrounding; It shares TD properties between TD system & surrounding
- **Boundary** -Imagined surface or an idealization of a real surface-Zero thickness, no mass/volume
- Depending on the objective of the analysis: Focus can be on the system or movement of the boundary

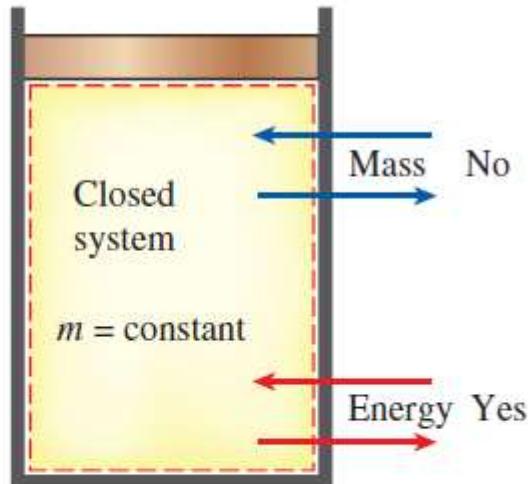


**FIGURE 1–18**

System, surroundings, and boundary.

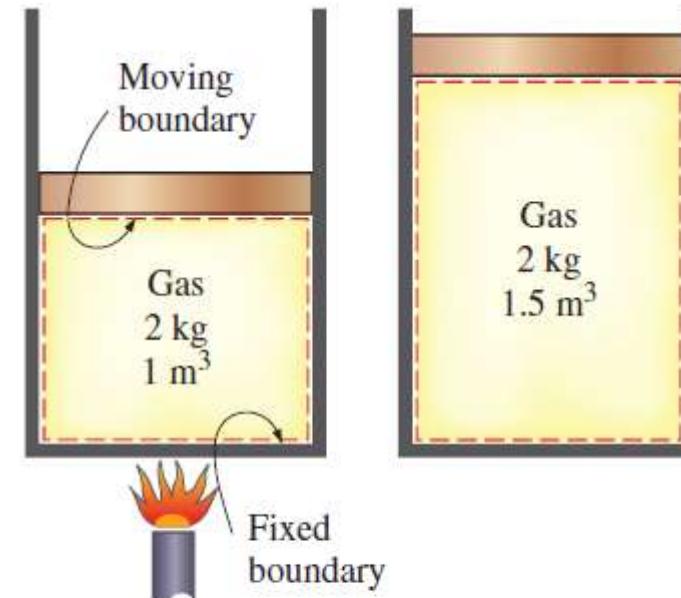
Fig: C & B: TD

# *Control Systems-Closed: Mass & Surface...*



**FIGURE 1–19**

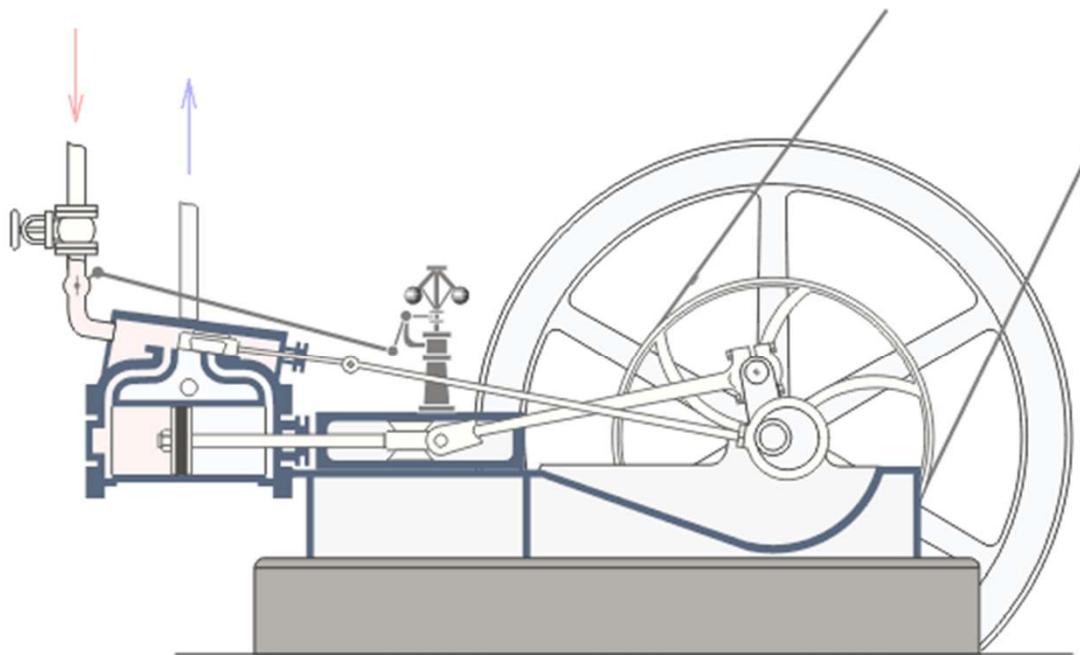
Mass cannot cross the boundaries of a closed system, but energy can.



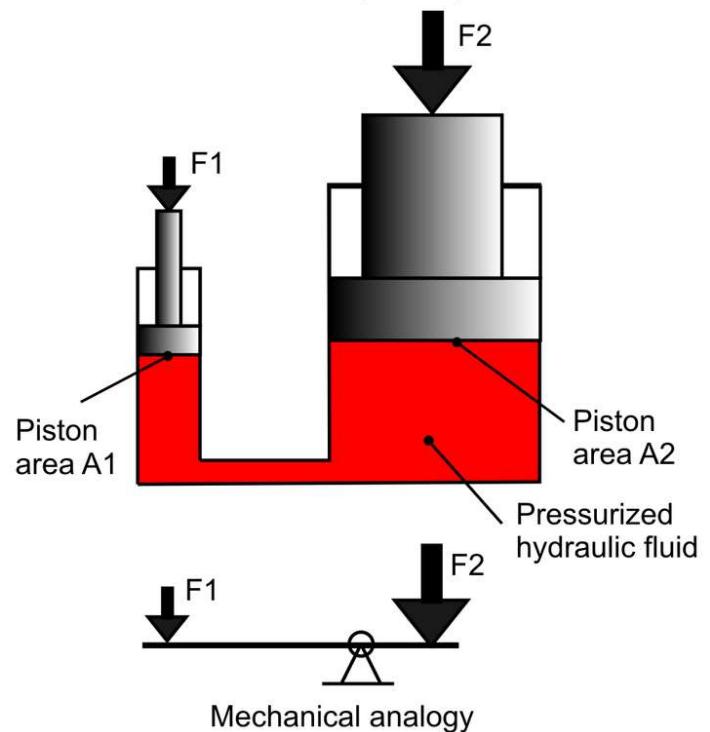
**FIGURE 1–20**

A closed system with a moving boundary.

# *Is the course title ESO: Pistons-analysis & applications?!*



Force increase with hydraulics  
 $F_2 = F_1 \cdot (A_2/A_1)$



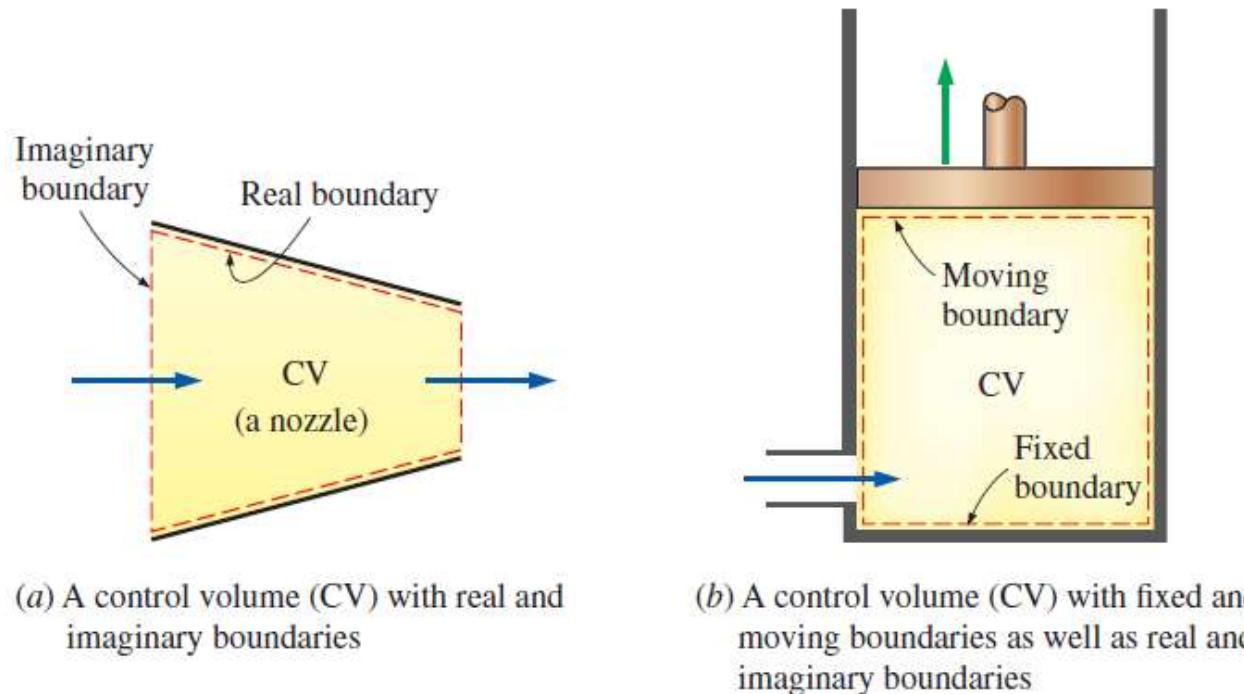
Cyclic linear motion of the piston → Rotatory motion

When **weights** above the piston are changed in **very small increments**, the **pressure** can be varied **infinitesimally** → Reversible process

[https://en.wikipedia.org/wiki/Reciprocating\\_motion](https://en.wikipedia.org/wiki/Reciprocating_motion)

[https://en.wikipedia.org/wiki/Hydraulic\\_machinery](https://en.wikipedia.org/wiki/Hydraulic_machinery)

# *Control Systems-Open: Volume & Surface...*



**FIGURE 1–22**

An open system (a control volume) with one inlet and one exit.

Fig: C & B: TD

## *Variants in TD systems*

- System open to selective components: semi-permeable membranes
- Flexible boundaries: Gas expansion in a balloon
- Adiabatic/Insulating wall Vs Diathermal/Conducting wall
- Idealization of systems encountered in reality

## *TD system-Emphasis starts with T & then...*

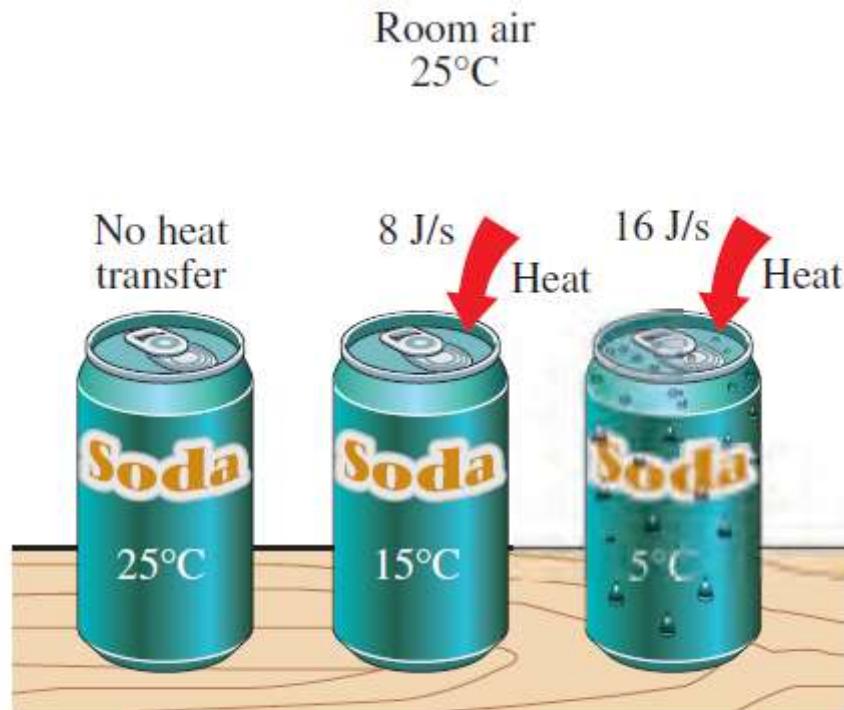
- Solid mechanics: Focus on strain of charge neutral systems; Electrodynamics focusses on effects of charge in mechanically unstrained situation...
- As the focus in TD is on T, we begin with charge neutral, elastically unstrained systems...
- But TD can deal with stress & strain, electrical charges/monopoles & fields, Magnetic dipoles & fields, surface stress & strain, surface tension & area...
- Eventually you will see that TD variables come in conjugate pairs where an (Intensive quantity) \* (Extensive quantity)=Energy
- Extensive quantities: mass, V, charge monopoles, magnetic dipoles, strains, area...
- Intensive quantities: gravitational potential, Pressure, fields, stress, surface tension...Specified at a given point; (extensive quantity/another exten.quan.)

# *Processes, Driving Forces & Steady State Fluxes*

Raj Pala,  
[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme  
Indian Institute of Technology, Kanpur.

## *Heat flux due to temperature difference*

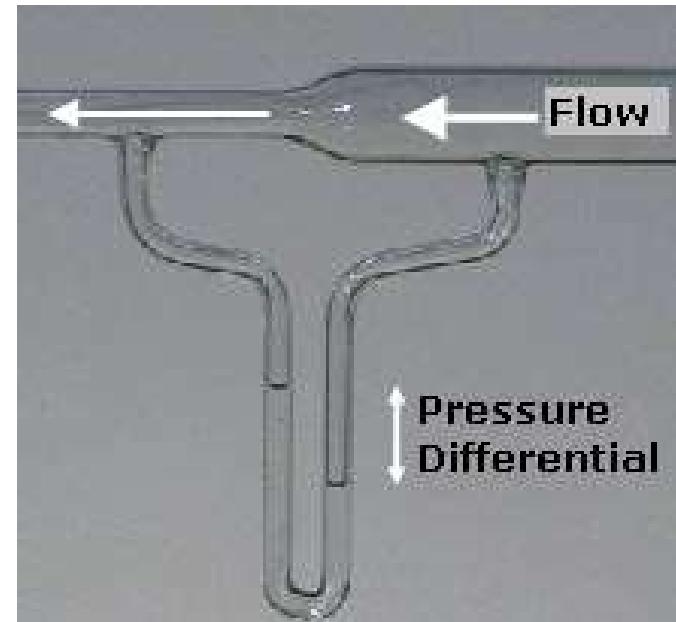


**FIGURE 2–15**

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

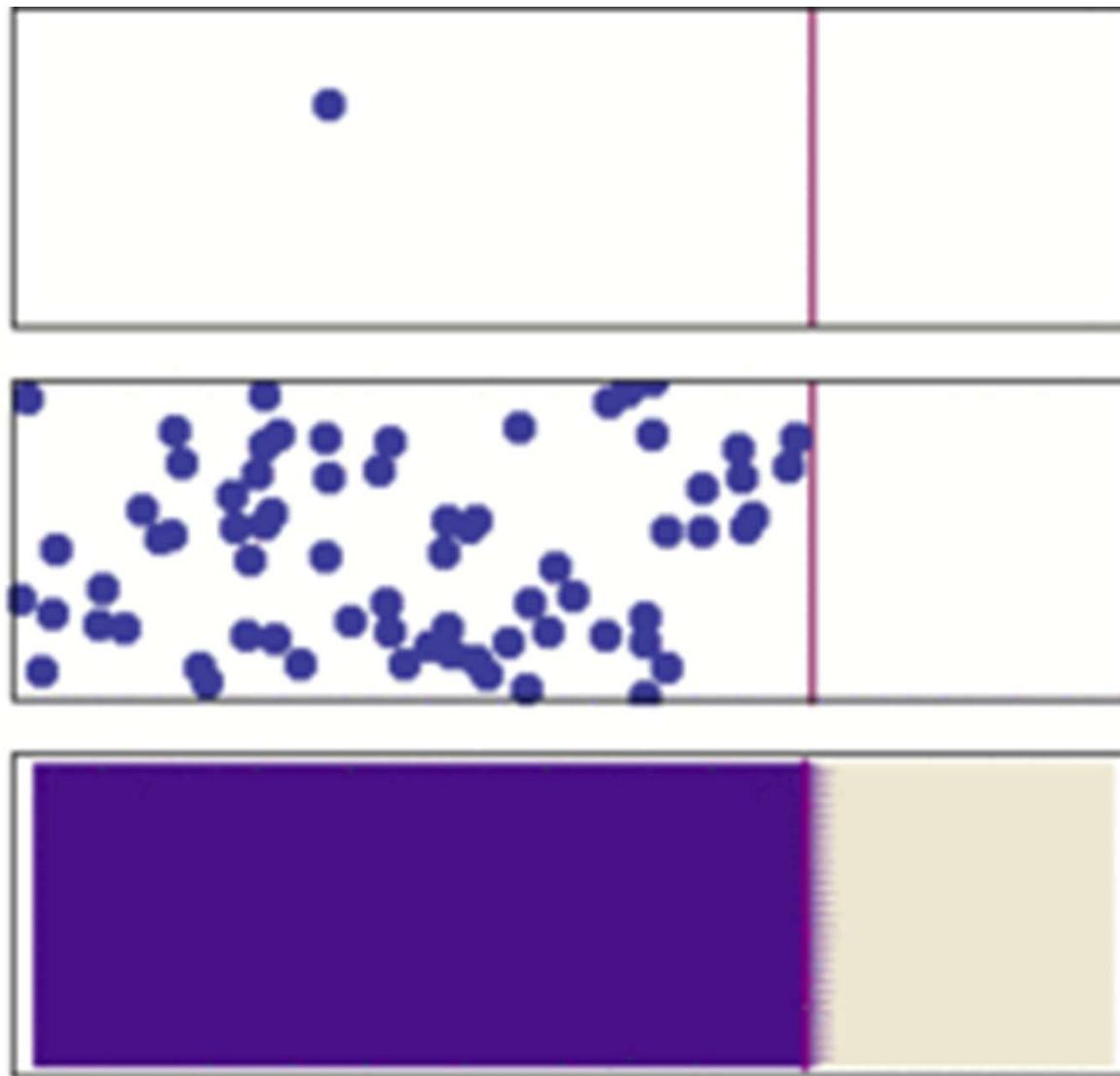
Fig: C & B: TD

## *Momentum flux/fluid flow due to pressure difference*

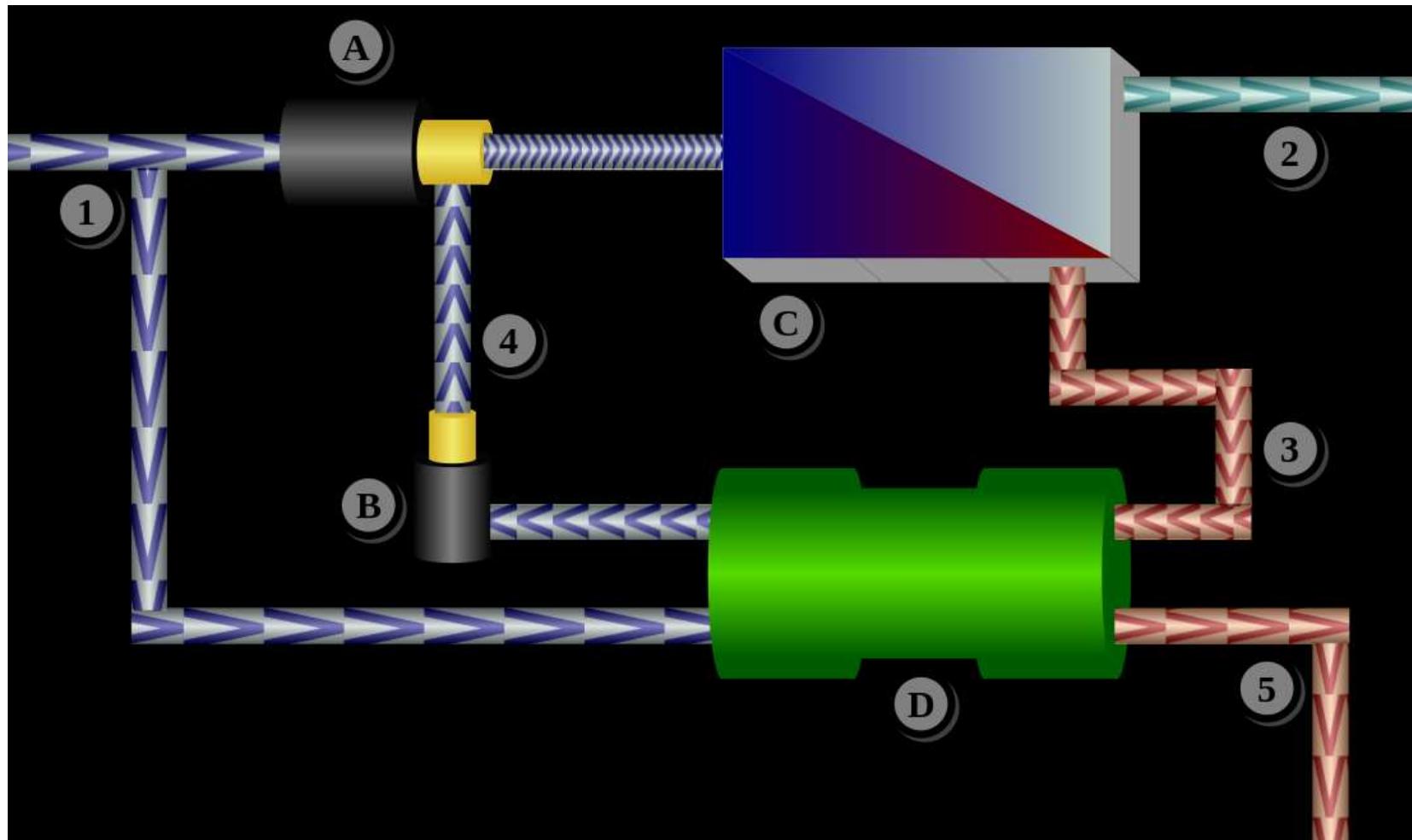


[https://en.wikipedia.org/wiki/Pressure\\_head](https://en.wikipedia.org/wiki/Pressure_head)

## *Mass flux due to difference in concentration*

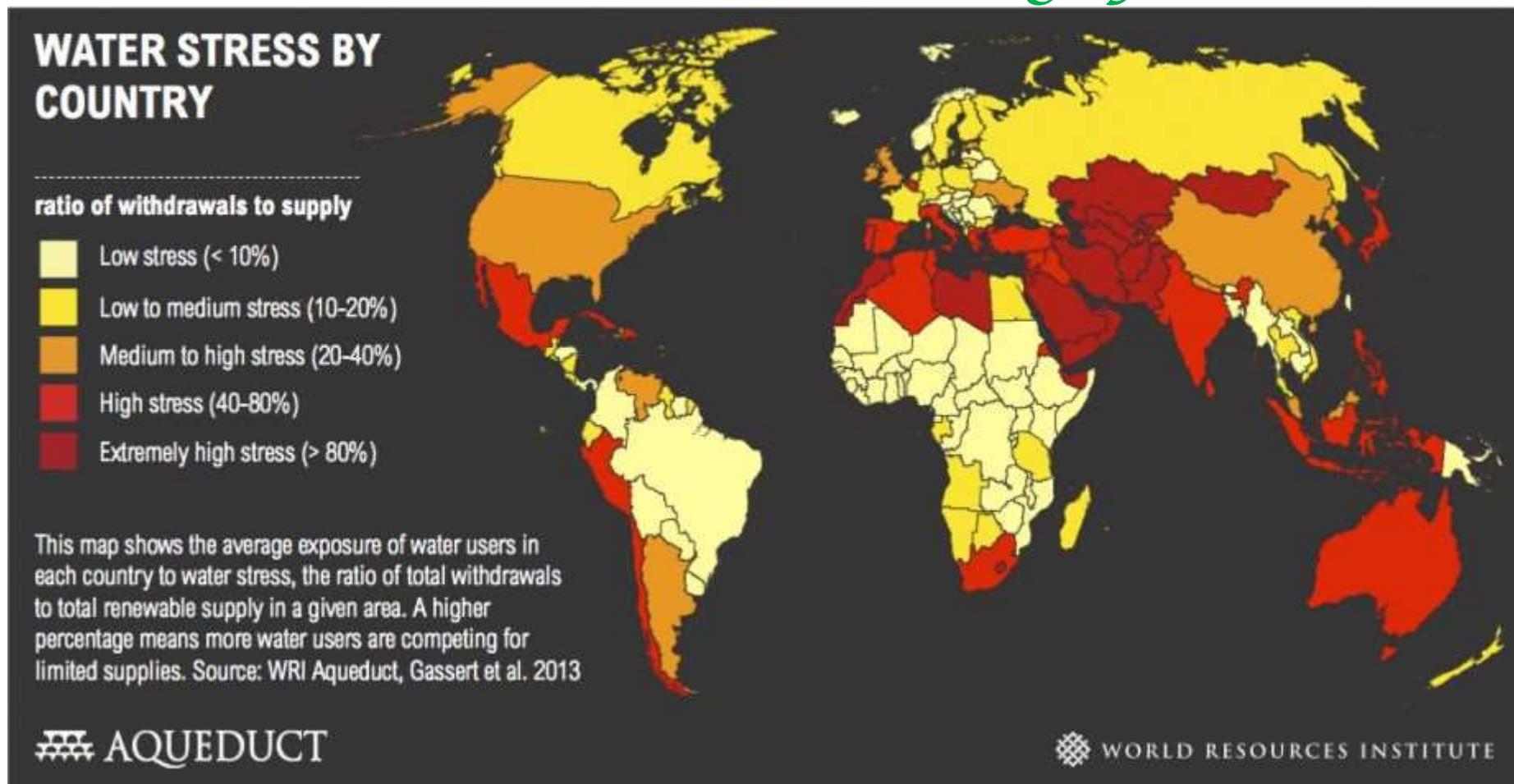


# *Reverse Osmosis Desalination: Mass flux due to difference in “chemical potential”*



1: Sea water inflow, 2: Fresh water flow (40%), 3: Concentrate flow (60%),  
4: Sea water flow (60%), 5: Concentrate (drain),  
A: Pump flow (40%),  
B: Circulation pump, C: Osmosis unit with membrane, D: Pressure exchanger  
[https://en.wikipedia.org/wiki/Reverse\\_osmosis](https://en.wikipedia.org/wiki/Reverse_osmosis)

# *Clean water: Grand challenge problem*



*Smalley's top ten ventures to save the world*

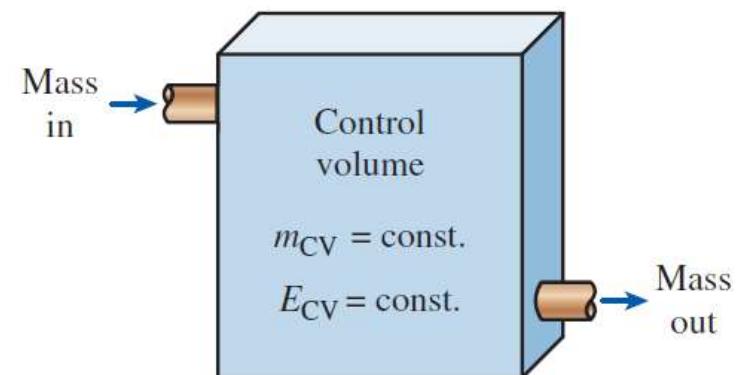
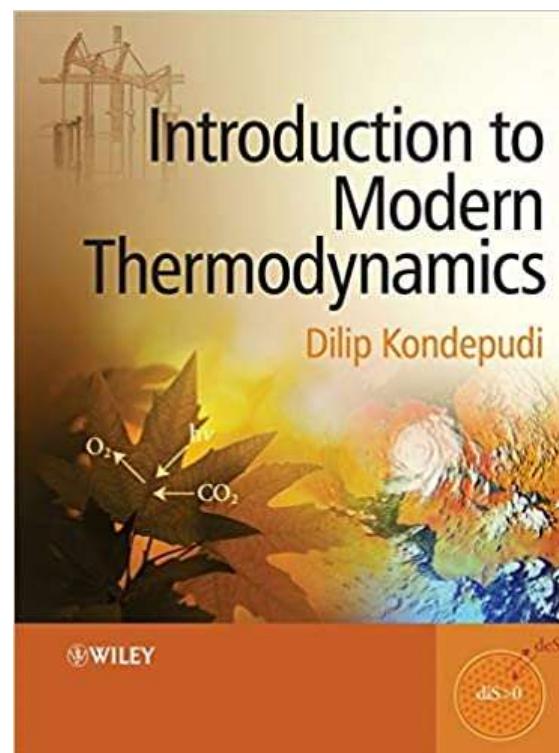
10. Population
9. Democracy
8. Education
7. Disease
6. Terrorism and War
5. Poverty
4. Environment
3. Food
2. Water
1. Energy!!!

