

## Slide 1

### Introduction

*Thermodynamics* is an engineering science topic, which deals with the science of “**motion**” (*dynamics*) and/or the transformation of “**heat**” (*thermo*) and energy into various other energy-containing forms.

**Examples**

- The transfer or motion of energy from hot gases emerging from a burner to cooler water in a hot-water heater.
- The transformation of the thermal energy, i.e., heat, contained in the hot gases in an automobile engine into mechanical energy, namely, work, at the wheels of the vehicle.
- The conversion of the chemical energy contained in fuel into thermal energy in a combustor.

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## Slide 2

**Applications**

- Understanding the nature and degree of energy transformations
- Determination of properties of substances using state equations
- Determination of stability of systems
- Determination of direction of spontaneous processes

**Limitations**

- Rates of transport processes cannot be determined using thermodynamic analysis alone

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## Slide 3

**Systems and Boundaries**

- A system is a region containing energy and/or matter that is separated from its surroundings by arbitrarily imposed walls or boundaries.
- A boundary is a closed surface surrounding a system through which energy and mass may enter or leave the system.
  - *Permeable* and process boundaries allow mass transfer to occur. Mass transfer cannot occur across *impermeable* boundaries.
  - A *diathermal* boundary allows heat transfer to occur across it. Heat transfer cannot occur across the *adiabatic* boundary.
  - A *movable/deforming* boundary is capable of performing “boundary work”. No boundary work transfer can occur across a *rigid* boundary.

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## Slide 4

- A *simple* system is a homogeneous, isotropic, and chemically inert system with no external effects, such as electromagnetic forces, gravitational fields, etc.
- *Surroundings* include everything outside the system.
- An *isolated* system is one with rigid walls that has no communication (i.e. no heat, mass, or work transfer) with its surroundings.
- A *closed* system is one in which the system mass cannot cross the boundary, but energy can, e.g., in the form of heat transfer.
- An *open* system is one in which mass can cross the system boundary in addition to energy.
- A *composite* system consists of several subsystems that have one or more internal constraints or restraints.

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## Slide 5

### ***Constraints and Restraints***

- Constraints and restraints are the barriers within a system that prevent some changes from occurring during a specified time period.
  - A *thermal* constraint can be illustrated through a closed and insulated coffee mug.
  - An example of a *mechanical* constraint is a piston-cylinder assembly containing compressed gases that is prevented from moving by a fixed pin.
  - A *permeability or mass* constraint can be exemplified by volatile naphthalene balls kept in a plastic bag.
  - The chemical constraint is an activation energy, which is the energy required by a set of reactant species to chemically react and form products. A substance which prevents the chemical reaction from occurring is a chemical restraint.

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## Slide 6

### ***Phase***

- A region within which all properties are uniform consists of a distinct phase.

### ***Examples***

- Solid ice, liquid water, and gaseous water vapor are separate phases of the same chemical species.
- Liquid mixtures that are miscible at a molecular level (such as those of alcohol and water for which molecules of one species are uniformly intermixed with those of the other)
- Air

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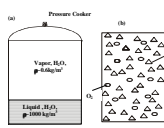
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Slide 7



(a) Pressure Cooker  
 Vapor:  $H_2O$   
 $p = 4.46 \text{ kg/cm}^2$   
 Liquid:  $H_2O$   
 $p = 4.46 \text{ kg/cm}^2$

(b)  $N_k$

- **Pure Substance**
  - A pure substance is one whose chemical composition is spatially uniform (Figure (a)).
- **Homogeneous Substance**
  - A system is homogeneous if its chemical composition and properties are macroscopically uniform. Single-phase systems containing one or more chemical components also qualify as homogeneous systems. (Figure (b)).

