L E C T U R E

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CY11001
Spring 2018

- Basic Concepts and Definitions
- 0th and 1st Laws of Thermodynamics

Lecture Slides @

http://10.57.2.100/moodle/login/index.php

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Thermodynamic Properties:

Intensive properties (do not depend on the size of the system, density, pressure)

Extensive properties (they do. Ex: mass, volume)

If each intensive property is constant throughout the system,

Homogeneous system

Heterogeneous system

a homogeneous part of a system is called a phase

How do we define a system? State of a System

Macroscopic state of a system can be specified by the values of a small number of macroscopic Properties/Parameters/Physical characteristics or attributes of a system - **Thermodynamic variables**

Thermodynamic variables which are <u>**experimentally measurable**</u>

- Composition – mass of each chemical species that is present in each phase,

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

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

- gravitational field

If the value of every thermodynamic property in system A is same as in system B – same thermodynamic state

Microscopic state of a system needs description about each molecules – a very complicated picture

Zeroth Law of Thermodynamics – Temperature

(Flower, 1931)

Temperature is a property associated with **random motion of many particles**.

Introduction of the concept of temperature in thermodynamics is based on the **the zeroth law of thermodynamics:**

A well-defined quantity called **temperature** exists such that two systems will be in thermal equilibrium if and only if both have the same temperature.
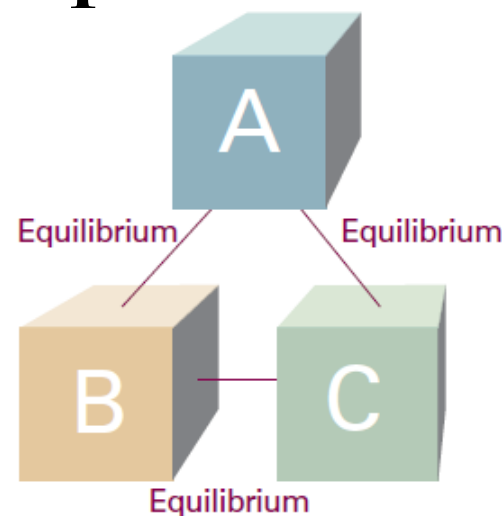
Fig. 1.3 The experience summarized by the Zeroth Law of thermodynamics is that, if an object A is in thermal equilibrium with B and B is in thermal equilibrium with C, then C is in thermal equilibrium with A.

Application of Zeroth Law of Thermodynamics: Thermometer

Thermodynamic Processes:

When one or more of the thermodynamic properties of a system changes, the state of the system also changes and system is undergoing a process

Isothermal (constant T),

Isobaric (constant p),

Isochoric (constant V)

Adiabatic

Exothermic & Endothermic

Cyclic

Reversible & Irreversible

Reversible process:

- *Ideal*
- Change must occur in *successive stages of infinitesimal quantities*
- *Infinite duration*
- *Virtual thermodynamic equilibrium,* at each of the small stages.
- Backward changes of the thermodynamic quantities in different stages will be the *same as in the forward direction but opposite in sign with respect to the forward direction*

Irreversible Process:

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

The Equation of State

An equation that relates macroscopic variables (e.g., *p, V,* and *T*) for a given substance *in thermodynamic equilibrium.*