*TD driving forces is indicate a lack of equilibrium & leads to fluxes*

- Heat flux due to temperature difference driving force/lack of thermal equilibrium
- Momentum flux/fluid flow due to “pressure difference”
- Mass flux due to difference in “chemical potential”
- Constant **driving force** → **steady state** flux
- Both steady and unsteady processes can be described via relationships involving fluxes to macroscopic variables like T, P...

# *Flow Processes are not in TD equilibrium*

- Steady-flow conditions ~ turbines, pumps, boilers, condensers, and heat exchangers or power plants or refrigeration systems
- TD of steady states will not be discussed here



**FIGURE 1–33**

Under steady-flow conditions, the mass and energy contents of a control volume remain constant.

Fig: C & B: TD

# *Thermodynamic Equilibrium*

Raj Pala,

[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

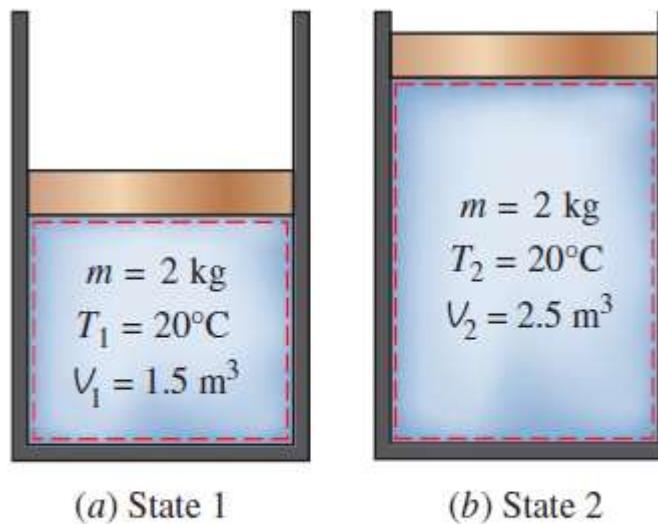
Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme  
Indian Institute of Technology, Kanpur.

# *Isolated systems & TD equilibrium*

- Systems that **cannot exchange BOTH matter and energy** with the surrounding- **Isolated**
- TD equilibrium=**None of the TD properties are changing with time at a measurable rate** (Methods of TD, H. Reiss)
- Equilibrium is unique & is irrespective of the irreversible pathways via which the system reaches the equilibrium state
- Uniqueness of the equilibrium state for simple systems is easy to rationalize because the TD properties are related via an equation of state,  $f(\text{TD variables})=0$
- Reproducibility and relevant TD variables/properties is not straight forward in complex systems: Solids like thermally treated steel/glass that are strained during processing, heterogeneous systems...

# *Equation of state*

- Ideal gas equation of state;  $PV=nRT$
- Total number of independent variables can be chosen via “Gibbs phase rule”, Degree of freedom (to be discussed in latter lectures);

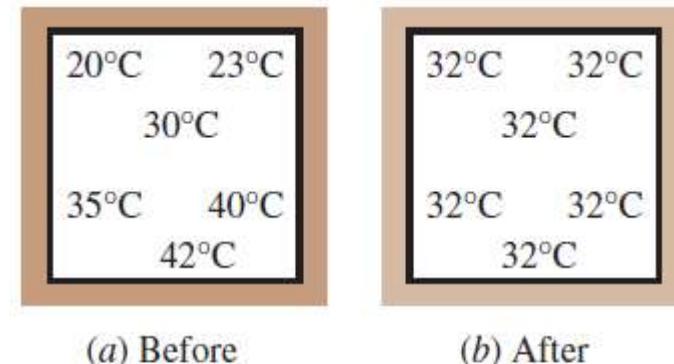


**FIGURE 1–26**  
A system at two different states.

Fig: C & B: TD

# *TD equilibrium state*

- At equilibrium state: no driving forces for change within the system.
- **Thermal equilibrium:** Temperature is uniform in the entire system & does not vary with time
- **Mechanical equilibrium:** Pressure is uniform in the entire system & does not vary with time
- **Chemical equilibrium:** Chemical composition of a system does not change with time, that is, no chemical reactions occur
- **Phase equilibrium:** For system with more than one phase, mass of different component in each phase does not change with time



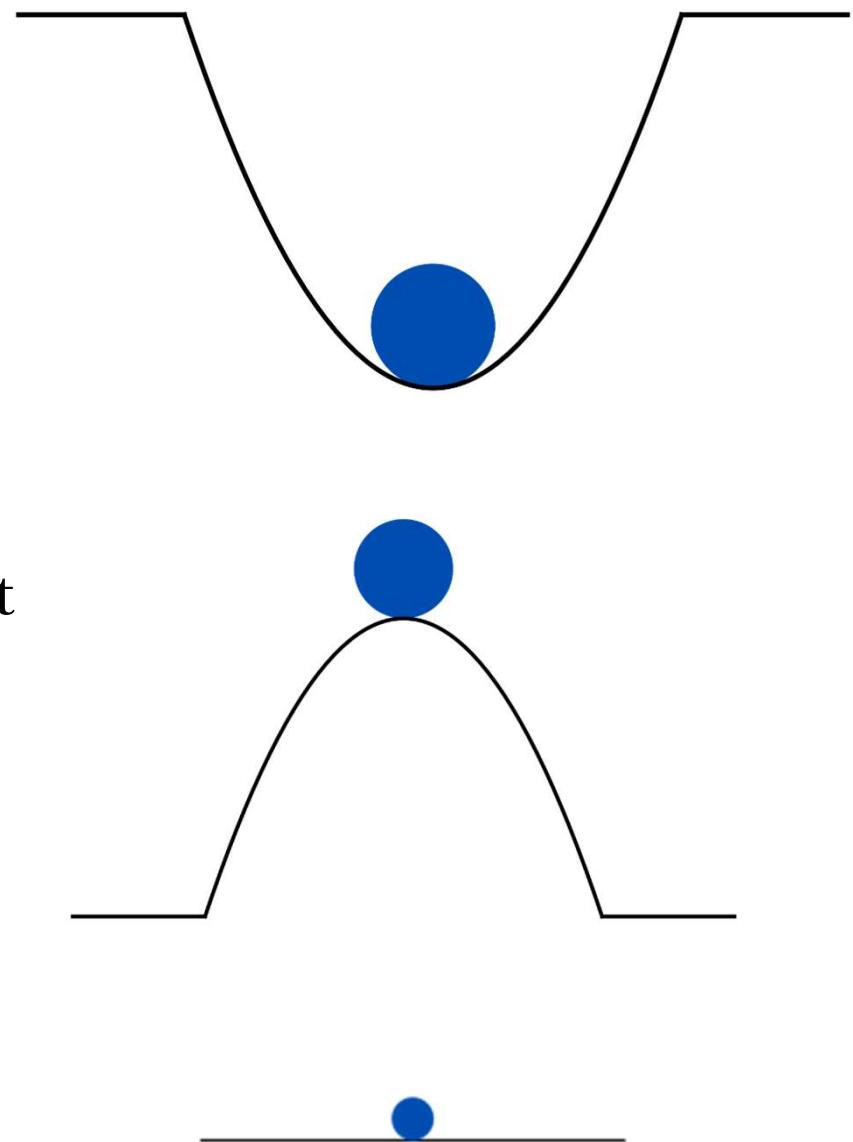
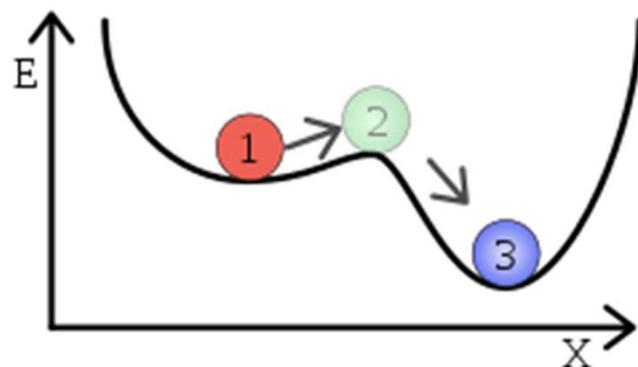
**FIGURE 1–27**

A closed system reaching thermal equilibrium.

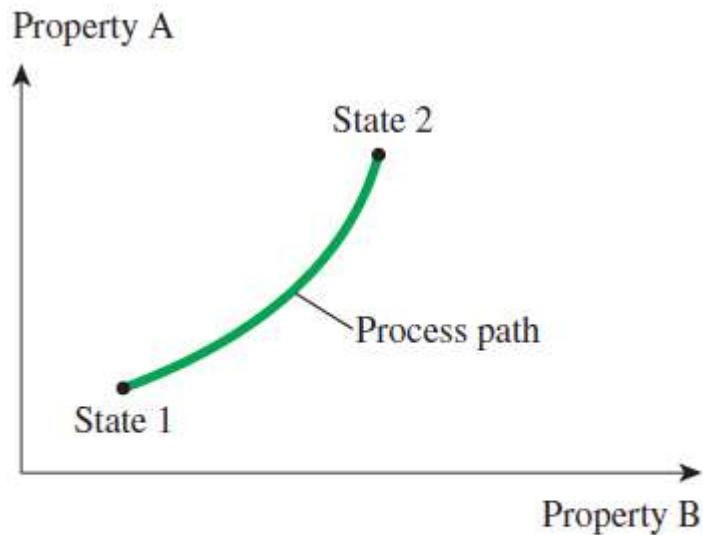
Fig: C & B: TD

# *Avatars of TD states*

- Stable equilibrium & fluctuations
- Unstable & neutral equilibrium are rare in TD
- Metastable states do occur;  
Metastability is an internal constraint

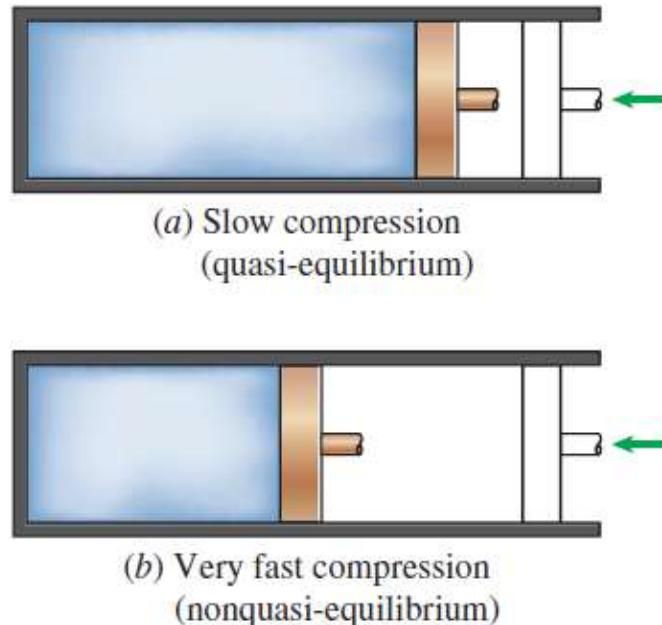


# *Transformation via quasi static/equilibrium states*



**FIGURE 1–29**

A process between states 1 and 2 and the process path.

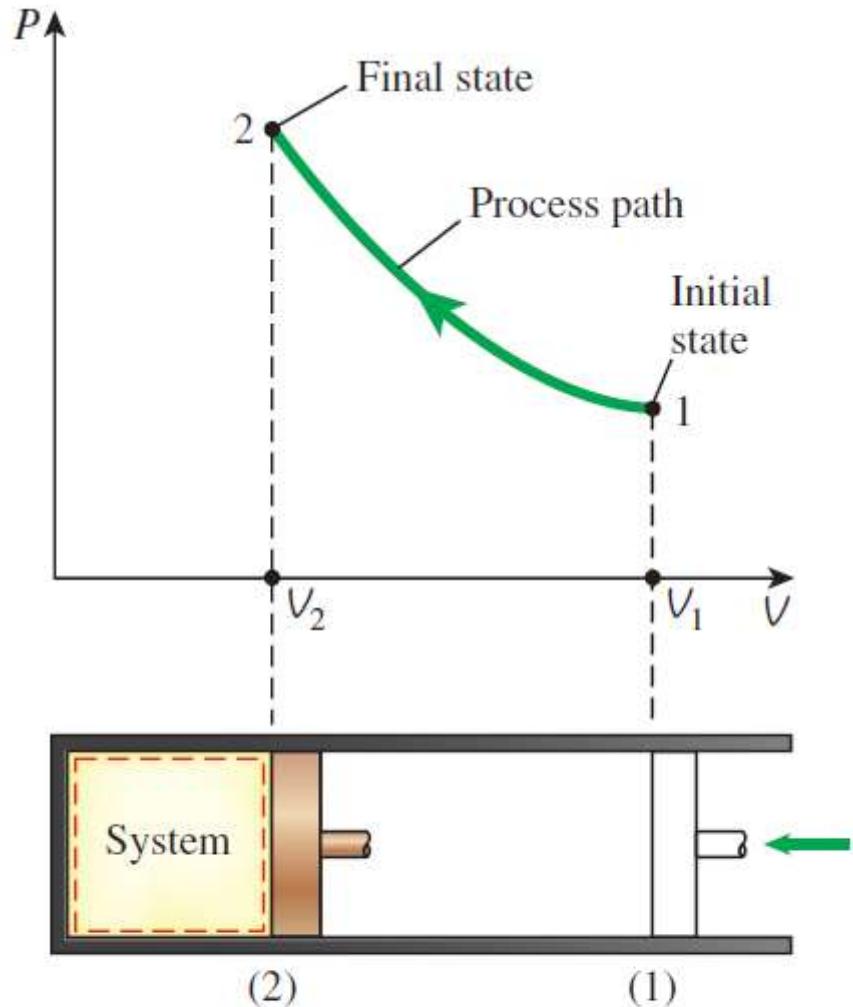


**FIGURE 1–30**

Quasi-equilibrium and nonquasi-equilibrium compression processes.

## *Typical TD processes*

- Isothermal process
- Isobaric process
- Isochoric (or isometric) process
- Cycle: Linear cyclic motion of a piston to rotary motion of the wheel...



**FIGURE 1–31**

The  $P$ - $V$  diagram of a compression process.

Fig: C & B: TD

# *Zeroth Law of Thermodynamics*

Raj Pala,

[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

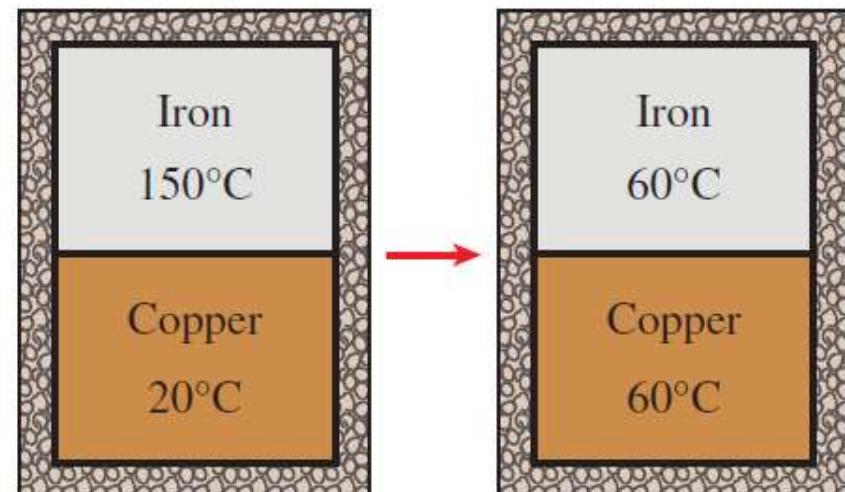
Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme  
Indian Institute of Technology, Kanpur.

# *What did Galileo think about Heat?!*

- *Is there is an “observation” when there is no observer?*
- Galileo (1564-1642) imagined heat to be a response of the senses
- Effectively, there is no such thing as “heat” if there is no one to experience it!
- Rene Descartes (1596-1650) of “Cartesian coordinates” & “I think, therefore I am” fame followed up with similar “ideas”
- Importance of instrumentation science and engineering: Meaning & measurements

# *Zeroth Law of Thermodynamics*

- If two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other
- Implication: Third body=Thermometer
- T is intensive & independent of mutual contact of bodies via “*diathermal*” interfaces (Note: “*dia*” in Greek means “through”)
- Law...?



**FIGURE 1–34**

Two bodies reaching thermal equilibrium after being brought into contact in an isolated enclosure.

## *Contribution of Indian Scientists to 0<sup>th</sup> Law?*

- A Text Book of Heat by **Saha & Srivastava** (1<sup>st</sup> Ed-1931); 2<sup>nd</sup> edition-1935 was reviewed by the originator of 0<sup>th</sup> Law **R. H. Fowler**
- “THE authors of this book have written a most stimulating version of the old song “Heat a Mode of Motion”, and written it, too, rather in the grand manner...

## *“A text book of heat” by Saha & Srivastava...*

... Their arrangement of matter follows classical lines. Formal thermodynamics is not introduced until more than half-way through the book. Before that point is reached, there are excellent descriptive chapters on thermometry, calorimetry, production of low temperature, heat engines, gases, changes of state, elementary kinetic theory and other topics. These are all treated in a most pleasing broadly descriptive manner, with a temperature based on the perfect gas scale and an occasional forward reference to the second law where unavoidable. The ideas of hot and cold and heat are here quite properly treated as familiar primary concepts which need not be further analysed—quantities which we must set to work to measure precisely—and the kinetic interpretation of heat is brought in naturally in its right place. The chapter on heat engines seems to me to be exceptionally satisfactory for the elementary treatment that is intended, being practically without reference to entropy, and using merely a perfect gas Carnot cycle as standard. An exceedingly pleasing feature is the section on the Otto cycle gas or oil engine, the Diesel engine and steam turbines. The latter, however, are not given credit for the full overall efficiency that has recently been attained.

## *Correlations & speculations...*

- R. H. Fowler was the Ph.D advisor of Paul Dirac, a pioneer of quantum mechanics (Central drama: Solvay conference-1927)
- In quantum mechanics the measurement “collapses the wave function”- Indeed there is no “observation” without the observer!
- Wonder if importance of measurements in QM had something to do with Fowler’s preoccupation about meaning of measurements in TD



# *Logic behind Thermometers & Temperature Scales*

Raj Pala,

[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme  
Indian Institute of Technology, Kanpur.

# *Thermometer... COVID times@IIT-K*



●○ REDMI NOTE 6 PRO  
MI DUAL CAMERA



●○ REDMI NOTE 6 PRO  
MI DUAL CAMERA

# *How to design a Thermometer?*

- Thermometer-1624 (*Recreaction Mathematique* by Leurechon)-  
Instrument to **measure** the degree of hotness/coldness...(Aristotle-original Bansal Sir of Kota Factory~**300 BC**, University of Bologna ~**1088**)
- Identify a material property that changes with temperature in a monotonous manner
- Material property should be easily measurable:  **$I(T)$ ,  $V(T)$**
- Nail down two “special temperatures”: Melting & Boiling point
- Coexistence of ice-water: Melting/ice point  $\rightarrow T_1$
- Coexistence of water-steam (without air): Boiling/steam point  $\rightarrow T_2$
- “**Triple point**” is more special i.e. **more reproducible**

## *More to monotony*

- Monotonous variation with temperature can be non-linear!
- Non-linear variation is due to “material properties”
- Problem with non-linear variation: One may agree with temperature measurement at the two distinct temperatures, but not in-between
- Fix: Monotonous **Linear** variation with temperature

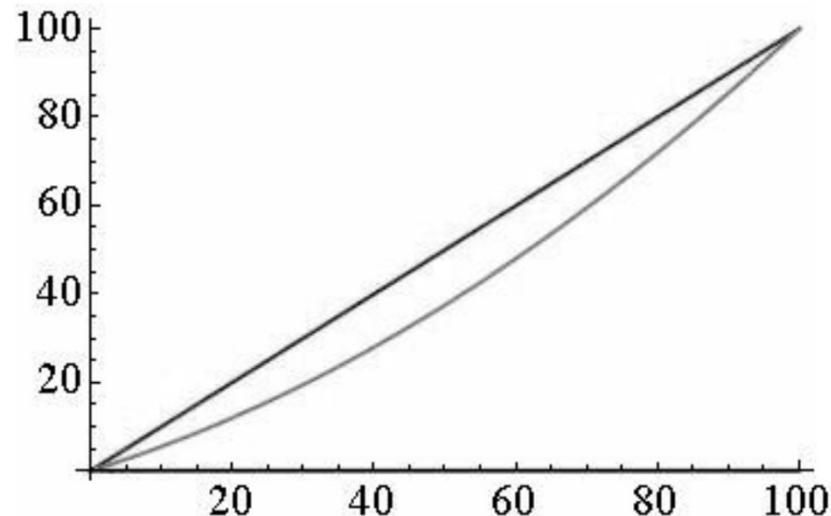
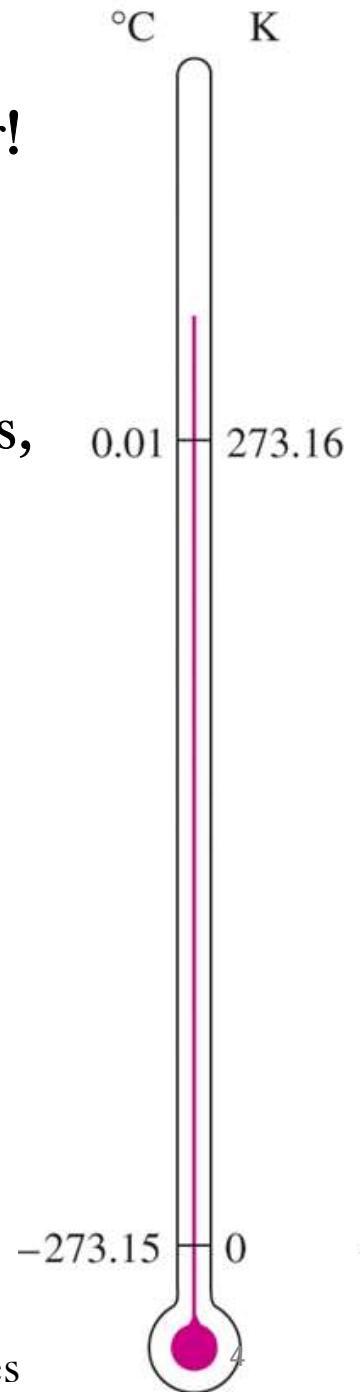


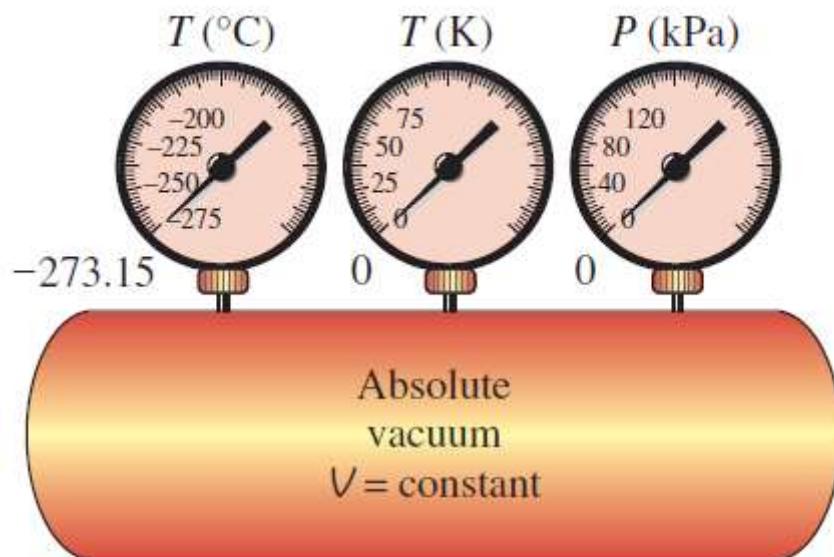
Fig: “Fundamentals of Physics” by R. Shankar



Figs: Cengel & Boles

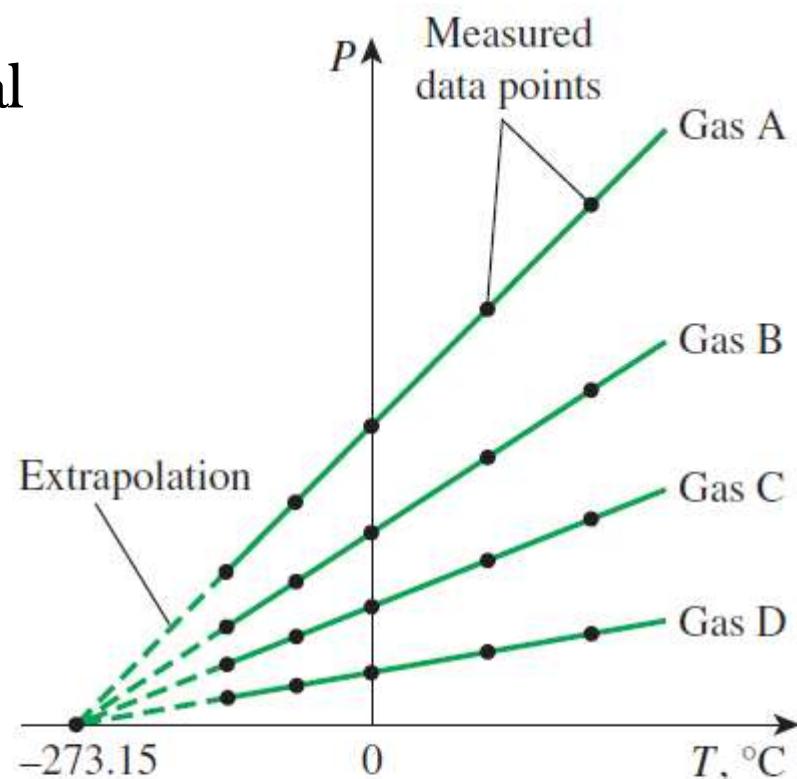
# *Monotonous Linear variation of a property*

- Gases have lesser interactions in general
- Ideally, the gases should be Ideal!