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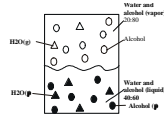
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Slide 8



Water and alcohol vapors:  
 $H_2O(g)$   
 $H_2O(l)$

Alcohol  
 Water and alcohol liquids:  
 Alcohol (l)  
 Water (l)

- **Heterogeneous Systems**
  - Heterogeneous systems may hold multiple phases with one component and multi-components in equilibrium.
  - Well-mixed single-phase systems are simple systems although they may be multicomponent, e.g., air.
  - The vapor-liquid system illustrated in the figure does not qualify as a pure substance.

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**Mixture**

- A system that consists of more than a single component (or species) is called a mixture, e.g., air.
- If  $N_k$  denotes the number of moles of the k-th species in a mixture, the mole fraction of that species  $X_k$  is given by the relation  $X_k = N_k/N$ , where  $N = \sum N_k$  is the total number of moles contained in the mixture.
- A mixture can also be described in terms of the species mass fractions  $m_k$  as  $Y_k = m_k/m$ , where  $m_k$  denotes the mass of species k and m the total mass.
- The molecular weight of a mixture M is defined as the average mass contained in a kmole of the mixture, i.e.,  $M = m/N = \sum N_k M_k / N = \sum X_k M_k$

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## Slide 10

### Properties

- A property is a characteristic of a system, which resides in or belongs to it, and it can be assigned only to systems in equilibrium.
- *Primitive* properties are those which appeal to human senses, e.g., T, P, V, and m. *Derived* properties are obtained from primitive properties, e.g., force, enthalpy, H and entropy, S.
- *Intensive* properties are independent of the extent or size of a system, e.g., P (kN m<sup>-2</sup>), v (m<sup>3</sup> kg<sup>-1</sup>), specific enthalpy h (kJ kg<sup>-1</sup>), and T (K).  
(Homogeneous function of order 0)
- *Extensive* properties depend upon system extent or size, e.g., m (kg), V (m<sup>3</sup>), total enthalpy H (kJ), and total internal energy U (kJ).  
(Homogeneous function of order 1)
- An extensive property can be converted into an intensive property provided it is distributed uniformly throughout the system by determining its value per unit mass, unit mole, or unit volume.
- An *extrinsic* quantity is independent of the nature of a substance contained in a system (such as kinetic energy, potential energy, and the strength of magnetic and electrical fields). An *intrinsic* quantity depends upon the nature of the substance (examples include the internal energy and density).

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## Slide 11

### State

- The condition of a system is its state, which is normally identified and described by the observable primitive properties of the system. The system state is specified in terms of its properties.
- **Stable State**
  - A stable equilibrium state, is associated with the lowest energy, and following perturbation, returns to its original state.
- **Unstable State**
  - A slight disturbance to either side of equilibrium will cause a system to move to a new equilibrium state.
- **Metastable State**
  - Stable to small perturbations but unstable to large perturbations.

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## Slide 12

- Mechanical equilibrium prevails if there are no changes in pressure.
- Thermal equilibrium exists if the system temperature is unchanged.
- Phase equilibrium occurs if, at a given temperature and pressure, there is no change in the mass distribution of the phases of a substance, i.e., if the physical composition of the system is unaltered.
- Chemical equilibrium exists if the chemical composition of a system does not change.
  - The species are allowed to react chemically, the restriction being that the number of moles of a species that are consumed must equal that which are produced, i.e., there is no net change in the concentration of any species
- The term *thermodynamic state* refers only to equilibrium states. The system state cannot be described for a *nonequilibrium* (NE) position, since it is transient.