$$p = f\,(V,T,n)$$

•Equation of state is not a theoretical deduction *from* thermodynamics, rather an experimental addition *to* it. An equation of state is as accurate as the experiments that led to its formulation. It holds *only* within the range of measurement.
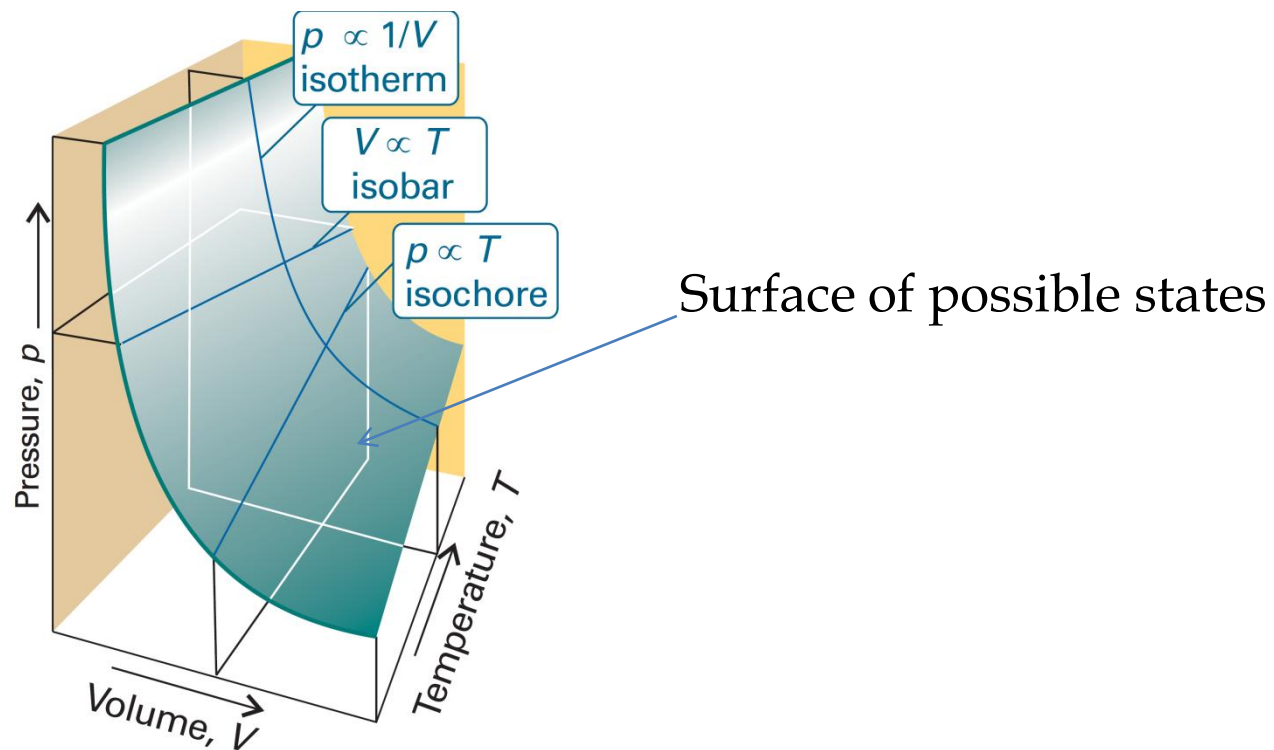
perfect/ideal gas equation, $pV = nRT.$

perfect/ideal gas, a gas that obeys $pV = nRT$ exactly under all conditions.

gas constant, R (with $R = N_A k$, where N_A is Avogadro's constant and k is Boltzmann's constant).

Table 1.2	The gas constant
R	
8.314 47	$J\,K^{-1}\,mol^{-1}$
$8.205\ 74 \times 10^{-2}$	$dm^3\,atm\,K^{-1}\,mol^{-1}$
$8.314\ 47 \times 10^{-2}$	$dm^3\,bar\,K^{-1}\,mol^{-1}$
8.314 47	$Pa\,m^3\,K^{-1}\,mol^{-1}$
1 62.364	$dm^3\,Torr\,K^{-1}\,mol^{-1}$
1.987 21	$cal\,K^{-1}\,mol^{-1}$

The Equation of State (Ideal Gas)

$p \propto 1/V$
isotherm

$V \propto T$
isobar

$p \propto T$
isochore

Pressure, p

Volume, V

Temperature, T

Surface of possible states

Selected Equations of State …

	Equation
Perfect gas	$p = \dfrac{RT}{V_m}$
van der Waals	$p = \dfrac{RT}{V_m - b} - \dfrac{a}{V_m^2}$
Berthelot	$p = \dfrac{RT}{V_m - b} - \dfrac{a}{TV_m^2}$
Dieterici	$p = \dfrac{RTe^{-a/RTV_m}}{V_m - b}$
Virial	$p = \dfrac{RT}{V_m}\left\{1 + \dfrac{B(T)}{V_m} + \dfrac{C(T)}{V_m^2} + \cdots\right\}$

The First Law of Thermodynamics:

- There exists an extensive state function E such that for any closed system, $\Delta E = q + w$

- In absence of any external field acting on the system and the system at rest, $\Delta E = \Delta U$ $\quad (K = V = 0)$

$$\boxed{\Delta U = q + w}$$

$$dU = \bar{d}q + \bar{d}w = \delta q + \delta w = dq + dw$$

- w, work done **on the system** by the surroundings

- q, heat **absorbed by the system** from the surroundings

- The conventions for the signs of q and w are set from the system's perspective

1st Law for Special Cases

- For isolated system, $\quad dU = 0; \qquad q = -w$
- For adiabatic process, $\quad q = 0; \qquad dU = w$
- For cyclic process, $\qquad \oint dU = 0; \qquad q = -w$