**FIGURE 1–36**

A constant-volume gas thermometer would read  $-273.15^{\circ}\text{C}$  at absolute zero pressure.



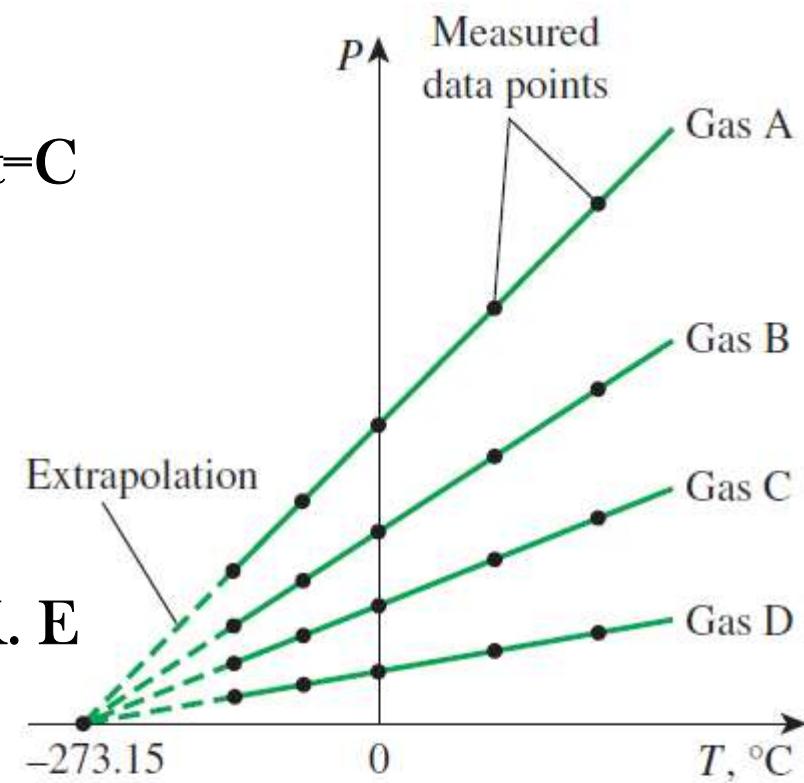
**FIGURE 1–35**

$P$  versus  $T$  plots of the experimental data obtained from a constant-volume gas thermometer using four different gases at different (but low) pressures.

$$T(\text{K}) = T(^{\circ}\text{C}) + 273.15$$

# *Kelvin scale is intuitive & natural!*

- All gases at low pressure:  $PV=\text{Constant}=C$
- Possible to keep reducing P & T
- Pressure cannot fall below zero!
- T (in Kelvin) is a measure of average K. E
- Hence, both  $T(K) \geq 0$  &  $P \geq 0$
- $T = \lim_{p \rightarrow 0} \left( \frac{pV}{R} \right)$



**FIGURE 1–35**

$P$  versus  $T$  plots of the experimental data obtained from a constant-volume gas thermometer using four different gases at different (but low) pressures.

$$T(K) = T(^{\circ}\text{C}) + 273.15$$

## *Temperature & 2<sup>nd</sup> TD law: Advertisement*

- Ideal gas:  $PV = \text{Monotonous Fxn}(T)$ ; Real gas:  $P(V-b) = \text{Mono. Fxn}(T)$ ...this  $\text{Fxn}(T)$  cannot have maxima/minima/stationary point
- Defining Temperature without referring to properties of materials/gases is possible via 2<sup>nd</sup> law of TD...

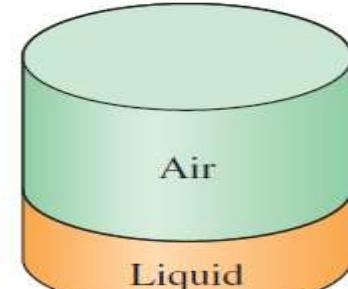
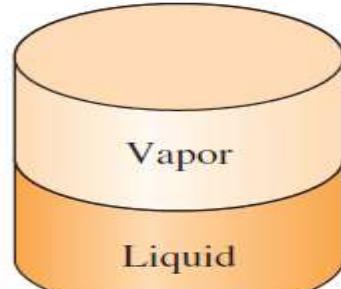
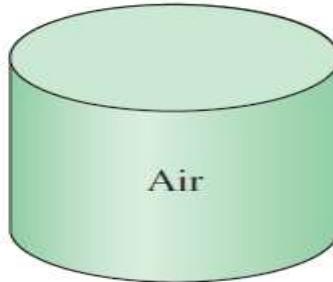
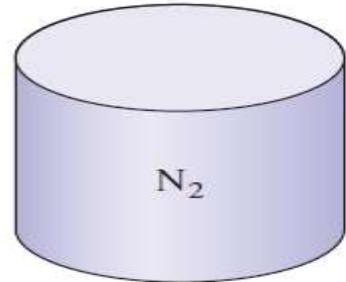
*PhaseBook-Introduction to structure,  
symmetry, EOS & Phase Diagrams*

Raj Pala,  
[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme  
Indian Institute of Technology, Kanpur.

## Pure substance approximation

- Chemical composition is “same” in the system under study



**FIGURE 3–1**

Nitrogen and gaseous air are pure substances.

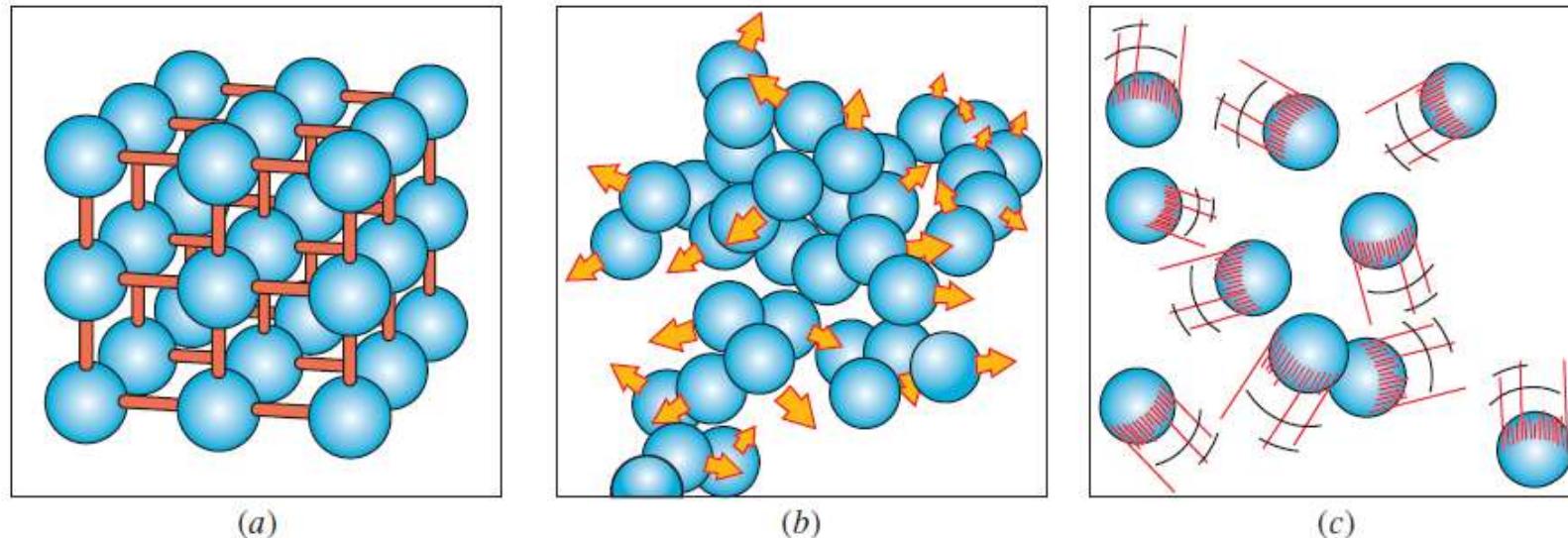
Figs: Cengel & Boles

**FIGURE 3–2**

A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous air is not.

- In practice, “pure” depends on properties & processes that are studied
- Gas separation (for e.g. CO<sub>2</sub> separation) by liquefaction: Is air pure?
- Compositions can be different at the surface, but if bulk properties are only important...Radiation Thermodynamics & Nuclear isotopes...

# *“Structure”-property correlations*



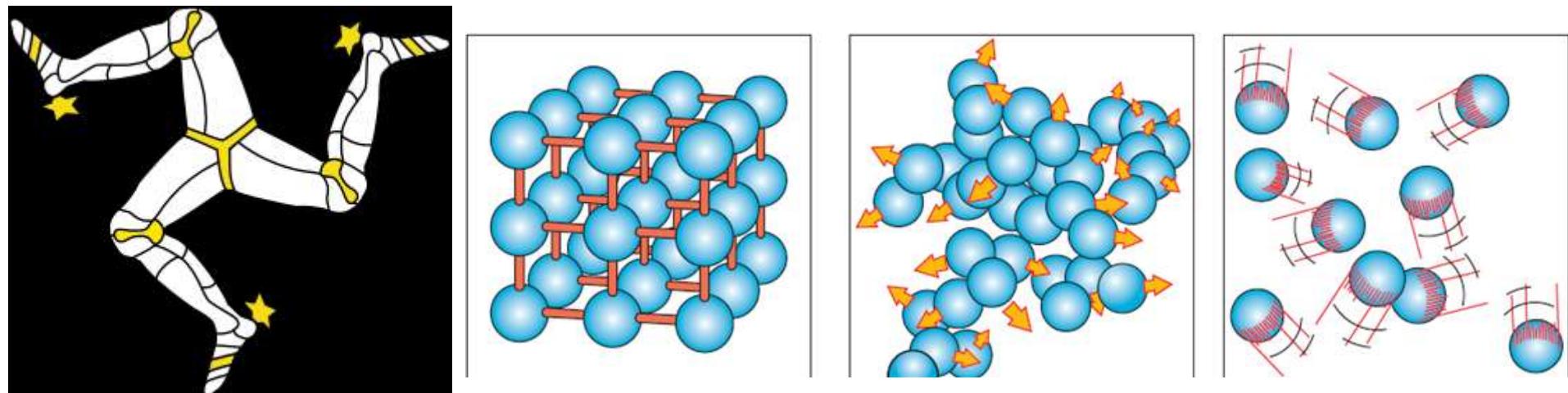
**FIGURE 3-4**

The arrangement of atoms in different phases: (a) molecules are at relatively fixed positions in a solid, (b) groups of molecules move about each other in the liquid phase, and (c) molecules move about at random in the gas phase.

- What makes gases ideal?
- “Ideal solids”, not just ideal gases
- What can make solids ideal?
- Despite strong interactions, solids can be discussed via an “unit cell”
- There are no “ideal liquids”; Why?

# *Structure & “Symmetry”*

- How do we describe structure beyond a high-school description?
- Which is more symmetric: Crystalline solid or gas?
- Solid (**fluids**) has discrete (**continuous**) translational symmetry
- Continuous translational symmetry is “broken” to discrete in solids
- Greater the number of symmetry operations=Greater symmetry



Figs: ebook- <https://en.wikipedia.org/wiki/Symmetry>; Cengel & Boles

## *Structure, Symmetry and the EOS*

- Symmetry & structure determines Equation of State (EOS)
- Ideal gas EOS:  $PV=RT$  (no structure)
- Van der waals EOS for non-ideal gas incorporates finite atomic “size”:

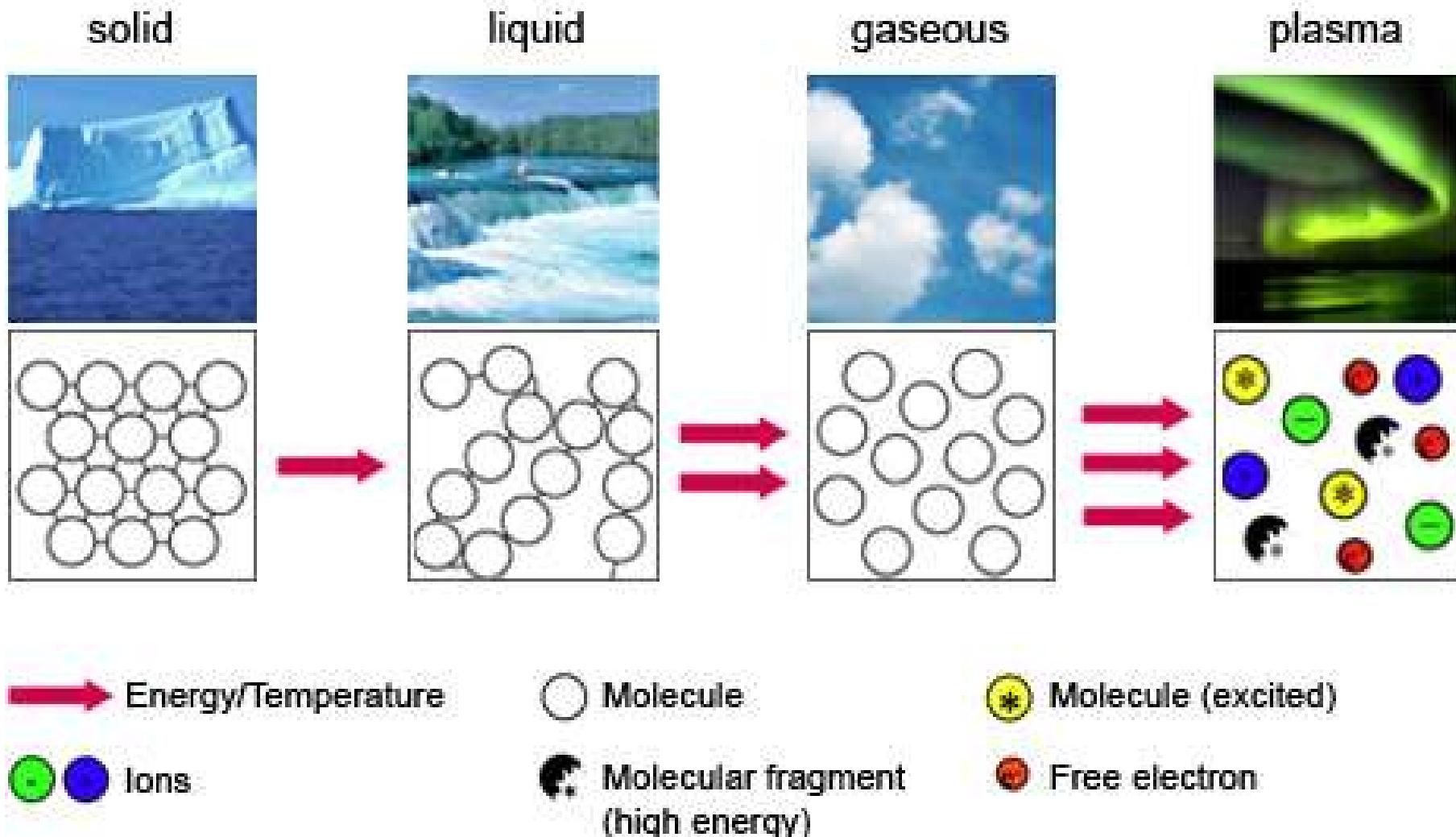
$$\left( P + \frac{a}{v^2} \right) (v - b) = RT$$

- EOS (Murnaghan) for condensed matter:  $P(V) = \frac{K}{K_0} \left[ \left( \frac{V}{V_0} \right)^{K_0} - 1 \right]$

$K_0$ =Modulus of incompressibility at ambient pressure

- More symmetric structures (like fluids) have more isotropic material properties; Isotropic =No directional dependence
- Beyond descriptive/qualitative words from high school, symmetry can be quantified by mathematical theory of point & space groups
- EOS determines material’s thermodynamic properties & processes

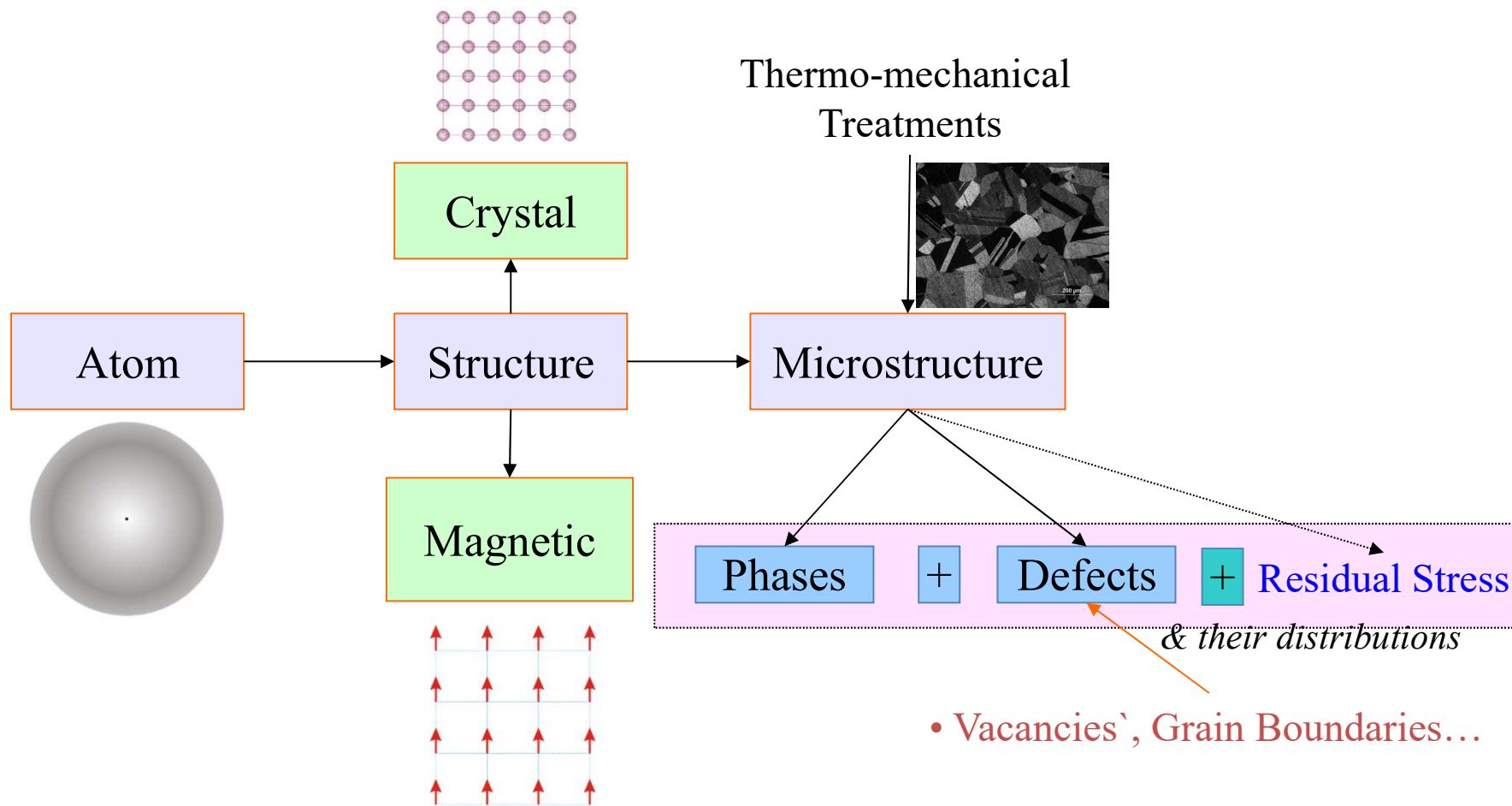
# *Energetic interactions & T are the primary determinant of “Structure”*



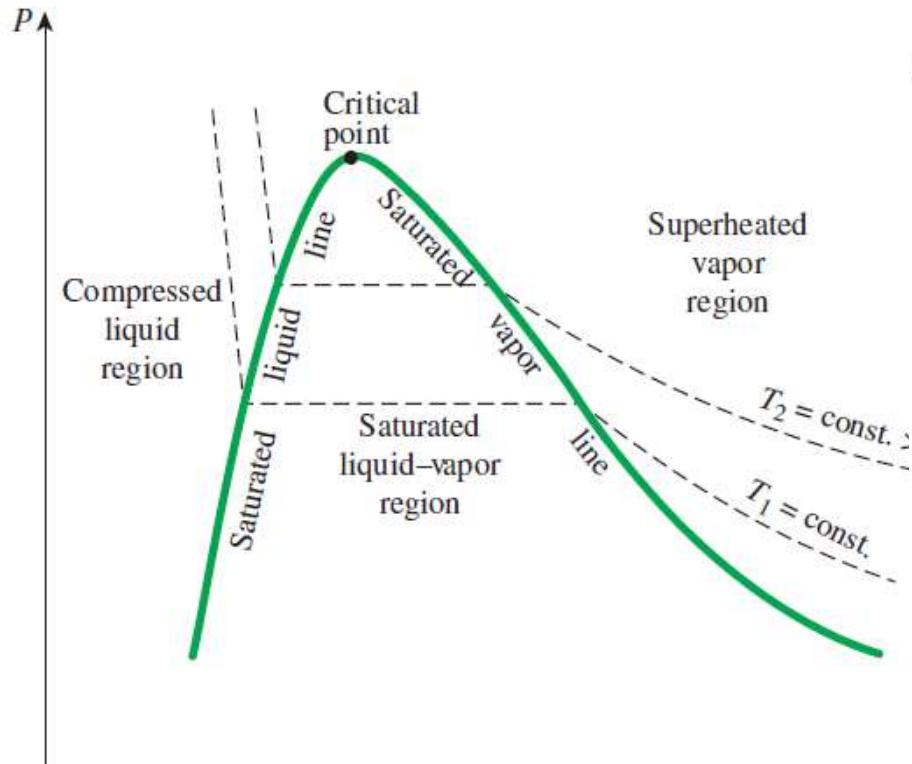
Ref: <https://physics.stackexchange.com/questions/79426/is-a-plasma-a-distinct-phase-of-matter>

## *TD in practice: “Structure” is multiscale*

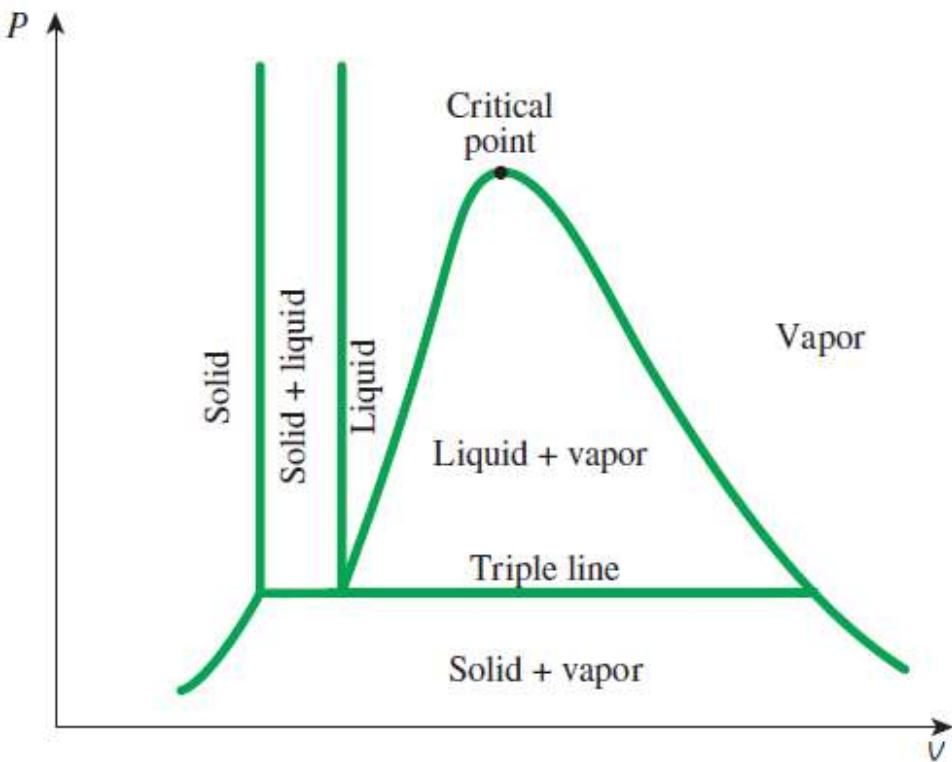
- “Structure” can be characterized at many levels: **Microstructure** (very important for engineering applications), atomic structure, electronic structure, nuclear structure... (am not considering “large” length scales)
- Relevant structure depends on application at under consideration