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### Slide 13

- **Equation of State**
  - A thermodynamic state is characterized by macroscopic properties called state variables denoted by  $x_1, x_2, \dots, x_n$  and  $F$ , of which, in general, at least one state variable, say  $F$ , is not independent of  $x_1, x_2, \dots, x_n$ .
  - Equation of the form  $F = F(x_1, x_2, \dots, x_n)$  is referred to as a *state postulate or state equation*.
  - For an ideal gas, the functional form of this relationship is given by the ideal gas law, i.e.,  $P = NRT/V$ , where  $R$  is known as the universal gas constant, the value of which is  $8.314 \text{ kJ kmole}^{-1} \text{ K}^{-1}$ .
  - At **standard temperature and pressure (STP)**, i.e. at 1 bar pressure and  $25^\circ\text{C}$  temperature, volume of 1 mole of ideal gas is  $24.78 \text{ m}^3$

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### Slide 14

- A process occurs when a system undergoes a change of state (i.e., its properties change) with or without interaction with its surroundings. A *spontaneous* process changes the state of a system without interacting with its environment.
  - For an *isothermal* process there are no temperature changes ( $dT=0$ )
  - For an *isobaric* process the pressure is constant ( $dp=0$ )
  - Volume remains unchanged during an *isometric* process ( $dV=0$ )
  - There is no heat transfer during an *adiabatic* process
  - If the final state is identical to the initial state, then the process is *cyclical*. Otherwise, it is *noncyclical*.

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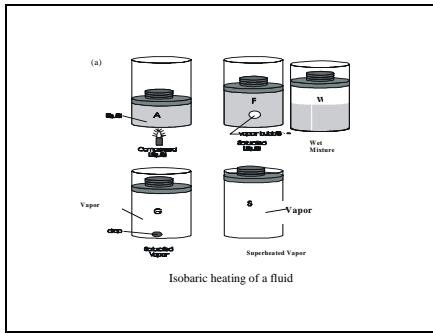
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### Slide 15



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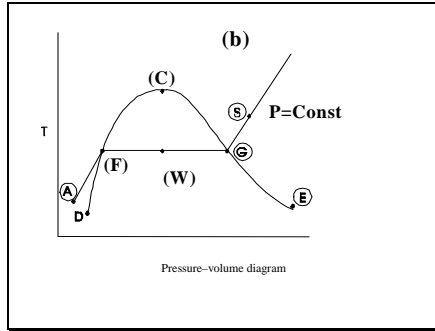
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Slide 16




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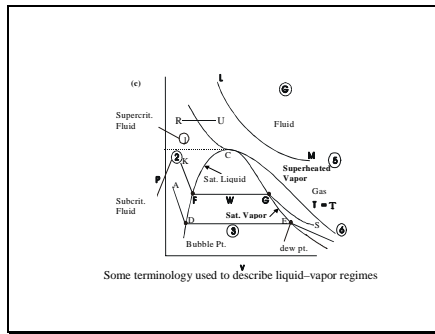
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Slide 17




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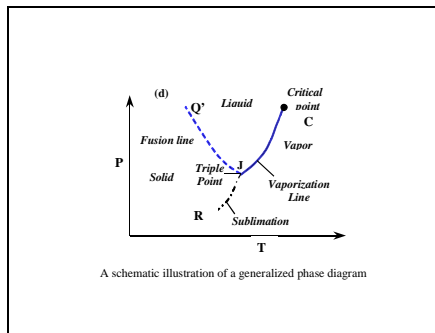
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Slide 18




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Slide 19

- **Microscopic Thermodynamics**
  - Matter**
    - All things are made of atoms – little particles that move around in perpetual motion attracting each other when they are a little distance apart, but repelling upon being squeezed into one another (*Feynman*)
    - Radius of atoms of the order of  $1 - 2 \text{ \AA}$  i.e.  $1 - 2 \times 10^{-10} \text{ m}$
    - For water molecules, separation between O and H atoms of the order of  $1 \text{ \AA}$
    - Intermolecular Force: negative, when attractive, positive, when repulsive