# Greater structure → More complex EOS & phase diagram

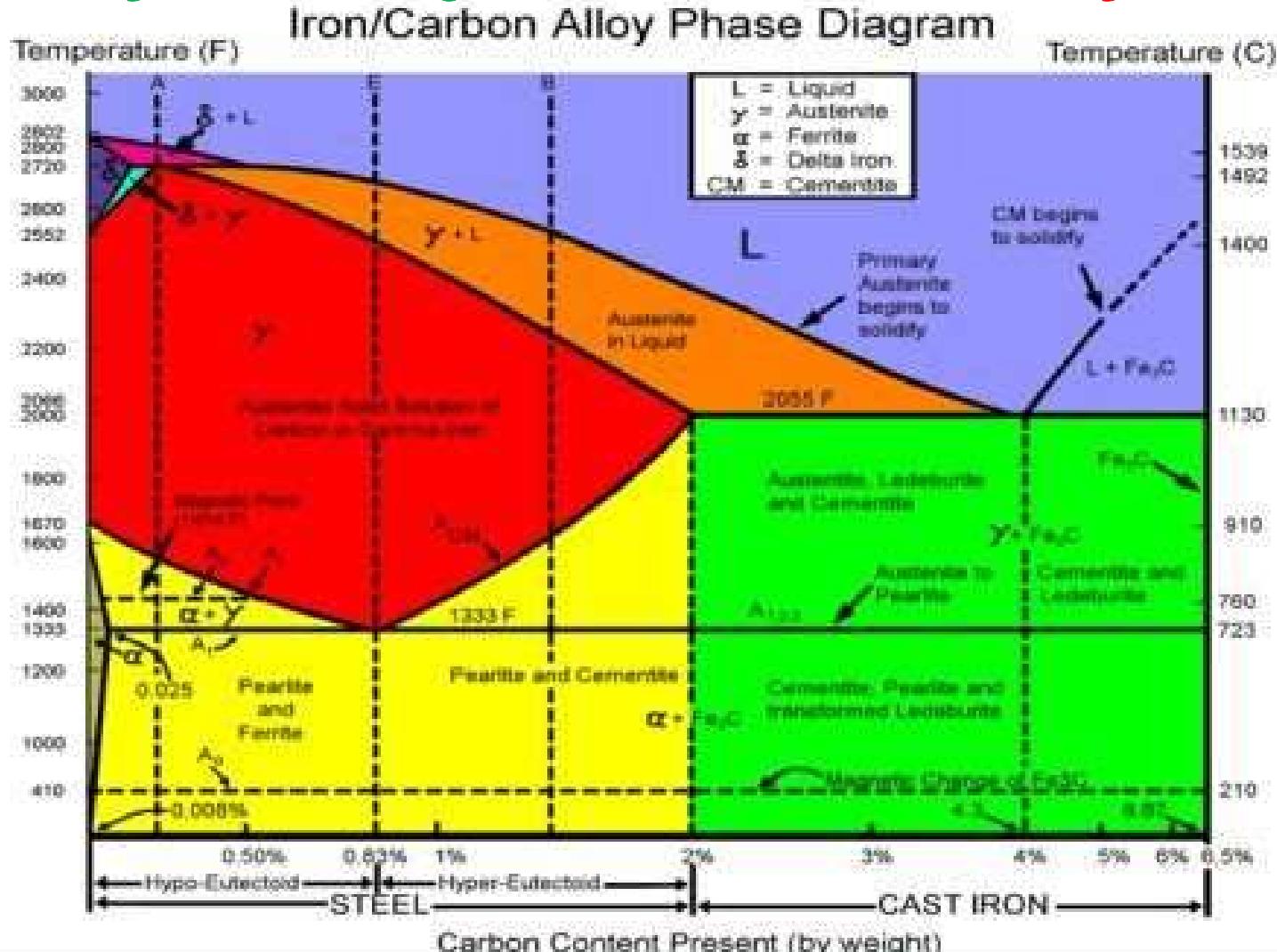


(b)  $P-v$  diagram of a pure substance



(a)  $P-v$  diagram of a substance that contracts on freezing

*Greater structure → More complex  
EOS & phase diagram + chemical complexity*



- Second most important phase diagram of in human civilization!
- Which is the first?  
<http://www.engineersgallery.com/iron-carbon-equilibrium-diagram/>

# *PhaseBook-Liquid Vapor Transition*

Raj Pala,

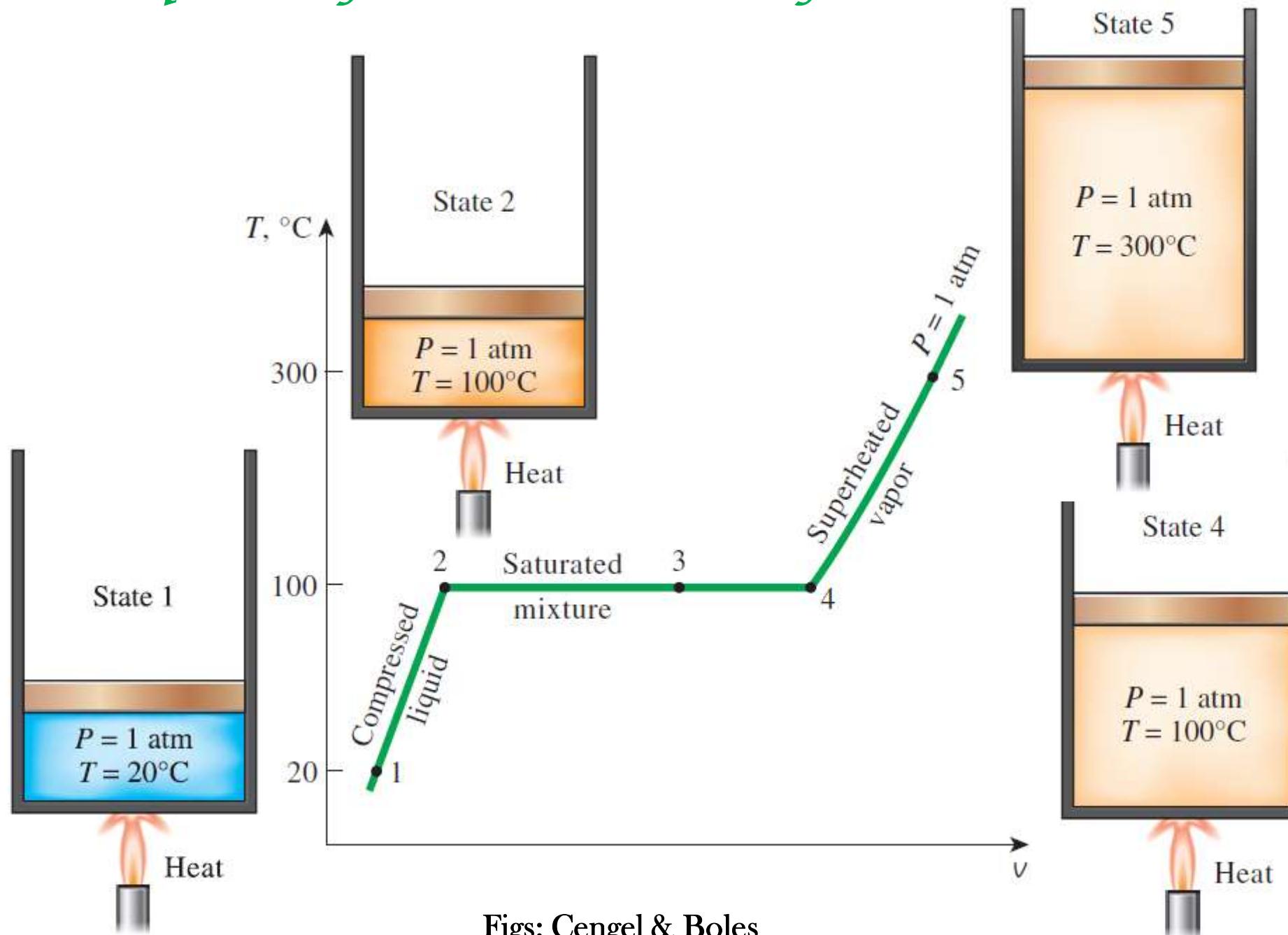
[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme  
Indian Institute of Technology, Kanpur.

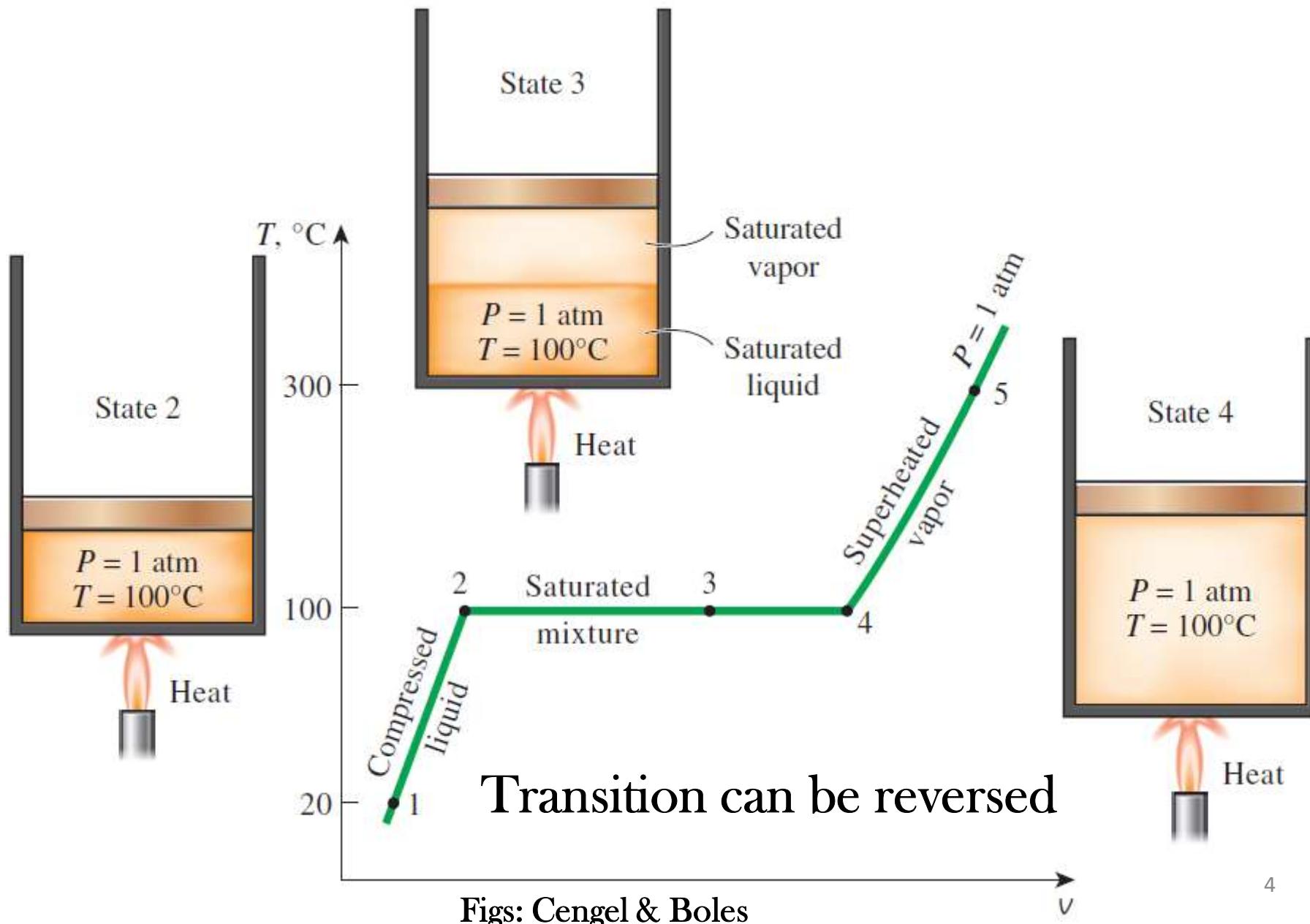
# *Liquid-Vapor Transition*

- Vapor Vs Gas?; Evaporation Vs. Boiling?
- Boiling: Vapor pressure=superincumbent pressure
- Evaporation can occur below boiling point too; Evaporation increases with temperature
- Many processes (like refrigeration, evaporative cooling, reactor control...) involve phase change-Latent heat especially of water is large

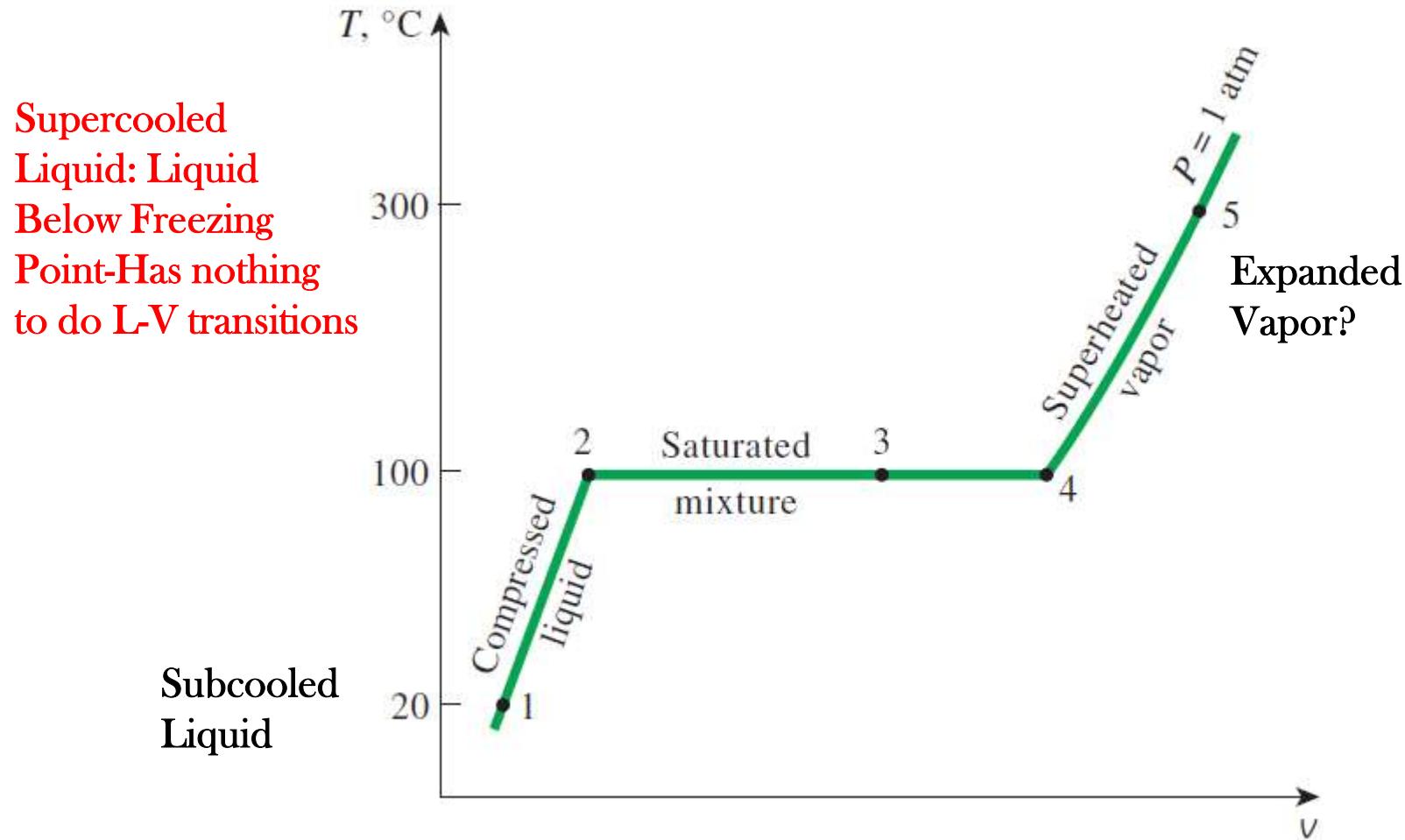
# Liquid-Vapor Transition-Physical Realization



# Liquid-Vapor Transition-Two phase region



# Liquid-Vapor Transition-Quirky terminologies



# *Boiling temperature Vs. Pressure*

- Boiling: Vapor pressure=superincumbent pressure

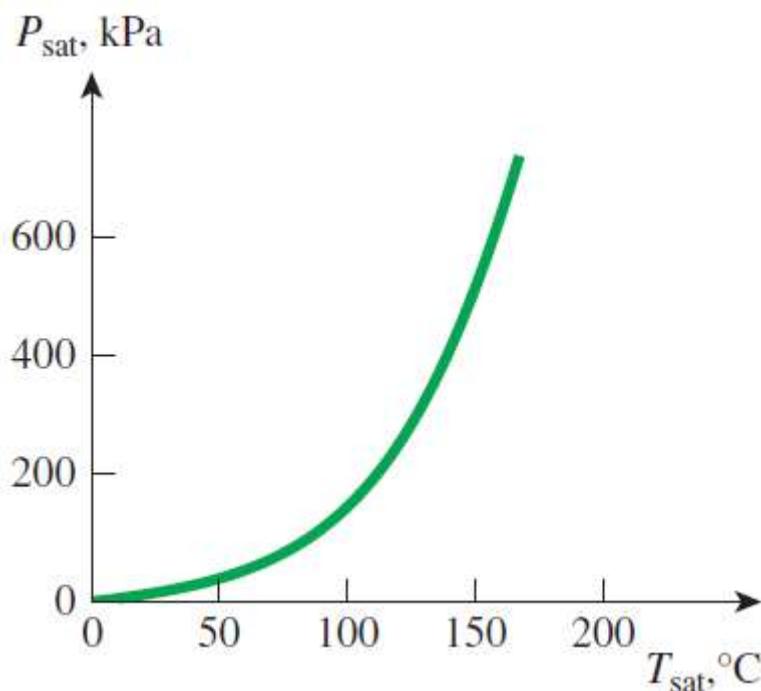


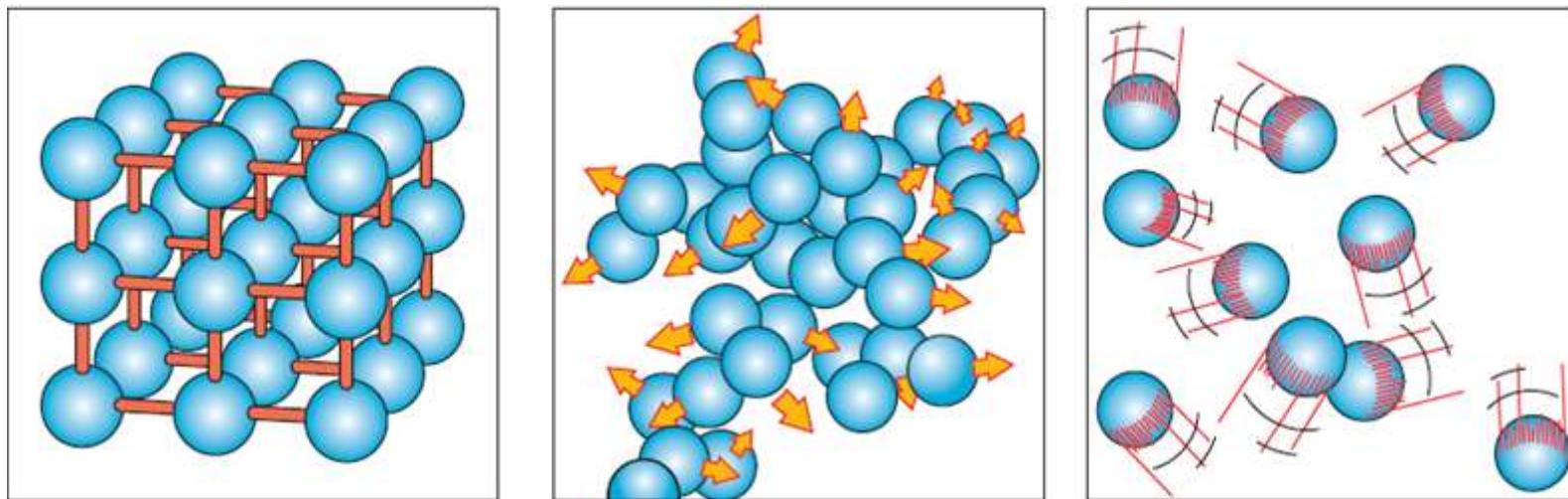
TABLE 3-1

Saturation (or vapor) pressure of water at various temperatures

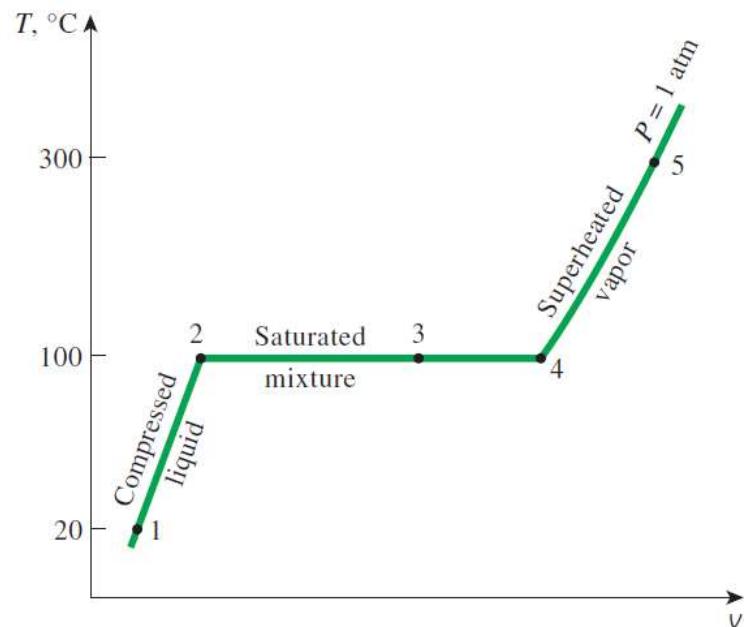
Temperature $T, ^\circ\text{C}$	Saturation Pressure $P_{\text{sat}}, \text{kPa}$
-10	0.260
-5	0.403
0	0.611
5	0.872
10	1.23
15	1.71
20	2.34
25	3.17
30	4.25
40	7.38
50	12.35
100	101.3 (1 atm)
150	475.8
200	1554
250	3973
300	8581

Fig & table: Cengel & Boles

# Revisiting structure-property correlations



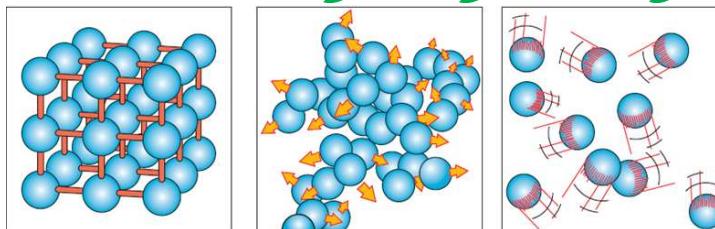
- Latent heat
- Latent heat of vaporization
- Latent heat of “fusion” (**Fusion=Freezing**)



7

Figs: Cengel & Boles

# *Intuitive structure-property correlations*



Substance	LHF (KJ/Kg)	M. Pt (°C)	LHV (KJ/KG)	B. Pt (°C)
Ethyl alcohol	108	-114	855	78.3
Ammonia	332.17	-77.74	1369	-33.34
Carbon dioxide	184	-78	574	-57
Helium			21	-268.93
Hydrogen	58	-259	455	-253
Lead	23	327.5	871	1750
Nitrogen	25.7	-210	200	-196
Oxygen	13.9	-219	213	-183
Refrigerant R134a		-101	215.9	-26.6
Refrigerant R152a		-116	326.5	-25
Silicon	1790	1414	12800	3265
Toluene	72.1	-93	351	110.6
Water	334	0	2264.705	100

*PhaseBook*  
*Liquid Vapor Transition: T-ν & P-ν Avatar*

Raj Pala,  
[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme,  
Indian Institute of Technology, Kanpur.

# *T-v diagram@different pressures for water*

- Both liquids and gases have continuous translational symmetry-reason behind the existence of critical temperature and pressure

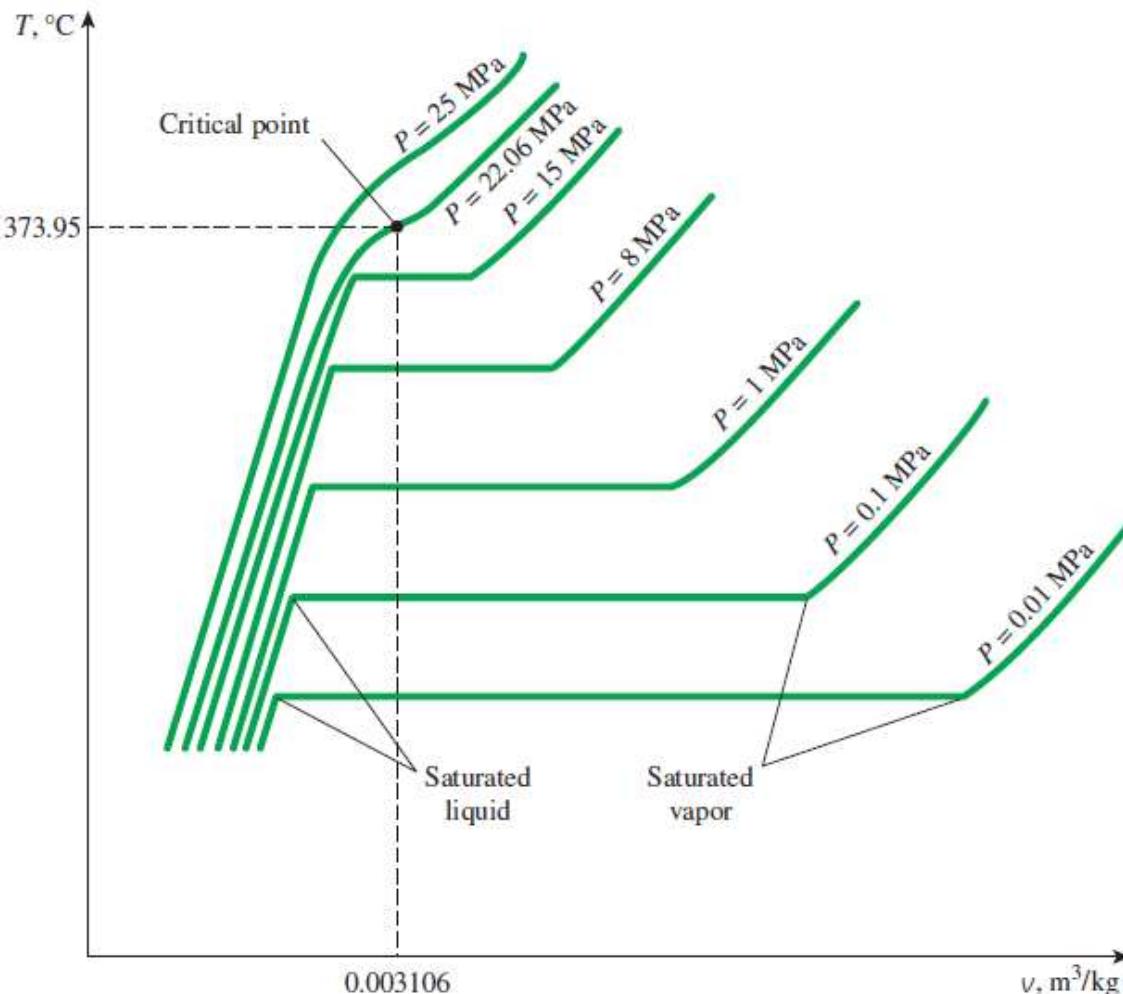
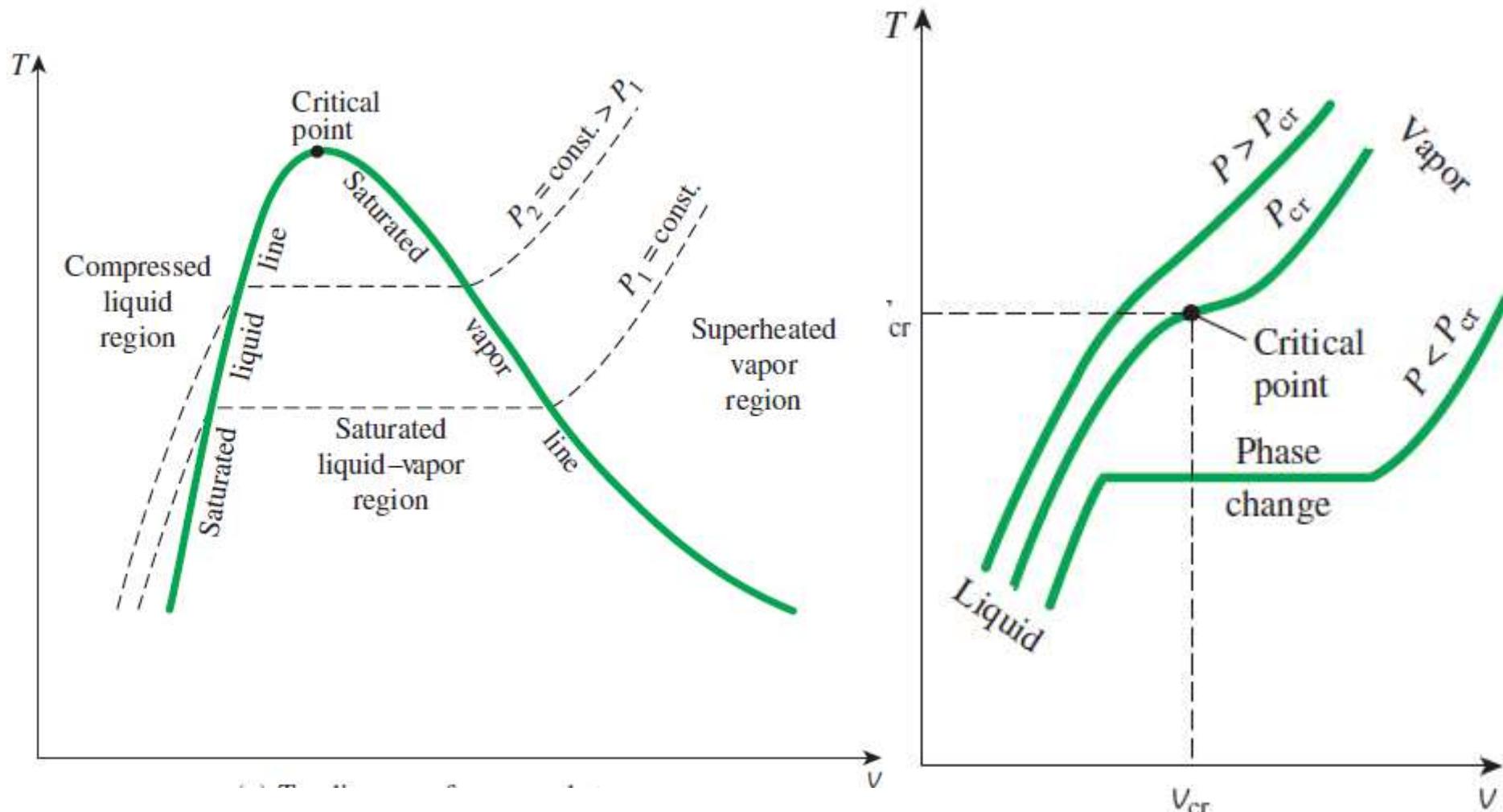


Fig: Cengel & Boles

# *T-v diagram@different pressures*



- Super critical solvents are important in Chemical engineering/Chemistry

Fig: Cengel & Boles

# $T$ - $v$ vs $P$ - $v$

- Intuition suggests as  $T$  increases,  $v$  increases; As  $P$  increases,  $v$  decreases

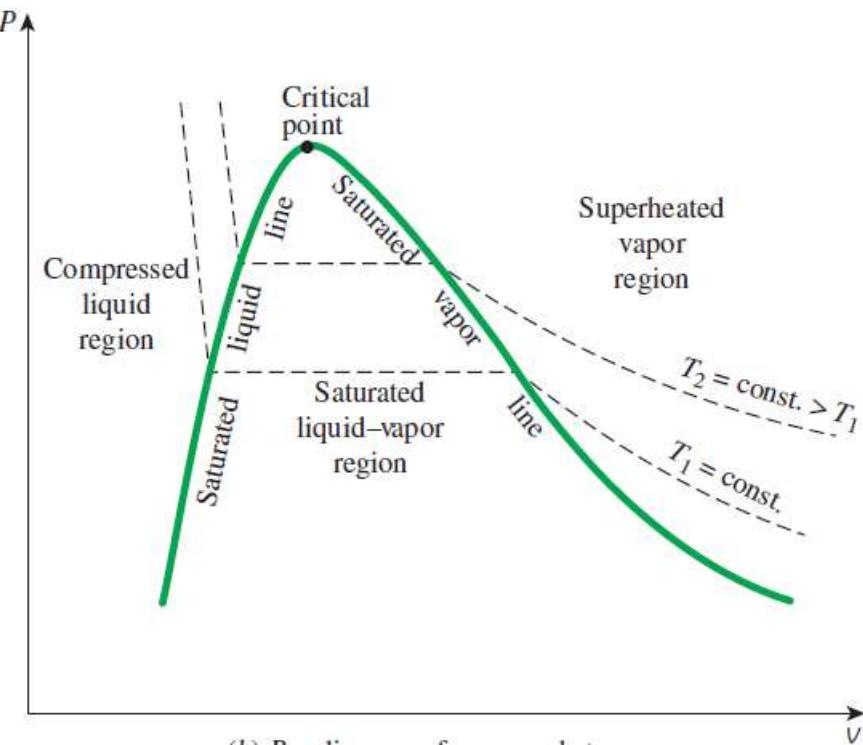
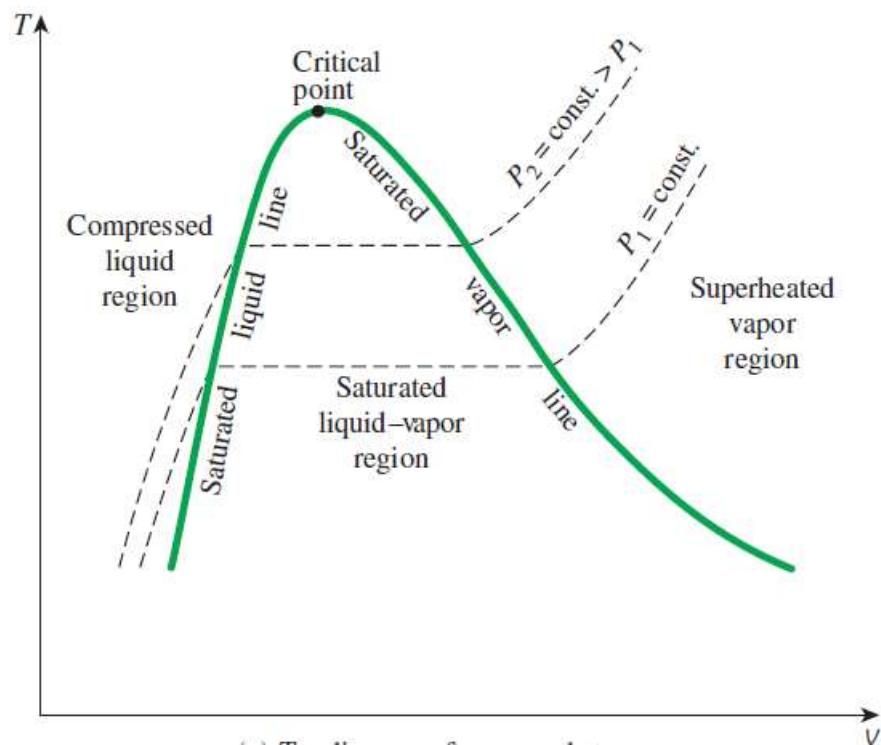


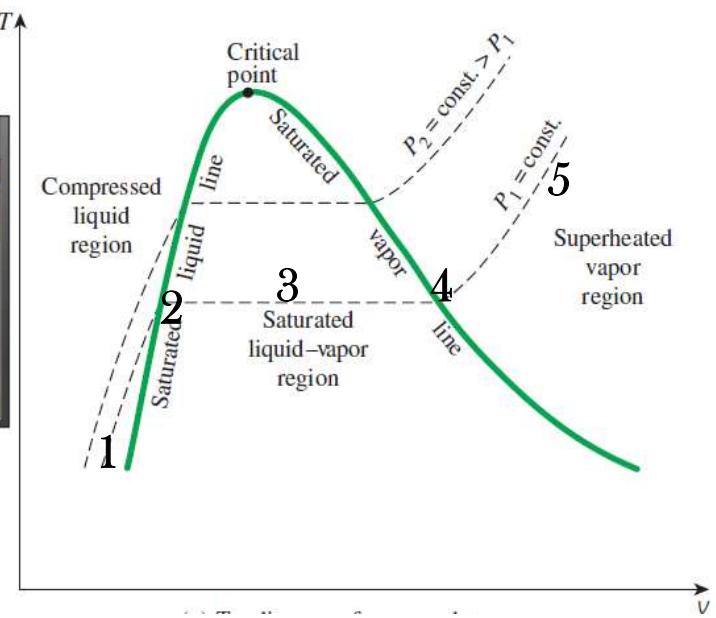
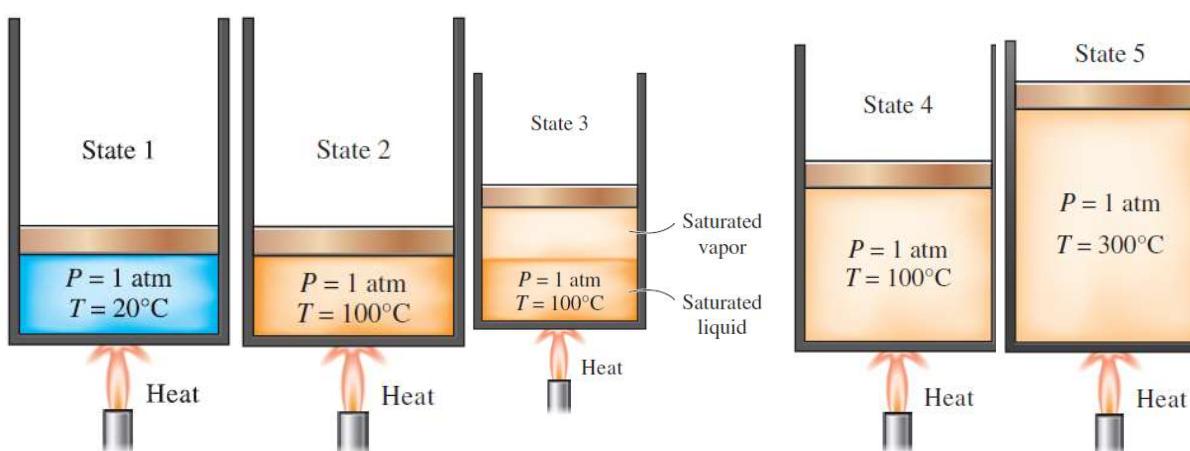
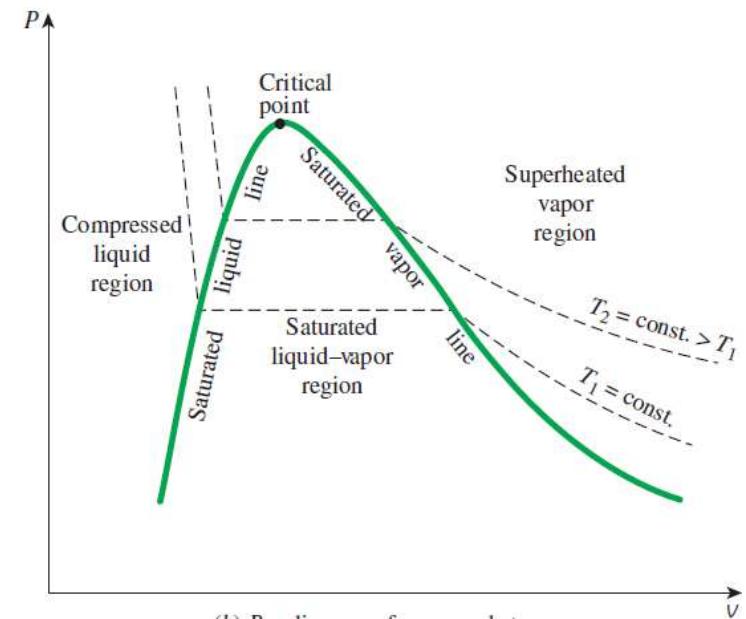
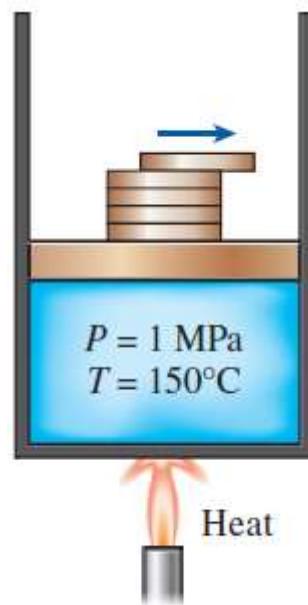
Fig: Cengel & Boles

*PhaseBook*  
*Solid-Liquid -Vapor Transitions*

Raj Pala,  
[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

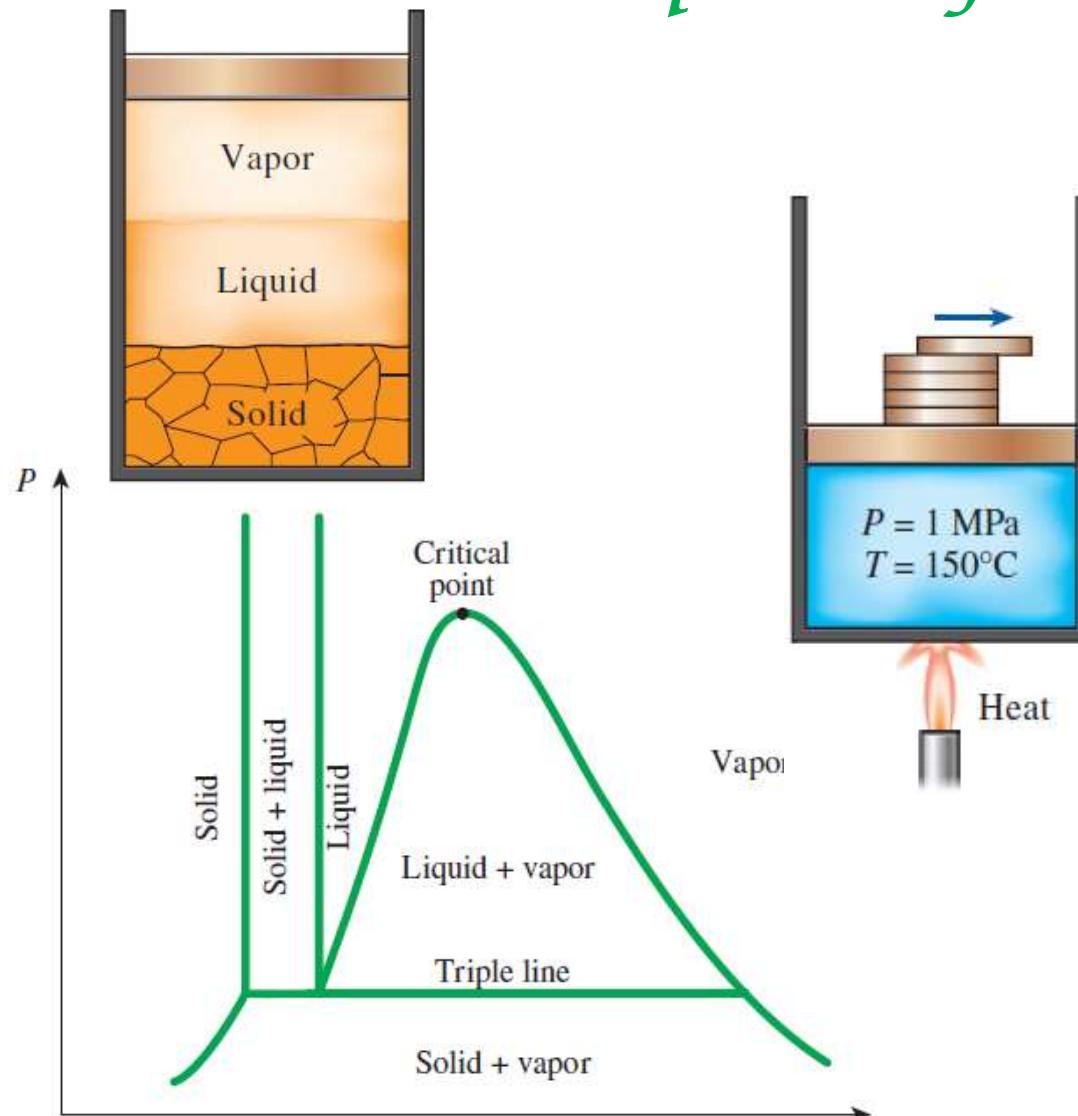
Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme,  
Indian Institute of Technology, Kanpur.

# Different ways of conducting experiments



Figs: Cengel & Boles, TD

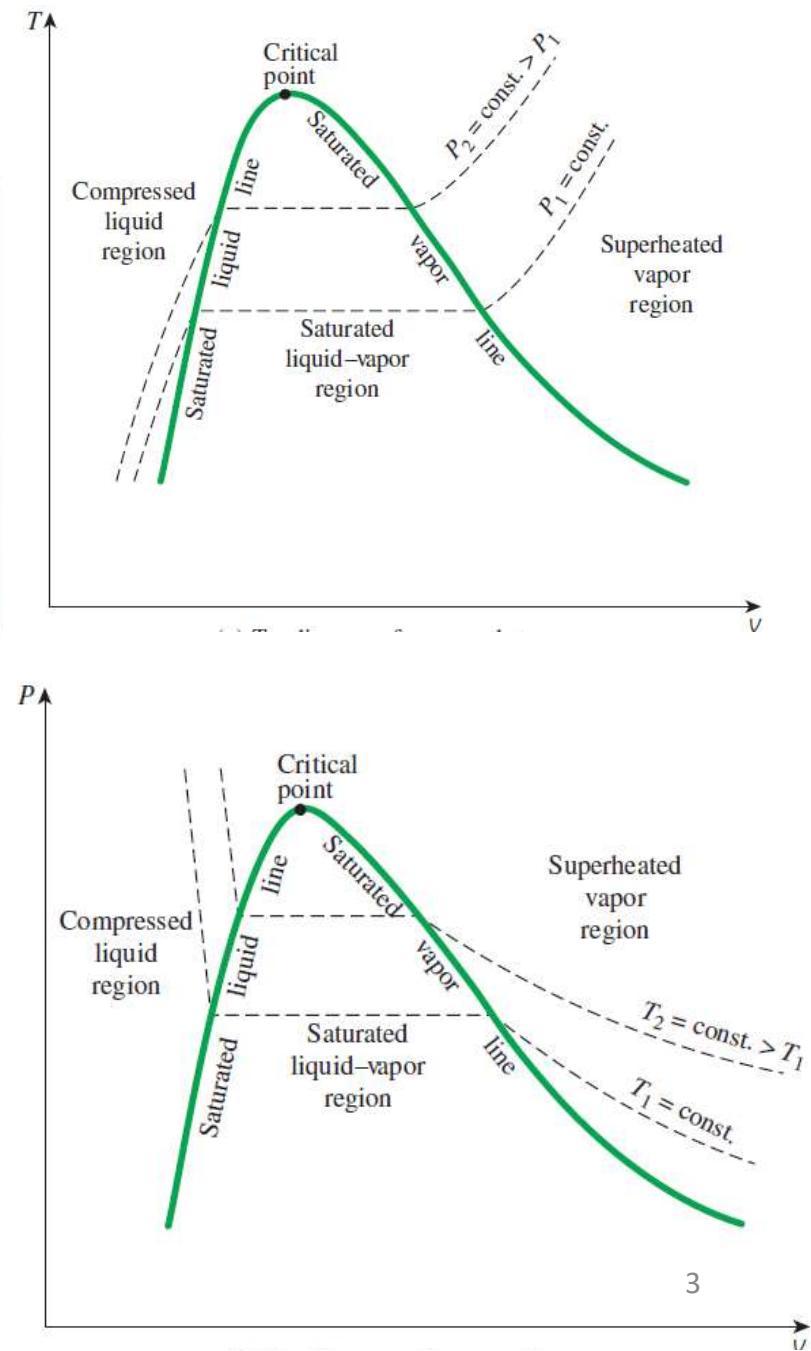
# Solid-Liquid-Vapor transitions



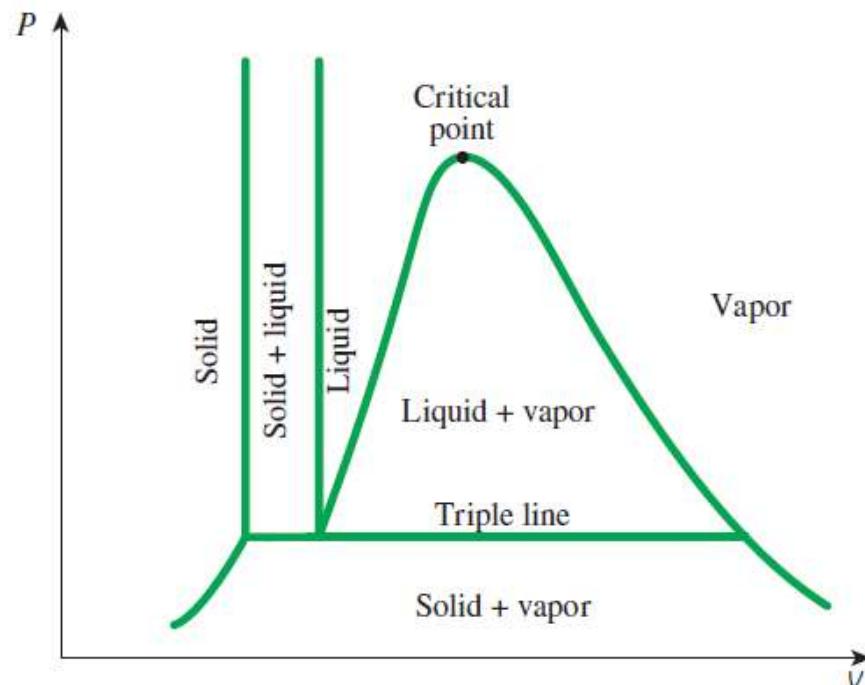
(a)  $P$ - $V$  diagram of a substance that contracts on freezing