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Slide 20

- **Intermolecular Forces**
  - For two molecules separated by a given distance, **stored potential energy and intermolecular force** are correlated (Analogous to gravitational potential and gravitational force between a pair of bodies)
  - For like molecular pairs (e.g.:  $\text{O}_2 - \text{O}_2$ ), **intermolecular force** given by **Lennard-Jones** empirical approach as
$$\Phi(r) = 4\epsilon \left( \left( \frac{r_0}{r} \right)^{12} - \left( \frac{r_0}{r} \right)^6 \right)$$
    - $\epsilon$ : characteristic interaction energy between molecules, i.e., the maximum attraction energy or minimum potential energy  $\Phi_{\text{min}}$  ( $\epsilon = \Phi_{\text{min}} = 0.77 k_B T_c$ , with  $k_B$ : Boltzmann constant;  $T_c$ : critical temperature)
    - $r_0$ : distance at which the potential is zero (approximately equal to the characteristic or collision diameter  $\sigma$ )

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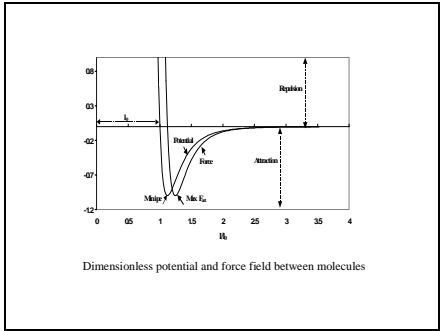
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Slide 21



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Slide 22

**Internal Energy and Temperature**

- The interactions of a molecule with its neighbors strongest at conditions corresponding to the minimum potential energy
- In solid state, most of the energy is in **vibration** mode
- In gaseous state, molecular distribution and motion is chaotic
- Polyatomic molecule containing 8 atoms has 38 degrees of freedom.
- Number of translation modes = 3
- Number of rotation modes = 2 (linear molecules); 3 (non-linear)
- Number of vibration modes = 38 - 5 (linear); 38 - 6 (non-linear)
- **Internal Energy = Translational + Rotational + Vibrational Energy**

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Slide 23

**Collision Number and Mean Free Path**

- Average distance traveled by the molecule during this time is called its mean free path  $l_{mean}$
- $l_{mean} = V_{avg} / (n \pi \sigma^2 V_{avg}) = 1 / (n \pi \sigma^2)$
- $\sigma$ : Collision Diameter (Closest distance between two molecules)
- $V_{avg}$ : Average Molecular Velocity
- The typical velocity distributions can be determined from the expression
- $(1/N) dN_v/dV = 4\pi^{-1/2} (m/2k_b T)^{3/2} v^2 \exp(-1/2 m v^2 / (k_b T))$
- $n$ : Number of molecules per unit volume
- Typical number of collisions  $\sim 10^{10} m^{-3} s^{-1}$

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Slide 24

**Collision Number and Mean Free Path**

- Alternative expression for velocity distribution
- In terms of K.E.:
- $N_v/N = 2\pi^{-1/2} (E/T)^{1/2} \exp(-E/R(T)) + (1 - \text{erf}((E/R(T))^{1/2}))$
- In terms of velocity:
- $N_v/N = 2\pi^{-1/2} (E/R(T))^{-1/2} \exp(-E/R(T))$
- Average molecular velocity:  $V_{avg} = 2\pi^{-1/2} V_{rms}$
- Most probable molecular velocity:  $V_{mps} = (2k_b T/m)^{1/2} = (2RT/M)^{1/2}$
- RMS molecular velocity:  $V_{rms} = (3k_b T/m)^{1/2} = (3RT/M)^{1/2}$
- $V_{rms}^2 = V_x^2 + V_y^2 + V_z^2$

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Slide 25

- **Pressure**
  - The pressure that we experience is due to a continuum of matter that strikes us incessantly
  - In the case of gases, large numbers of molecules travel at high speeds at standard conditions and impinge on surfaces, thereby creating pressure
  - The pressure in a container can be altered by changing the molecular velocity (hence, temperature), the number of molecules per unit volume ( $n$ ), or the number of moles per unit volume ( $n$ )