- Liquid is not possible below triple line

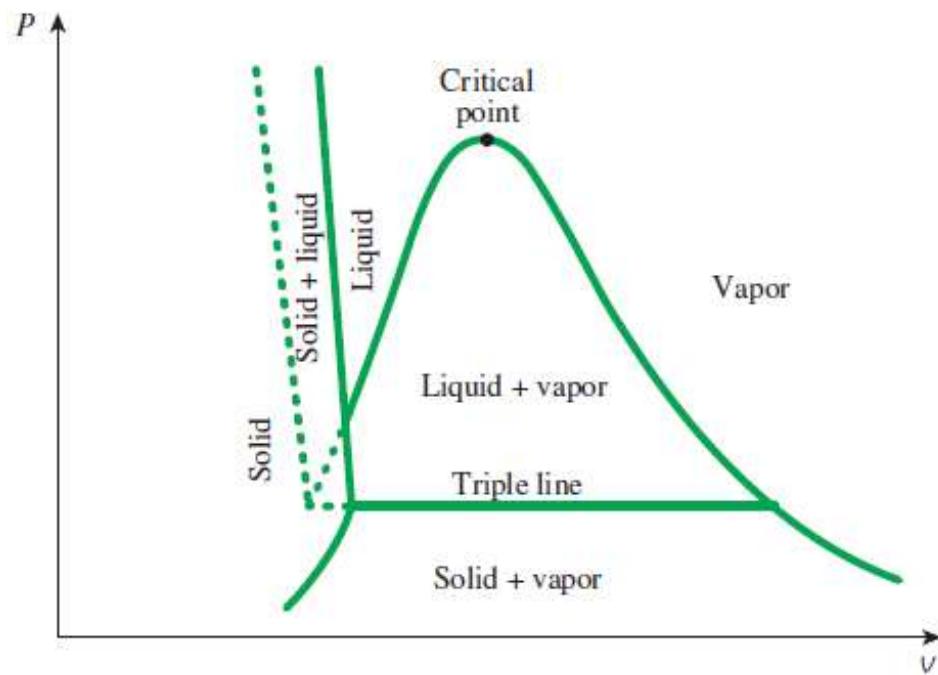
Figs: Cengel & Boles



# *Solid-Liquid-Vapor transition for water*



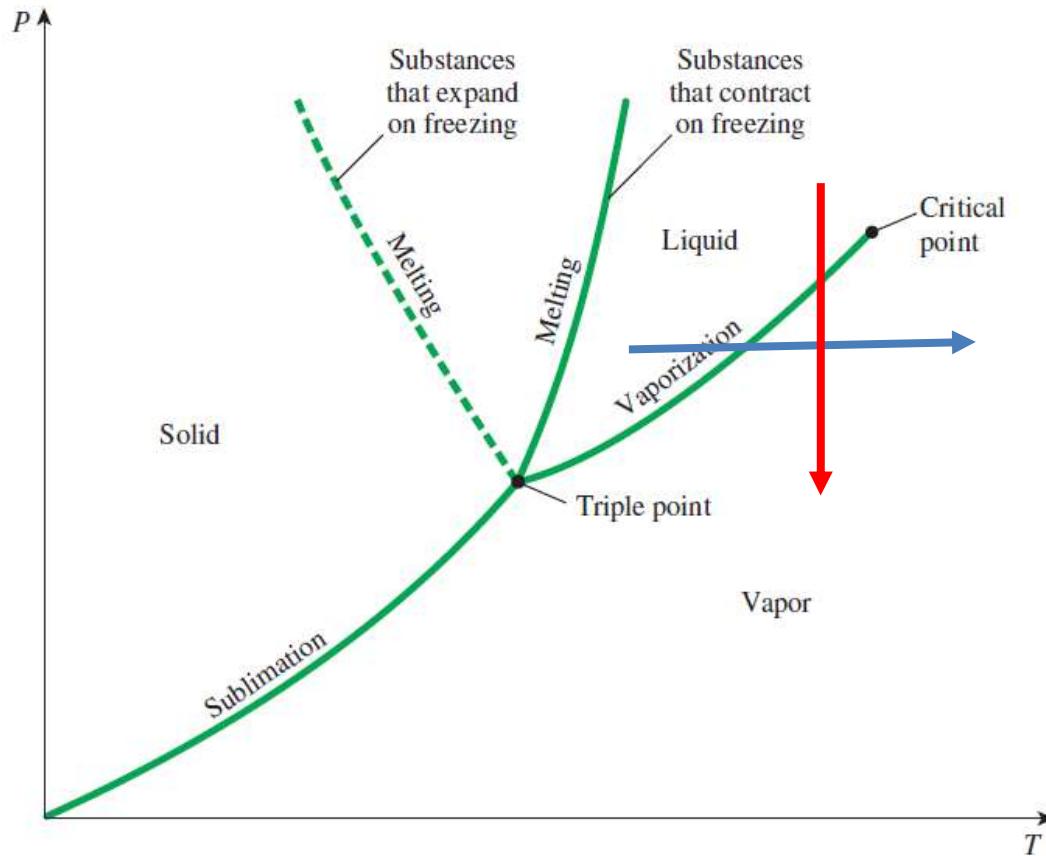
(a)  $P$ - $v$  diagram of a substance that contracts on freezing



(b)  $P$ - $v$  diagram of a substance that expands on freezing (such as water)

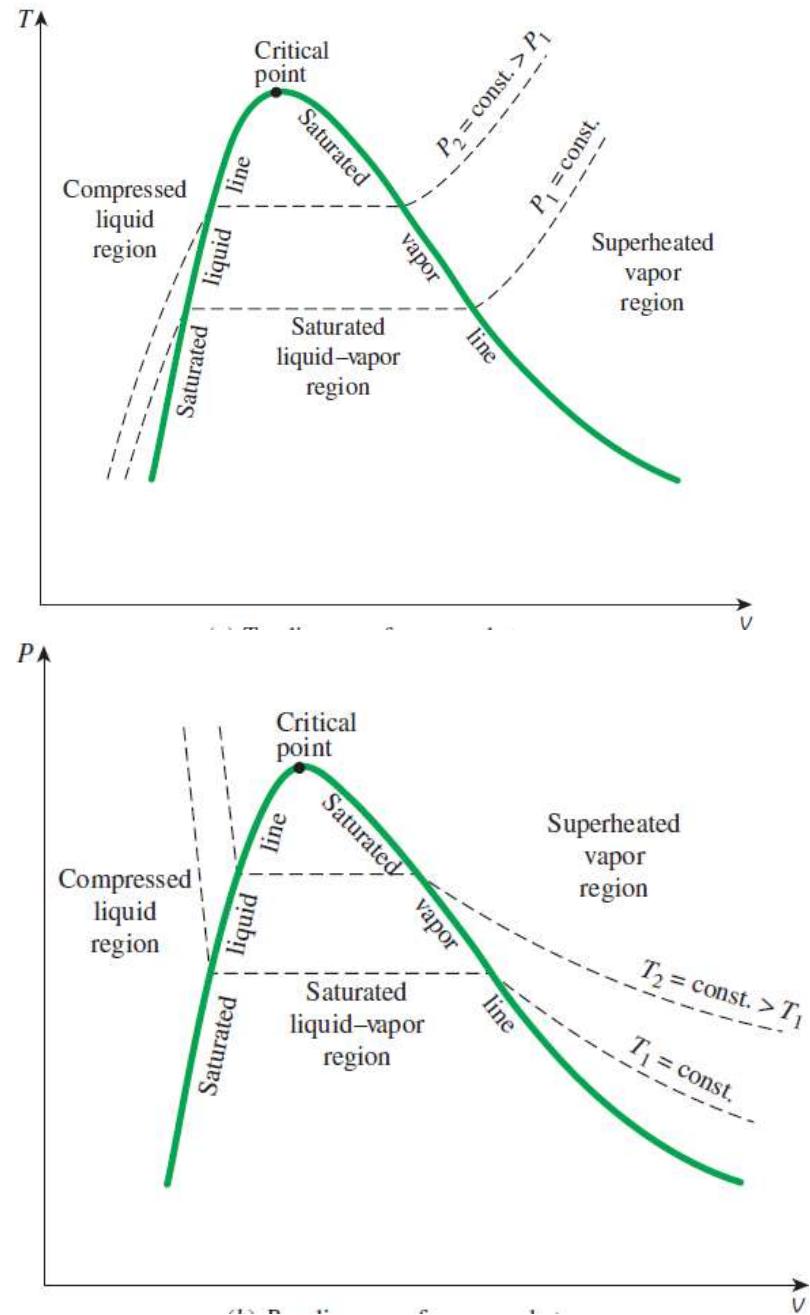
- Ice floats on water!

# $P$ vs. $T$ for Solid-Liquid-Vapor transitions



- 2-phase line in (P-v) appears as a point in (P-T)
- Triple line in (P-v) appears as a Triple point in (P-T)
- “Simple compressible substance”?
- No surface, electrical & magnetic effects
- No phase transition
- We will define it further after some more “work”

Fig: Cengel & Boles



# *Ice is cool!*

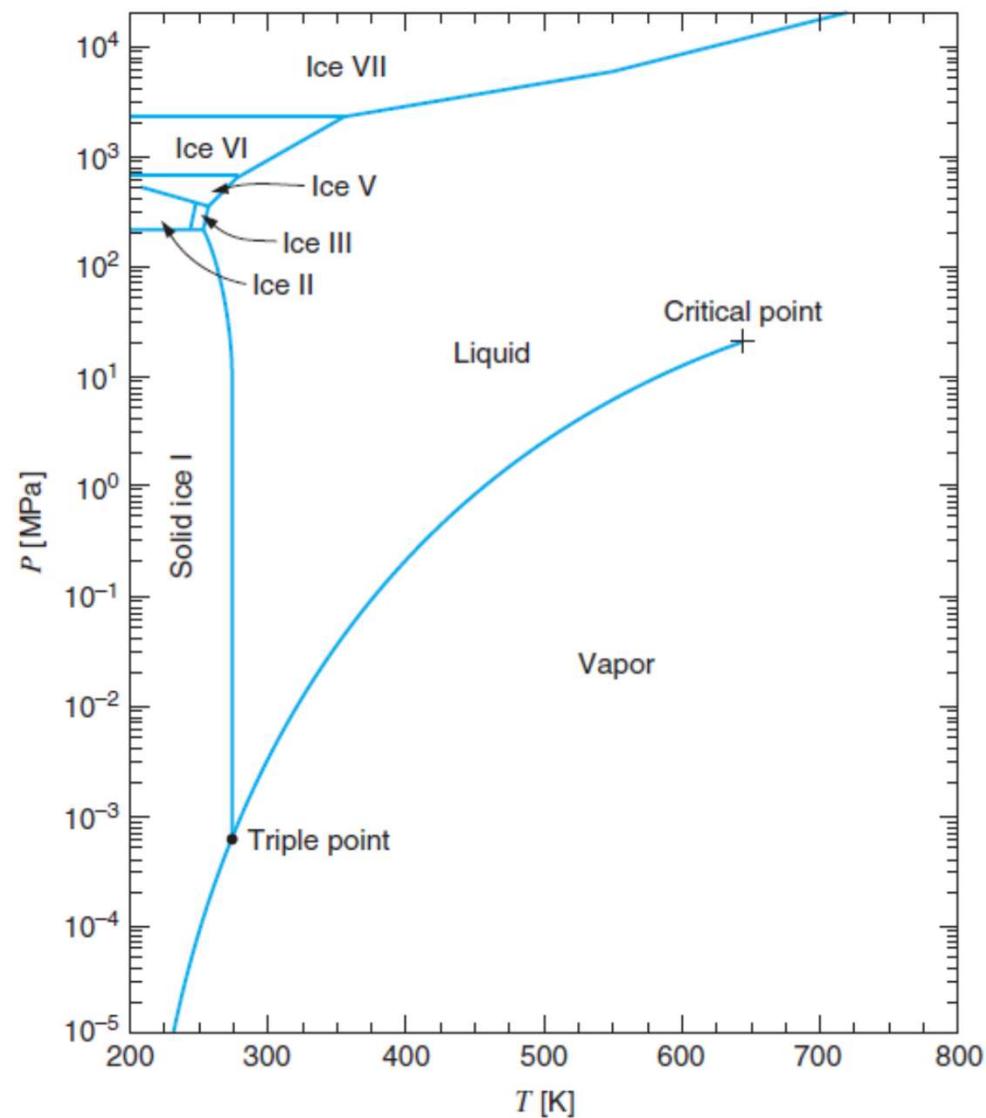
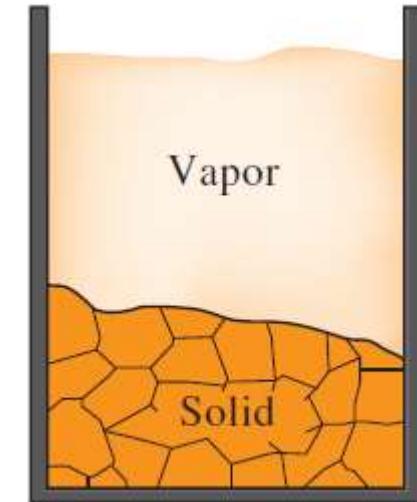
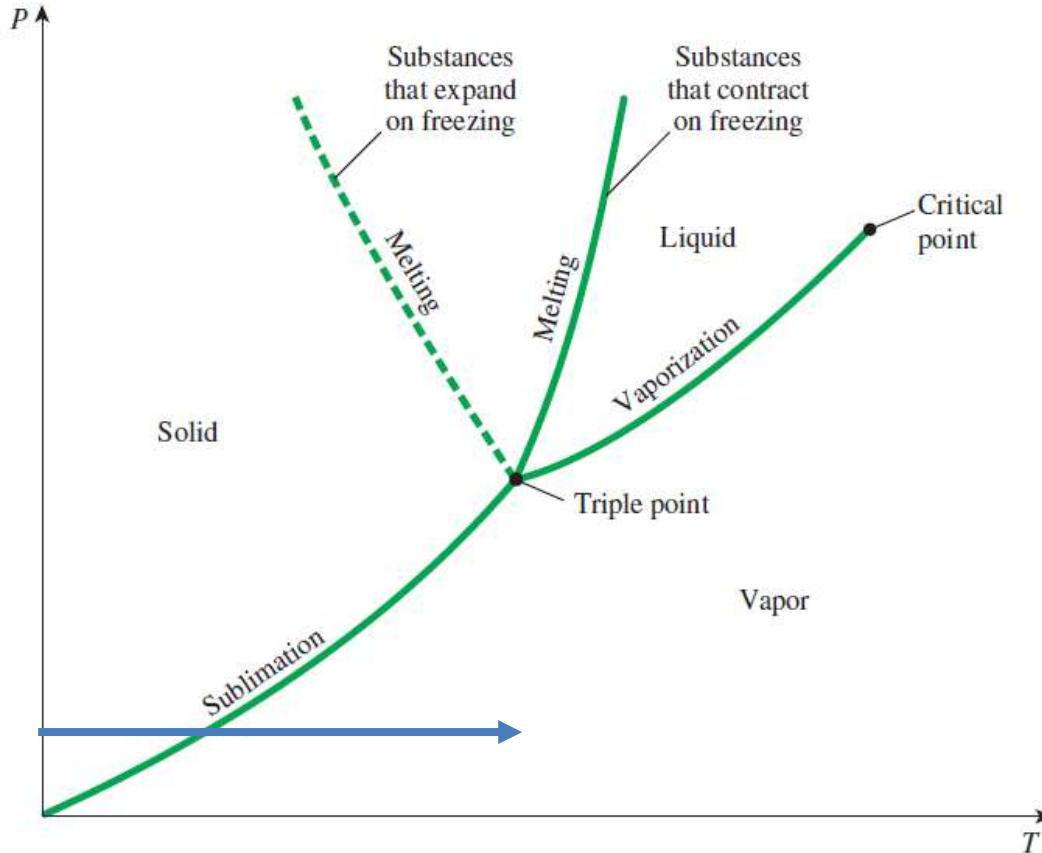


Fig: Borgnakke & Sonntag, TD

# *Sublimation*



- Both liquids and gases have continuous translational symmetry; Solid have discrete translational symmetry
- Sublimation vs. vaporization
- Sublimation:  $\text{CO}_2$  (dry ice), Camphor, Naphthalene...

Fig: Cengel & Boles

## *Sublimation in “dry ice”*

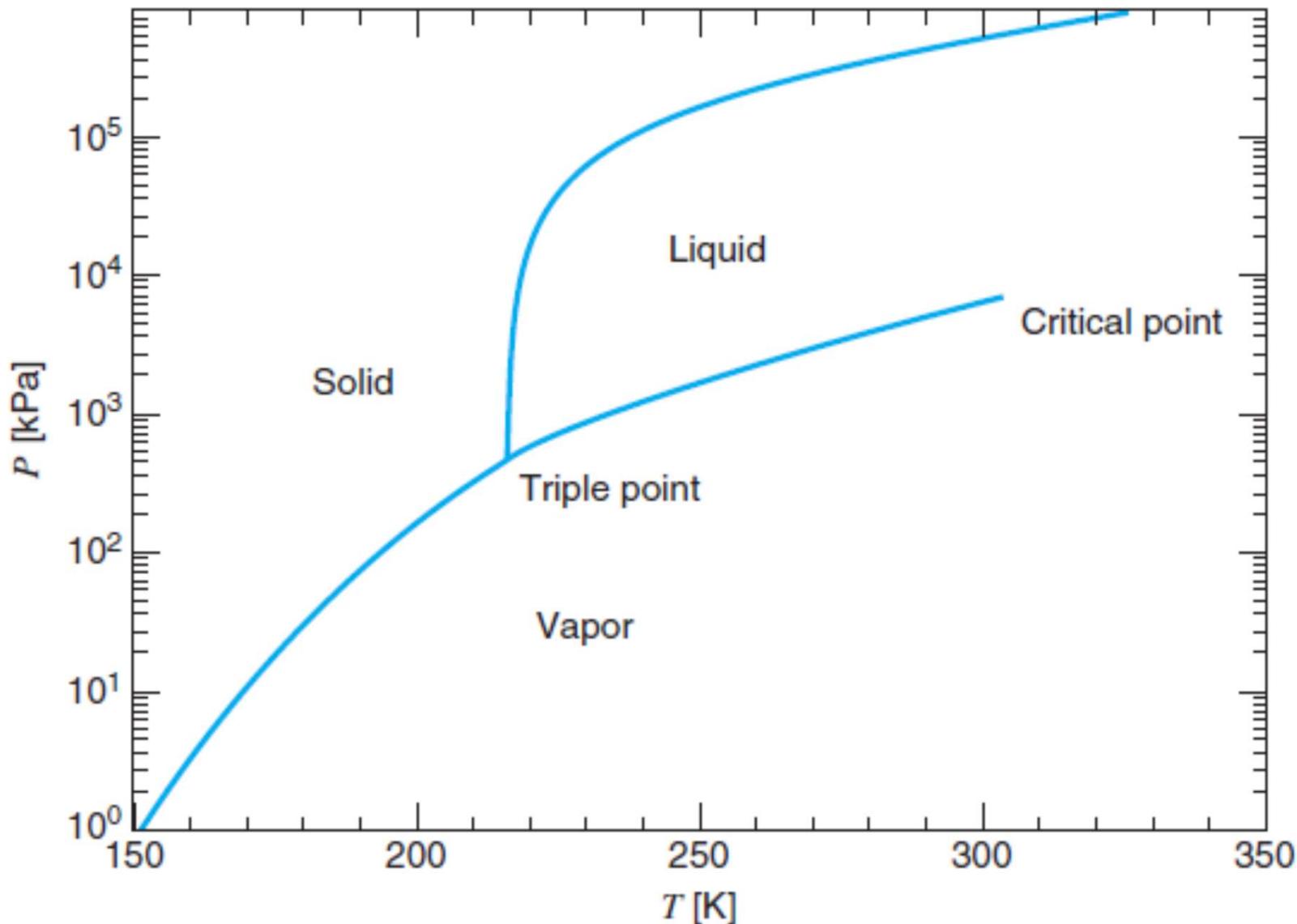


Fig: Borgnakke & Sonntag, TD

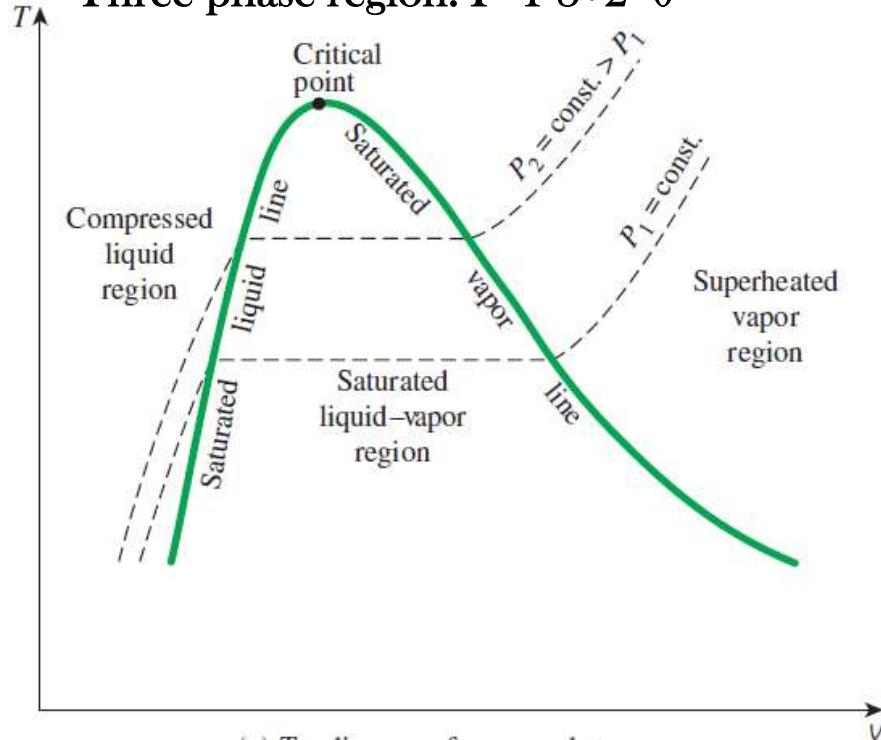
*PhaseBook*  
*Advertising Gibbs Phase Rule*

Raj Pala,  
[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

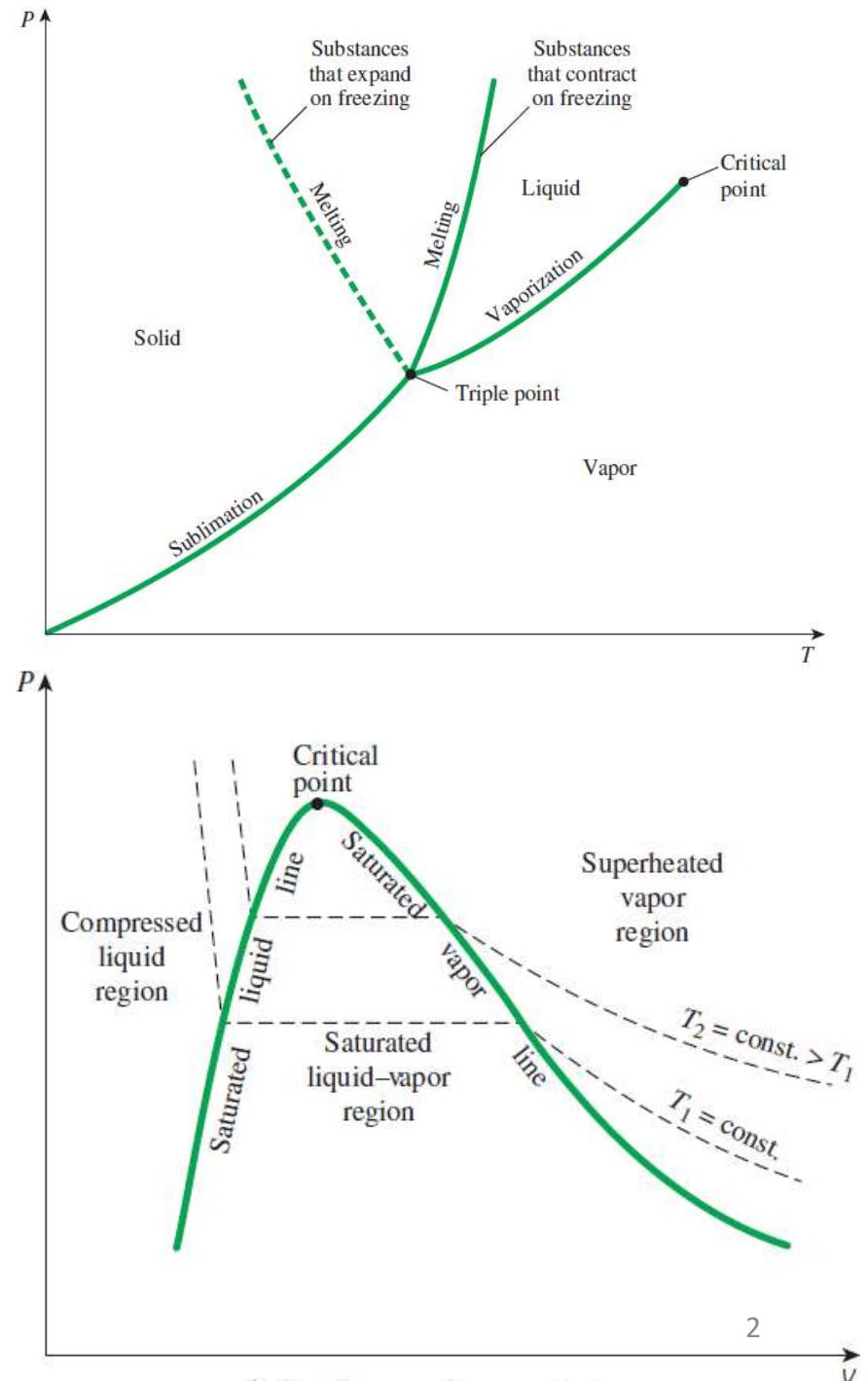
Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme,  
Indian Institute of Technology, Kanpur.

# Patterns & book keeping

- “Gibbs phase rule”:  $F = C-P+2$
- $F$ =Degrees of Freedom;
- $C$ =Component,  $P$ =#phases;
- $F$ =#independent intensive variables ( $P$ ,  $T$  **not v!**);
- Single phase region:  $F=1-1+2=2$
- Two-phase region:  $F=1-2+2=1$
- Three-phase region:  $F=1-3+2=0$



Figs: Cengel & Boles, TD

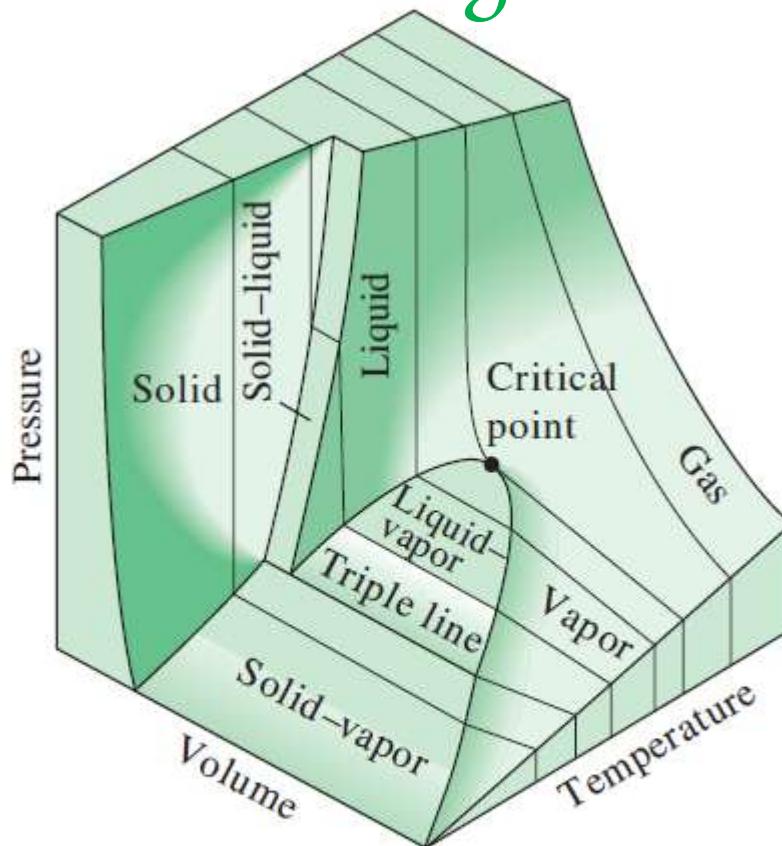


*PhaseBook*  
*Frowning Faces & 3D Phase Diagrams*

Raj Pala,  
[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme,  
Indian Institute of Technology, Kanpur.

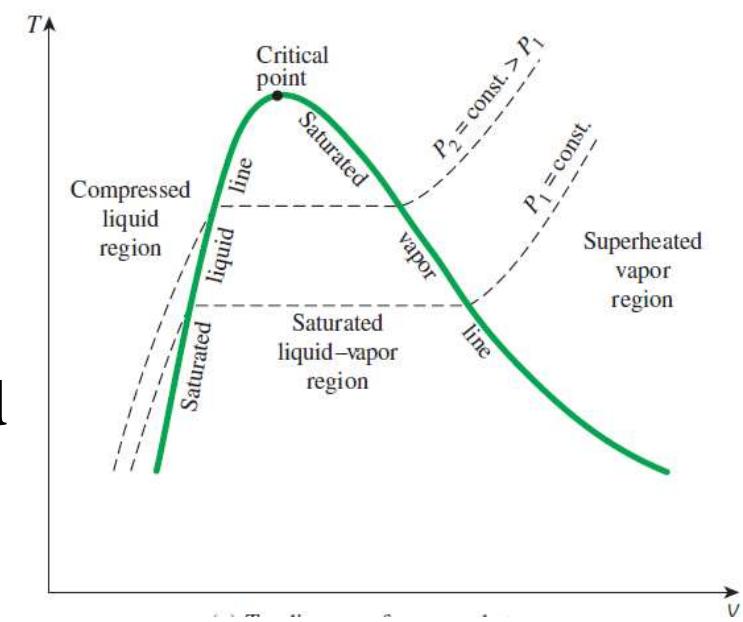
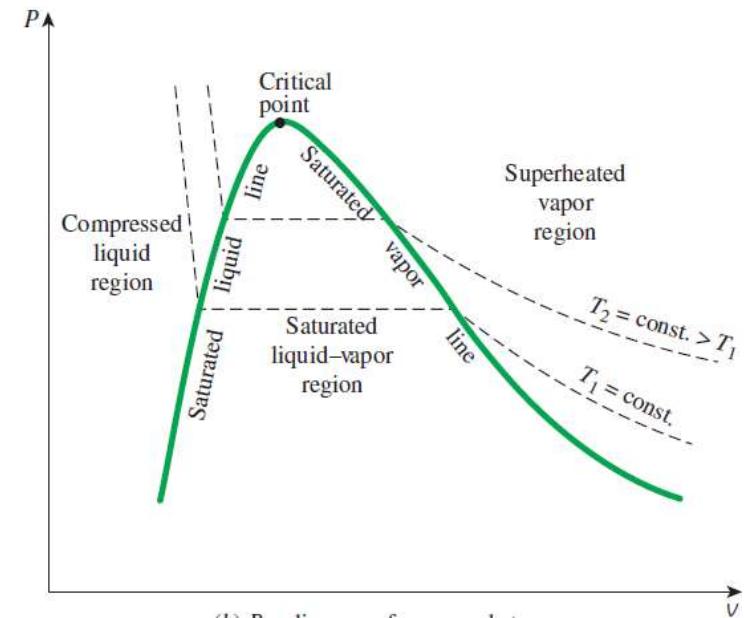
# Correlating 2D diagrams to 3D: $P(v,T)$



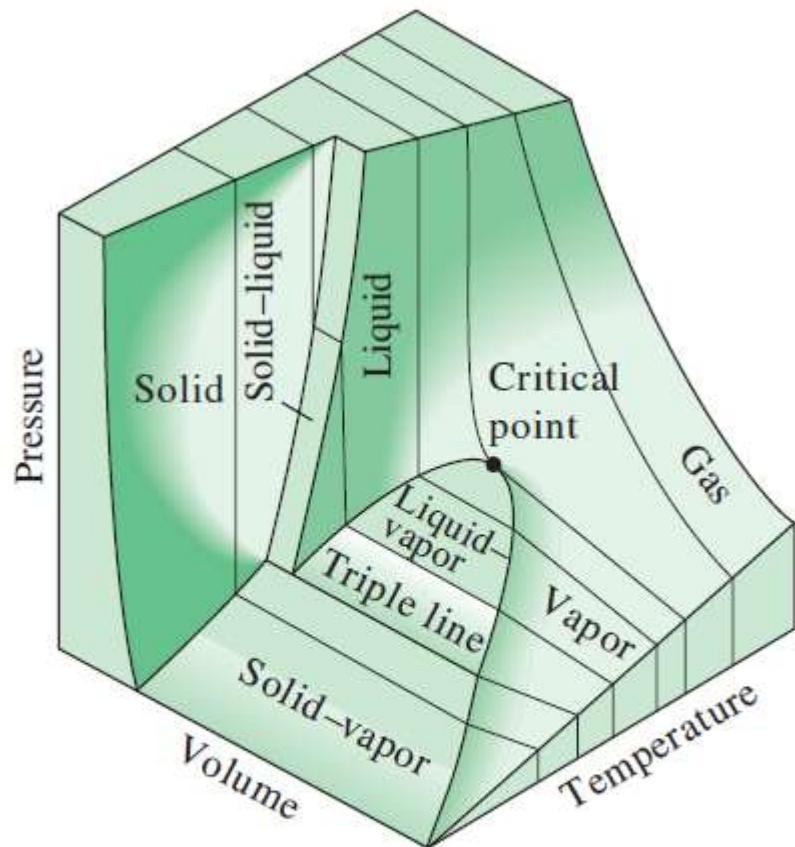
**FIGURE 3–23**

$P$ - $v$ - $T$  surface of a substance that  
*contracts* on freezing.

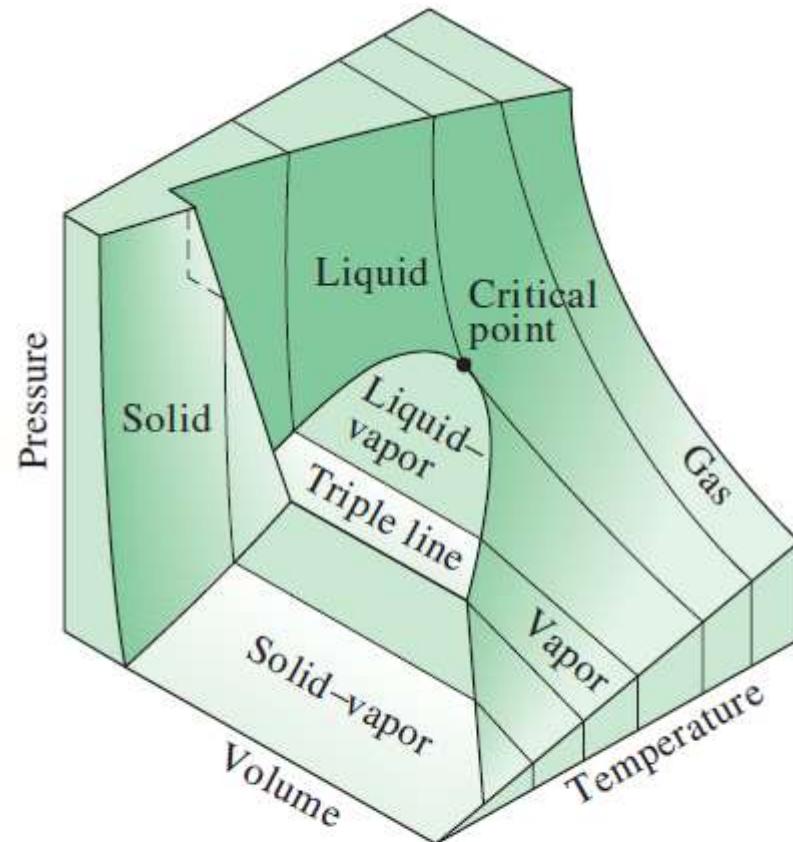
- Different set of lines needs to be indicated to correlate constant pressure processes...



# *Exercise in visual arts!*



**FIGURE 3–23**  
*P-v-T* surface of a substance that  
*contracts* on freezing.



**FIGURE 3–24**  
*P-v-T* surface of a substance that  
*expands* on freezing (like water).

# *Equation of state*

Raj Pala,

[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme,  
Indian Institute of Technology, Kanpur.

# What is *not* an equation of state?



- Why care?
- ...Filling your cooking gas cylinder
- Can the Table of P, T & v be replaced by equation?

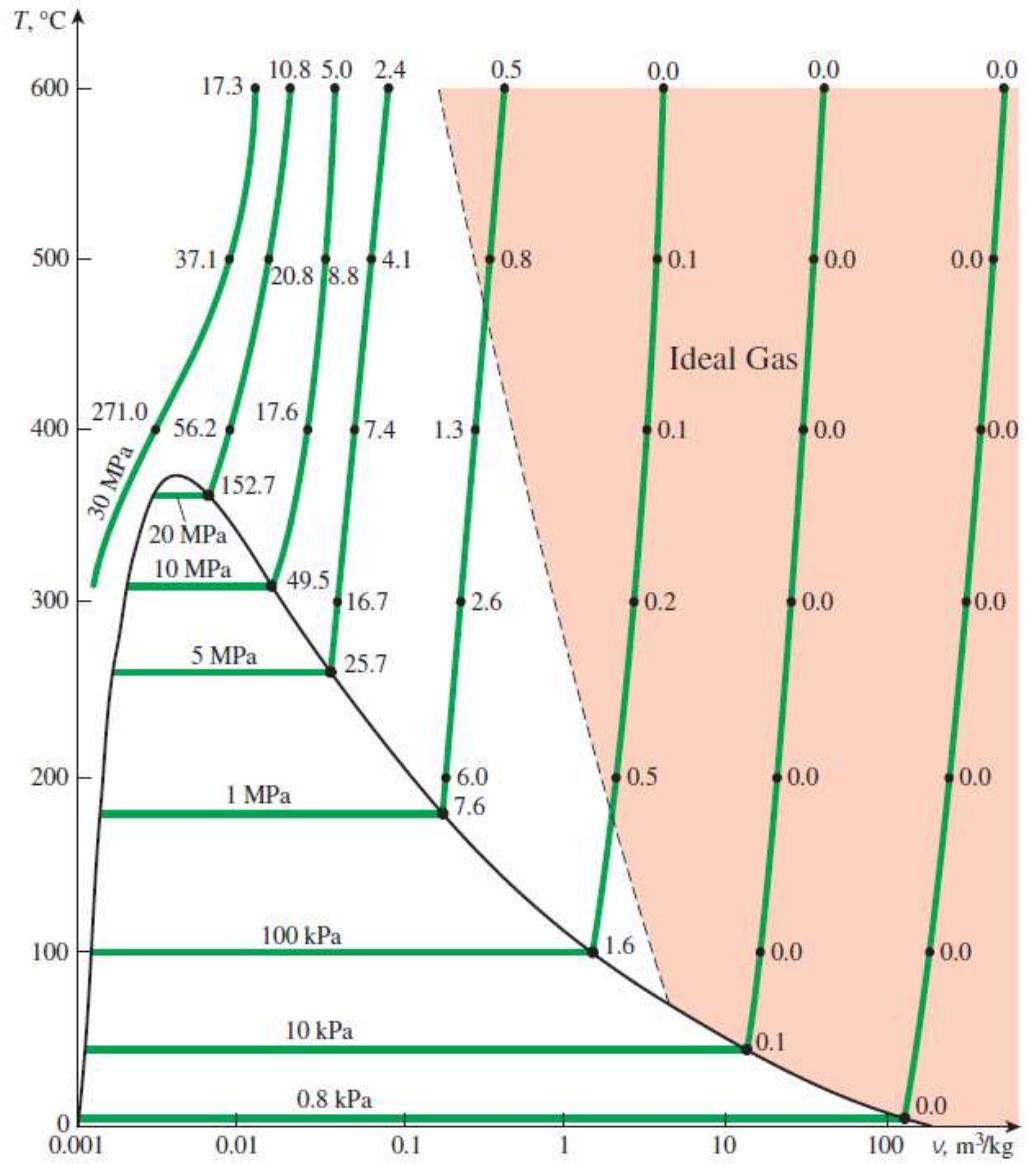
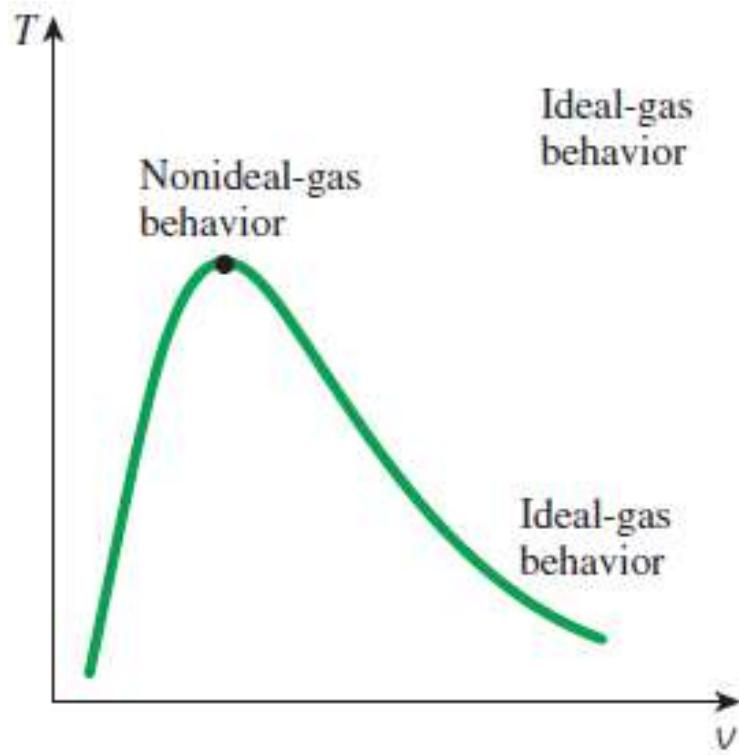
Fig: <https://www.shutterstock.com/>; Wiki

Table 18-1 Classical Physics

Maxwell's equations	
I. $\nabla \cdot E = \frac{\rho}{\epsilon_0}$	(Flux of $E$ through a closed surface) = (Charge inside)/ $\epsilon_0$
II. $\nabla \times E = - \frac{\partial B}{\partial t}$	(Line integral of $E$ around a loop) = $- \frac{d}{dt}$ (Flux of $B$ through the loop)
III. $\nabla \cdot B = 0$	(Flux of $B$ through a closed surface) = 0
IV. $c^2 \nabla \times B = \frac{J}{\epsilon_0} + \frac{\partial E}{\partial t}$	$c^2$ (Integral of $B$ around a loop) = (Current through the loop)/ $\epsilon_0$ $+ \frac{\partial}{\partial t}$ (Flux of $E$ through the loop)
Conservation of charge	
$\nabla \cdot J = - \frac{\partial \rho}{\partial t}$	(Flux of current through a closed surface) = $- \frac{\partial}{\partial t}$ (Charge inside)
Force law	
$F = q(E + v \times B)$	
Law of motion	
$\frac{d}{dt}(p) = F$ , where	$p = \frac{mv}{\sqrt{1 - v^2/c^2}}$ (Newton's law, with Einstein's modification)
Gravitation	
$F = -G \frac{m_1 m_2}{r^2} \mathbf{e}_r$	

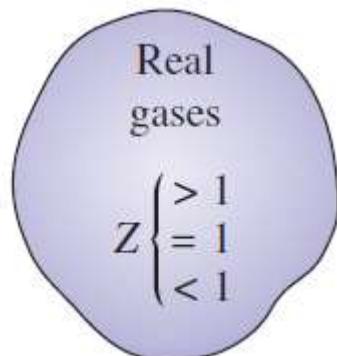
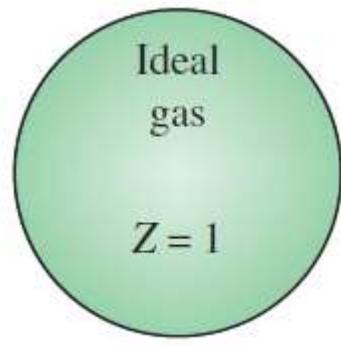
# *Ideal “gas” behavior & ...*

- $PV=nRT$
- Operational P & T
- Higher T, lesser relative interaction energy



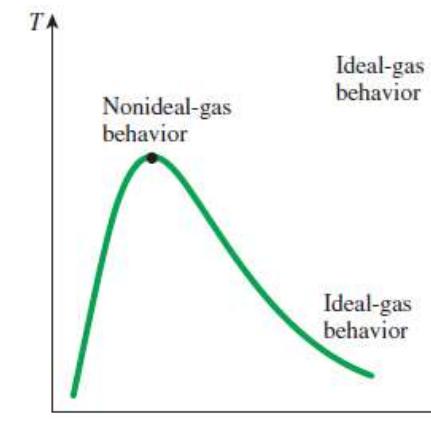
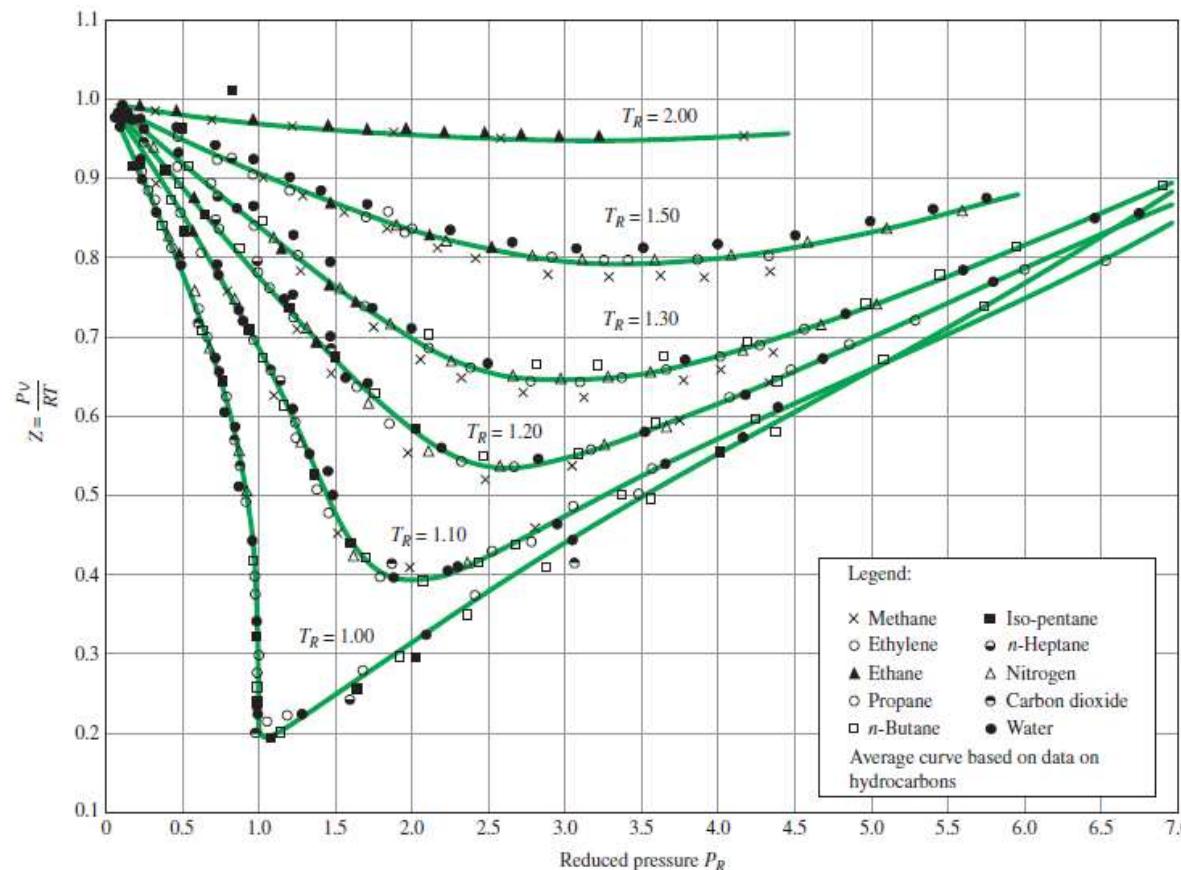
Figs: Cengel & Boles, TD

# Non-Ideality & Compressibility factor



$$PV = ZRT$$

$$Z = \frac{PV}{RT} \quad Z = \frac{V_{\text{actual}}}{V_{\text{ideal}}}$$



$$P_R = \frac{P}{P_{\text{cr}}} \quad T_R = \frac{T}{T_{\text{cr}}}$$

Reduced pressure      Reduced temperature

$$V_R = \frac{V_{\text{actual}}}{RT_{\text{cr}}/P_{\text{cr}}} \quad \text{Pseudo-reduced specific volume}$$

Fig: Cengel & Boles

# *Van der waals EOS*

- “Finite size” of gases
- Interactions: Electrodynamical & excluded volume
- Constraints on EOS: Inflection at critical point
- Noble Prize for Physics-1910

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

$$a = \frac{27R^2 T_{\text{cr}}^2}{64P_{\text{cr}}} \quad b = \frac{RT_{\text{cr}}}{8P_{\text{cr}}}$$