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Slide 26

- **Ideal Gas**
  - Molecules of mass  $m$ , velocity  $v$  impinging on a surface of area  $l^2$
  - Time interval between two successive molecular collisions =  $1/V_x$
  - Molecule imparted by each collision =  $mV_x$
  - Using  $V_x^2 = (1/3)V^2$ , **pressure**=force per unit area =  $mV^2/3l^3$
  - Using number of molecules per unit volume,  $n'=N/V$ ,  
$$P = n' m V^2 / 3 = 2N (TE) / 3V = (2/3)(3/2)N' k_B T / V = NRT / V$$

*(Ideal Gas Law)*

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Slide 27

- **Real Gas**
  - Intermolecular forces important, i.e.,  $P = P_0 - \Delta P_{attr}$
  - $\Delta P_{attr}$  proportional to the attractive force between experienced by each molecule within  $n'$  and all the interior molecules per unit volume ( $n'$ )
  - $\Delta P_{attr} \propto n'^2 \propto 1/v^2 \propto a/v^2$
  - $P = RT/v - a/v^2$
  - Ideal gas assumption is valid if  $v/\sqrt{a} \gg 0.9/T_k^2$

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## Slide 28

- **Work**
  - Gas molecules within a piston-cylinder assembly exert a force on piston wall
  - This unbalanced force causes piston displacement, till the force is balanced by a constraining force
  - For a volume change  $dV$ , work done =  $PdV$
  - Process is mechanically reversible
  - **Work transfer is a result of organized molecular motion in the direction of piston displacement**

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## Slide 29

- **Heat**
  - Heat (energy) transfer occurs due to temperature gradient
  - Heat transfer takes place due to transfer of energy from higher energy molecules to lower energy ones by impingement
  - **Heat transfer causes the random motion of molecules to increase in all directions**

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## Slide 30

- **Chemical Potential**
  - Chemical potential drives mass (or species) transfer in a manner similar to the thermal potential that drives heat transfer from higher to lower temperatures
  - For two chambers containing multiple species in different concentrations, random molecular motion implies that equal number of molecules are transported from each chamber
  - Different concentrations of a particular species causes net transfer of the species from higher to lower concentration (**diffusion**)
  - A higher species mole fraction implies a higher chemical potential for that species
  - Species transfer ceases when concentration (chemical potential) difference ceases

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## Slide 31

- **Phase Equilibrium**
  - If the water is heated, its molecular energy and intermolecular distances increase
  - Rotating molecules near the water surface attain sufficient rotational energy to overcome the attractive forces, and move (or escape) into the space occupied by air and/or water vapor (**Evaporation**)
  - Water vapor molecules can approach the liquid surface and be pulled (or captured) into the liquid phase by the strong attractive forces exerted by the liquid molecules (**Condensation**)
  - At saturation pressure (function of temperature) the two rates are equal

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## Slide 32

- **Entropy**
  - The energy of random molecular motion is indicated by temperature
  - Random motion which occur in all directions and in all velocities cannot be converted into work directly
  - Entropy is a measure of the number of "random" states in which molecules store energy
  - Assuming all of these states to be equally probable, the entropy  $S$  is defined as a quantity proportional to the logarithm of the number of macro states  $\Omega$ , in which energy is stored i.e.,  $S \propto \ln\Omega$

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## Slide 33

- **Entropy**
  - The larger the volume for a set number of molecules, the greater the number of quantum states within which energy storage is possible
  - Hence, for a given energy content, as volume decreases, entropy decreases
  - Total number of states do not change even though energy level for each group has increased due to work input
  - During heat transfer, molecules can be placed in higher energy states and hence number of states increase
  - **It is the energy gain due to heat transfer, which results in entropy increase.**
  - Mixing causes an increase in number of energy states and hence, entropy

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## Slide 34

- **Mathematical Prerequisites for Subsequent Chapters**

- Exact (Perfect) and Inexact (Imperfect) Differentials
- Homogeneous Functions
- Taylor Series
- LaGrange Multipliers
- Composite Function
- Stokes and Gauss Theorems
- Leibnitz Formula

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