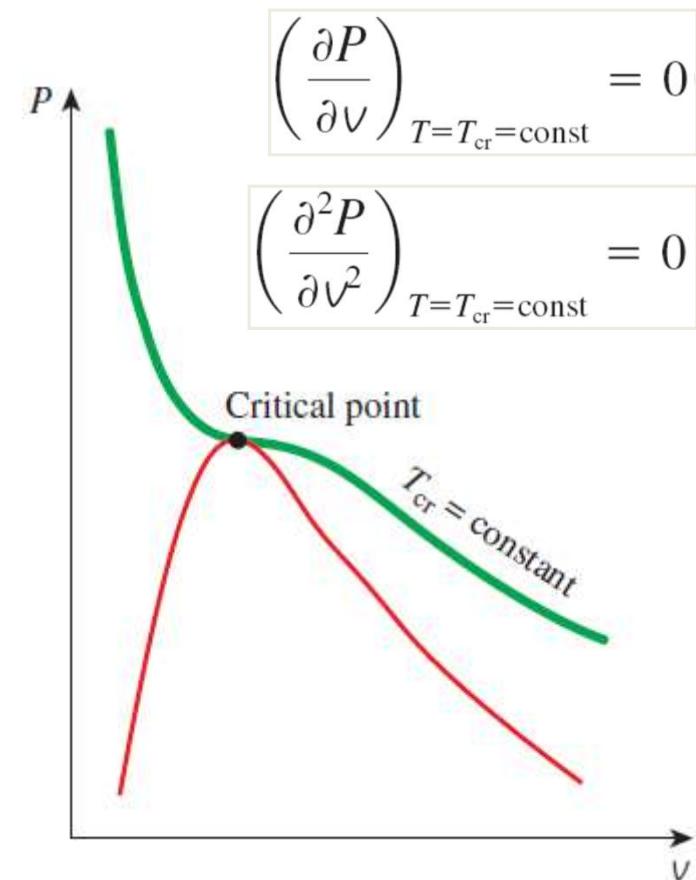


Fig: Cengel & Boles

# Who is the second man on Moon?-All other EOS!

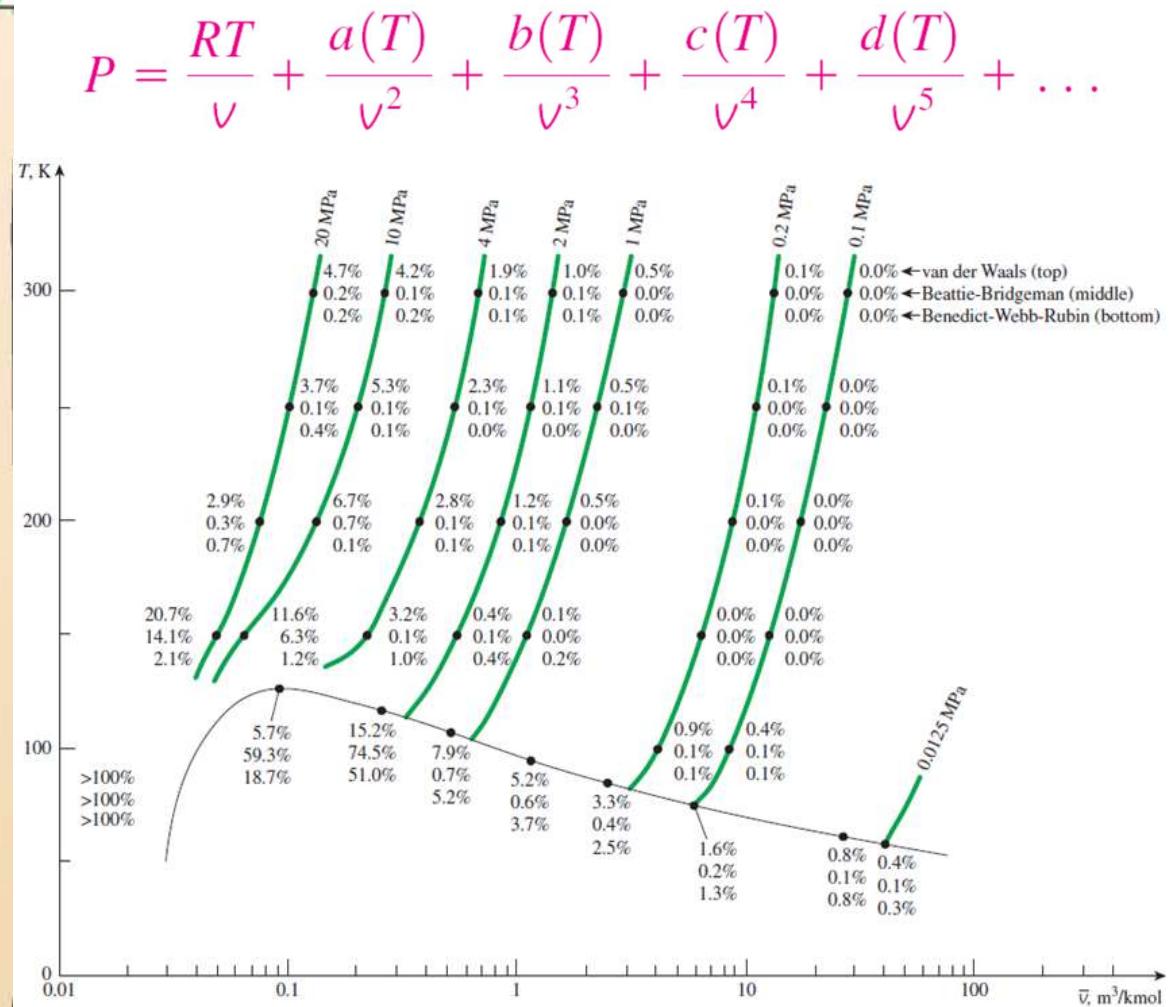
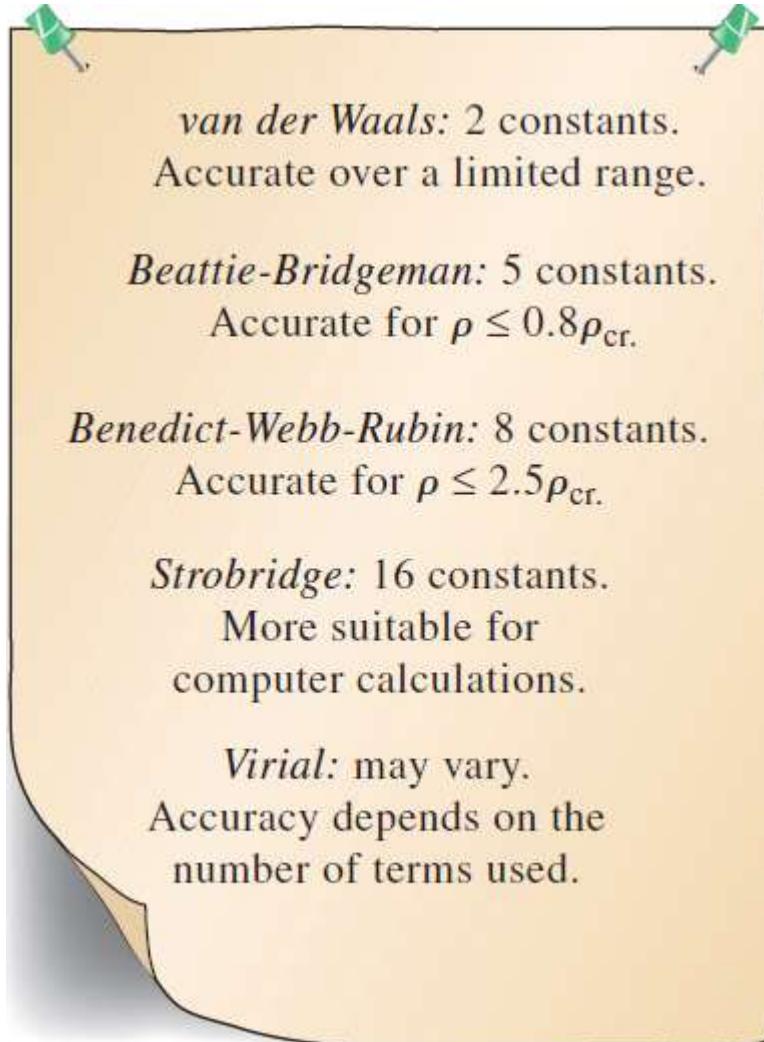


Fig: Cengel & Boles

- $a(T), b(T) \dots$  Virial Coefficients
- Statistical Thermodynamics/Mechanics: Maria Goeppert Mayer-2<sup>nd</sup> woman to win Physics Nobel Prize (for Nuclear Shell Model)

*All Work, No Heat!*  
*Brief review of elementary classical Mechanics Notions*

Raj Pala,  
[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme,  
Indian Institute of Technology, Kanpur.

## *Newton 1<sup>st</sup> & 2<sup>nd</sup>*

- 1<sup>st</sup> Law of inertia: Momentum of an *isolated* object is unchanged
- 2<sup>nd</sup> :  $\mathbf{F} = m\mathbf{a}$
- “Inertial mass” is the proportionality constant between force & acceleration; “Inertial mass” is measured somehow; Force is what that satisfies  $\mathbf{F} = m\mathbf{a}$ ; “Circular logic”
- Source of force field; e.g. Gravitation;  $F = \frac{-Gm_1m_2}{r^2}$ ;  $m_1$  and  $m_2$  are Gravitational masses
- Principle of equivalence: Inertial and Gravitational masses are equivalent
- Force field (like electrical & magnetic) need not involve masses

# *Work*

- Intuitive notion of physiological work-performed against resisting force
- $W = F * d$
- Can the work done in this purely mechanical system be recovered?
- Already lifted mass, in principle, can be lowered to lift another mass

## *Potential & Kinetic Energy in simple mechanical system*

- Cricket ball in Bumrah's hand has potential energy...
- At a particular position, ball has the potential to gain kinetic energy when accelerated/applied force
- Potential energy=Stored energy capacity of a mechanical system (e.g. system=object in a force field)
- Kinetic energy=Capacity to do work, present in the object in the form of motion of the object; Cricket ball with kinetic energy can move against a resisting gravitational force
- Work mediates **transformation** of Kinetic energy to Potential energy
- **Conservation** of energy & Work-Energy theorem

## *Potential Energy interconversion to Kinetic Energy*

- Hydroelectric energy/power
- Solar energy did the lifting of water, gave water (in the form of cloud) its potential energy
- Potential energy released is transformed to kinetic energy of rain, which is seldom used for work
- However, water falling from high altitude can be used for doing work
- Typically, hydroelectric power plants can convert ~85% of potential energy from stored water into electrical energy
- Energy density is less; Energy release per unit mass or volume is less

# *What is a simple mechanical system?*

- No “friction”; No heat; No temperature
- Mechanical quantities vs. thermodynamical quantities
- How do we extend notions of work, work-energy theorem, conservation and conversion of energy as seen in simple mechanical systems to thermodynamical systems?
- ESO-Thermodynamics!

*Let us get to Work with Ideal Gas!*

Raj Pala,

[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

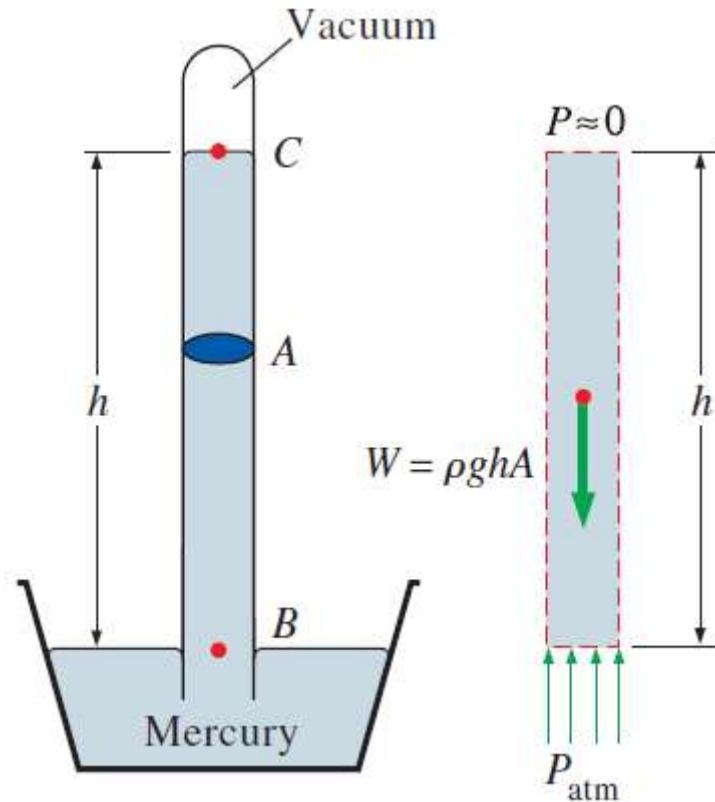
Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme,  
Indian Institute of Technology, Kanpur.

# *All work & No heat!*

- Mechanical quantities vs. thermodynamical quantities
- ESO-TD: Extend notions of work, work-energy theorem, conservation and conversion of energy as seen in simple mechanical systems to thermodynamical systems
- First step...

*What does  $1.03 \times 10^4$  kg acted by Earth's gravitational field of  $9.80 \frac{m}{s^2}$  over a square meter mean?*

- Atmospheric pressure
- $1.013 \times 10^4 \frac{N}{m^2} = 760 \text{ mm Hg}$



# *Resistance Movement: A Toy Model*

- Closed chamber ( $L^*L^*L$ ) with piston containing  $N_{AvA}$  ideal gas atoms
- Ideal gas atomic energy=Only Kinetic Energy
- Pressure exerted by gas on the piston= $P_{\text{external}}$ ; No acceleration
- Work= $F_{\text{external}} * (\Delta x) = \frac{F_{\text{resisting}}}{A} * A * (\Delta x) = P_{\text{external}} * (\Delta V)$
- $F_{\text{external}} = \text{"Average steady" force on the wall} = F_{\text{gas-NA atoms}}$
- $F_{\text{gas-1 atom}} = \text{"Stochastic" force due to single atom collision}$
- $F_{\text{gas-1 atom}} = (\text{momentum change per collision}) * \left( \frac{\text{Collisions}}{\text{Second}} \right)$
- $F_{\text{gas-1 atom}} = (2 * m * \text{velocity}_{\text{ideal gas atom}}) * \frac{\text{velocity}_{\text{ideal gas atom}}}{2L_{\text{Chamber}}}$
- $F_{\text{gas-N atoms}} (\text{"Average steady"}) = F_{\text{gas-1 atom}} * \frac{N_A}{3}$
- $P_{\text{external}} = \frac{F_{\text{external}}}{L^2} = \frac{F_{\text{gas-NA atoms}}}{L^2} = \frac{N_A m v^2}{3 L^3}$

## $\mathcal{P}$ from “first principles” & empirical connection to $\mathcal{T}$

- Charles’ Law:  $\mathbf{PV} = N_{\text{AvA}} * K_{\text{Boltzmann constant}} * T = R_{\text{gas constant}} * T$
- $P_{\text{external}} * V = \frac{F_{\text{external}}}{L^2} * L^3 = \frac{N_A mv^2}{3L^3} * L^3 = \frac{N_A mv^2}{3} = N_A * K_B * T$
- $\frac{mv^2}{2} = \frac{3K_B * T}{2}$  !!!
- What has been accomplished: Meaning of measured macroscopic TD variables  $P$  &  $T$  in terms of “derived” microscopic mechanical variables
- What is the second step: Warming up to looking at “energy inwards”

*Warming up to looking at “Energy inwards”!*

Raj Pala,

[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme,  
Indian Institute of Technology, Kanpur.

# *Let us get to Work with Ideal Gas!*

- $P_{\text{external}} * V = \frac{F_{\text{external}}}{L^2} * L^3 = \frac{N_A m v^2}{3L^3} * L^3 = \frac{N_A m v^2}{3} = N_A * K_B * T$
- $PV = N_{\text{AvA}} * K_{\text{Boltzmann constant}} * T = R_{\text{gas constant}} * T$
- $\frac{mv^2}{2} = 3 * \left(\frac{K_B * T}{2}\right)$  !!!-Equipartition theorem-3 DOF
- $v$ =Average velocity of an ideal gas atom; It is NOT C.O.M velocity!
- What has been accomplished: Meaning of measured macroscopic TD  $T$  in terms of microscopic mechanical variable  $v$

## *Energy of a “continuum” in classical mechanics*

- Continuum: “a **continuous** sequence in which adjacent **segments** are not **perceptibly** different from each other...”
- We are not resolving material segments into atoms/electrons...
- Energy due to the motion of the Center Of Mass: Kinetic energy
- Energy due to position of the C.O.M in a force-field: Potential Energy
- From mechanics to thermodynamics...?
- Is the “energy content” of Bumrah’s ball at 150 km/h same when he is bowling in Australian winter and Kanpur summer?
- Is the “energy content” of Cu metal block elevated to 1000 m different when it is at 50°C and 500 °C?
- In addition to K. E & P.E, how does T affect the energy content?

# *Work-Energy theorem of classical mechanics*

- The net work done on a particle equals the change in the particle's kinetic energy:  $W_{\text{net}} = K_B - K_A$
- $dW_{\text{net}} = \vec{F} \cdot \vec{dr}$
- $\vec{F} = \frac{\overrightarrow{dv}}{dt}$
- How do we extend work-energy theorem to thermodynamics?

## *Joule's Experiments (1843 to 1848)*

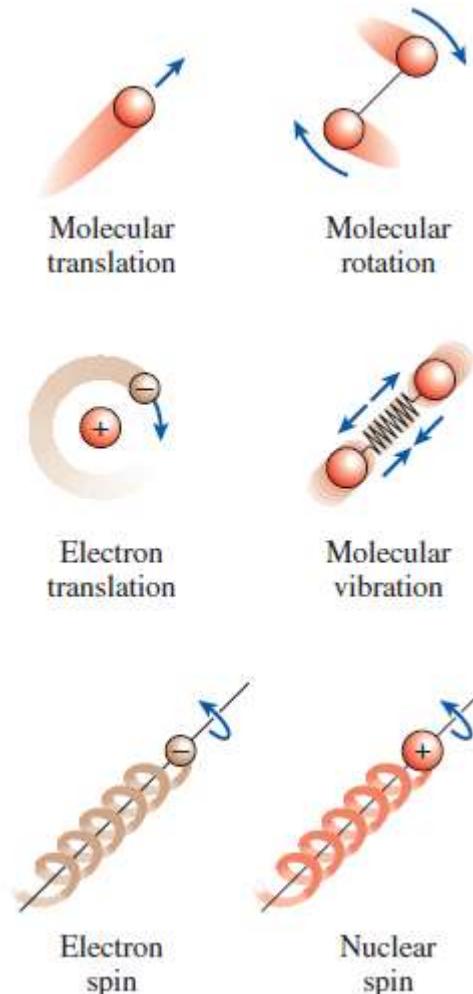
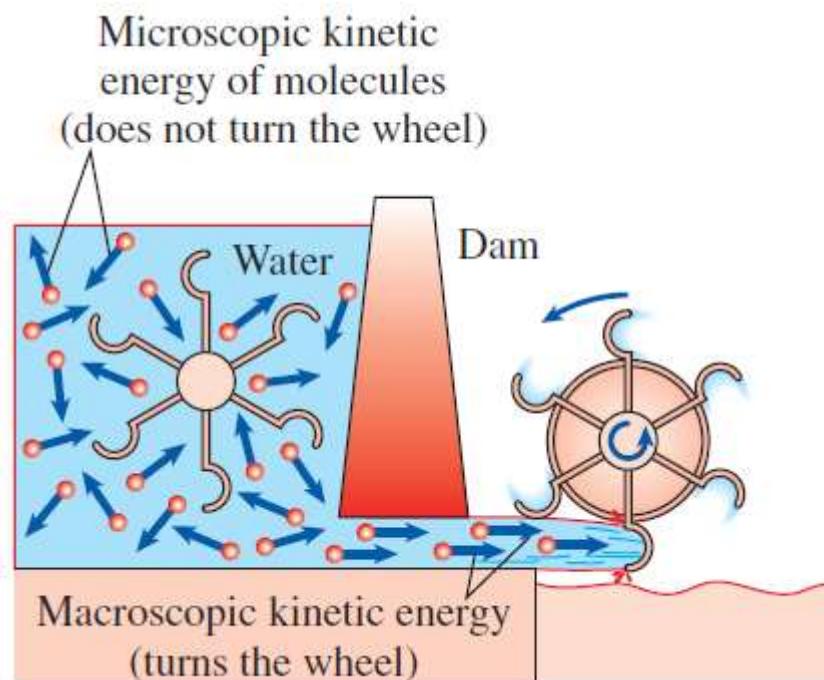
- <https://demonstrations.wolfram.com/JoulesExperiment/>
- What happens to the work done on the system contained within a adiabatically walled container whose C.O.M Kinetic & Potential Energy does not change?
- Temperature increased!
- By equipartition theorem, temperature is correlated to average velocity of atoms of the liquid in the adiabatically walled contained
- Note: Not C.O.M velocity; Atomic velocities are random and are correlated to temperature

## *Microscopic DOF provides additional ways of storing energy*

- Beyond C.O.M “directional positional change” (potential E) & “directional motion” (kinetic E), there is “internal energy” due to “random” motion atoms
- In Joule's experiment, the work done on the system within the adiabatically walled container increased the capacity of the system to store heat, with the increase corresponding to an increase in temperature
- Joule also found that similar amount of other forms of work (like electrical) also gave raise to similar increase in temperature
- All work can be converted to heat resulting in increase of temperature!<sup>6</sup>

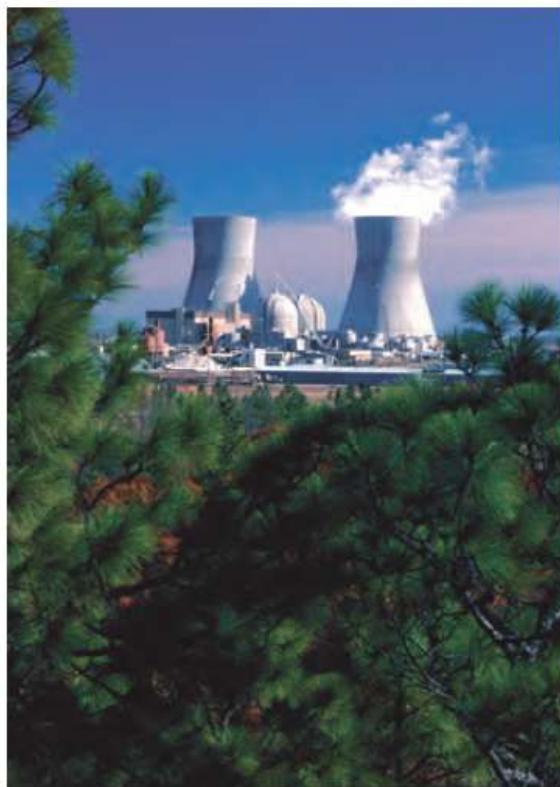
# *Relevant microscopic DOF depends on $T$*

- Excitable DOF
- Typically, engineering systems are “cold” in terms of electronic and nuclear DOF



Figs: Cengel & Boles 7

# *Multi Scale Nature of Energy*



**FIGURE 2–3**

At least six different forms of energy are encountered in bringing power from a nuclear plant to your home: nuclear, thermal, mechanical, kinetic, magnetic, and electrical.

# *Advertising First Law of Thermodynamics: Extending Work-Energy beyond mechanics*

$$\Delta U = \text{Change in Internal Energy } U = \text{"Heat & work exchange"} = "q - W"$$

# *Mechanical Energy of Flowing Fluid Elements An Introduction*

Raj Pala,  
[rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

Department of Chemical Engineering,  
Associate faculty of the Materials Science Programme,  
Indian Institute of Technology, Kanpur.

# *Internal Energy & Advertising First Law of Thermodynamics: Extending Work-Energy beyond mechanics*

$$\Delta U = \text{Change in Internal Energy } U = \text{"Heat \& work exchange"} = "q - W"$$

# *What is Mechanical “Engineering” Energy?*

- “Form of energy that can be converted to mechanical work completely and directly by an ideal mechanical device like ideal turbine”  
(Cengel & Boles: TD)
- We will book keep energy via “control mass”, “control volume”, energy flow across “control surface” but for now, we will look at energy per unit mass

# Forms of energy for flowing fluids

$$KE = m \frac{V^2}{2} \quad (\text{kJ}) \quad \text{Kinetic energy}$$

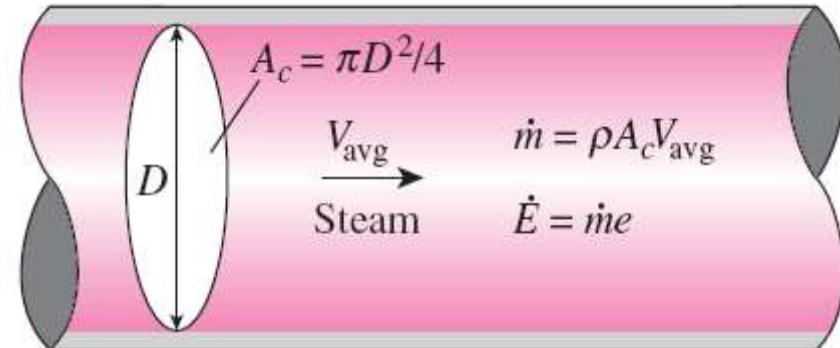
$$ke = \frac{V^2}{2} \quad (\text{kJ/kg}) \quad \text{Kinetic energy per unit mass}$$

$$PE = mgz \quad (\text{kJ}) \quad \text{Potential energy}$$

$$pe = gz \quad (\text{kJ/kg}) \quad \text{Potential energy per unit mass}$$

$$E = U + KE + PE = U + m \frac{V^2}{2} + mgz \quad (\text{kJ}) \quad \text{Total energy of a system}$$

$$e = u + ke + pe = u + \frac{V^2}{2} + gz \quad (\text{kJ/kg}) \quad \text{Energy of a system per unit mass}$$



Mass flow rate

$$\dot{m} = \rho \dot{V} = \rho A_c V_{\text{avg}} \quad (\text{kg/s})$$

Energy flow rate

$$\dot{E} = \dot{m} e \quad (\text{kJ/s or kW})$$

# *Mechanical energy of flowing fluids*

$$e_{\text{mech}} = \frac{P}{\rho} + \frac{V^2}{2} + gz$$

Mechanical energy of a flowing fluid per unit mass

$$\dot{E}_{\text{mech}} = \dot{m}e_{\text{mech}} = \dot{m}\left(\frac{P}{\rho} + \frac{V^2}{2} + gz\right)$$

Rate of mechanical energy of a flowing fluid

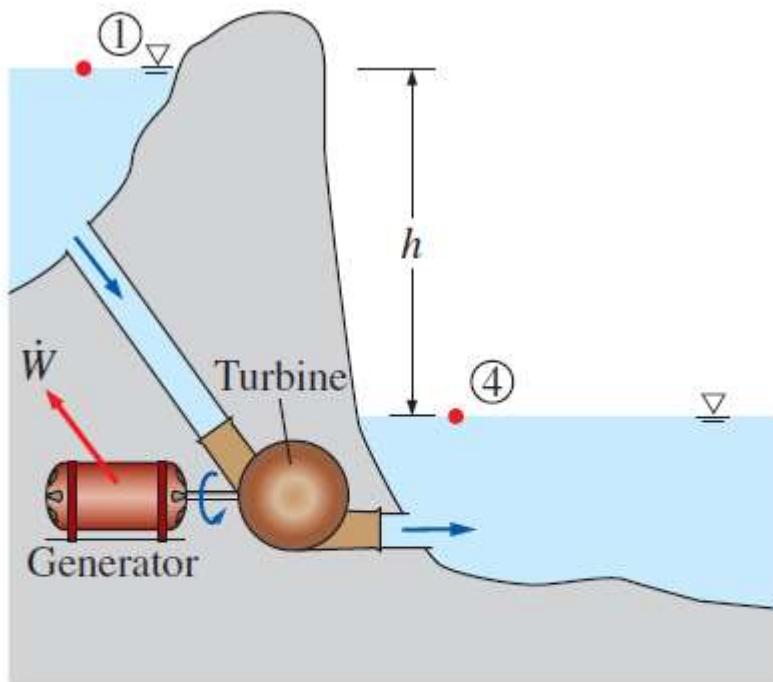
Mechanical energy change of a fluid during incompressible flow per unit mass

$$\Delta e_{\text{mech}} = \frac{P_2 - P_1}{\rho} + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1) \quad (\text{kJ/kg})$$

Rate of mechanical energy change of a fluid during incompressible flow

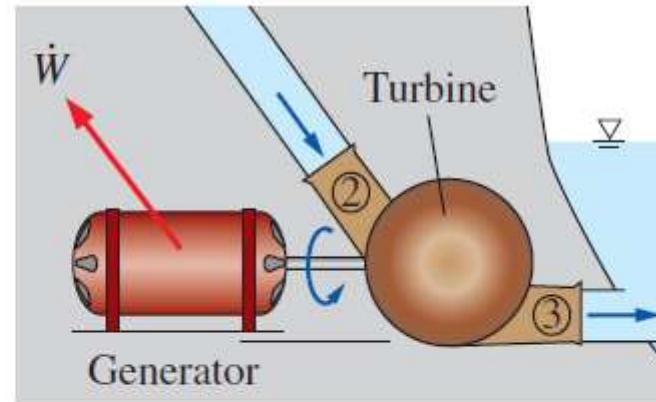
$$\Delta \dot{E}_{\text{mech}} = \dot{m}\Delta e_{\text{mech}} = \dot{m}\left(\frac{P_2 - P_1}{\rho} + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1)\right) \quad (\text{kW})$$

# Coupling mechanical energy to work



$$\dot{W}_{\max} = \dot{m} \Delta e_{\text{mech}} = \dot{m} g (z_1 - z_4) = \dot{m} g h$$

since  $P_1 \approx P_4 = P_{\text{atm}}$  and  $V_1 = V_4 \approx 0$   
 (a)



$$\dot{W}_{\max} = \dot{m} \Delta e_{\text{mech}} = \dot{m} \frac{P_2 - P_3}{\rho} = \dot{m} \frac{\Delta P}{\rho}$$

since  $V_2 \approx V_3$  and  $z_2 = z_3$   
 (b)