

Basic Concepts of Thermodynamics

change of state – a change in any of the macroscopic thermodynamic properties

E, *V*, *N*, *T*, *P*, or μ ; a change to a different set of equilibrium conditions

path - a progression in changes in the state of a system (e.g., changes in variables like *E*, *V*, *N*, *T*, *P*, and μ) that describes the process of moving from one equilibrium state to another

adiabatic process – a process in which there is no heat transfer between the system and its surroundings

isothermal process – a process that occurs at constant temperature T

isochoric process – a process that occurs at constant volume V

isobaric process – a process that occurs at constant pressure P

<u>T156</u> isentropic process – a process in which the entropy S is constant

	Boundary or reservoir	Process		
	Closed	Constant mass		
	Thermally insulated	Adiabatic		
	Rigid	Constant volume (isometric)		
	Closed and rigid	Constant density (isochoric)		
	Closed, rigid, insulated	Constant energy		
	Heat reservoir	Constant temperature (isothermal)	(41)	
<u>T1726</u>	Mechanical reservoir	Constant pressure (isobaric)		
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Thermodynamic Equilibrium

A system in Thermodynamic Equilibrium satisfies the stringent requirements:

- Mechanical Equilibrium: no unbalance forces acting on any part of the system or the system as a whole.
- Thermal Equilibrium: no temperature differences between parts of the system or between the system and the surrounding.
- Chemical Equilibrium: no chemical reactions within the system and no motion of any chemical species from one part to another part of the system.

	The conditions for equilibrium between two single-component systems are						
	(1) $T_1 = T_2$	ther	mal equilibrium				
	(2) $P_1 = P_2$ (3) $\mu_1 = \mu_2$	mec cher	hanical equilibrium nical equilibrium		4		
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Basic Concepts of Thermodynamics

State & Property

- The description of the condition of a system at a given instant is called its **State**.
- A **Property** is a quantity whose numerical value depends on the state but not on the history of the system. The origin of properties include those
 - directly measurable
 - e defined by laws of thermodynamics
 - (3) defined by mathematical combinations of other properties.
- Two states are identical if, and only if, the properties of the two states are identical.
- Intensive properties are independent of the size or extent of the system. Extensive properties depend on the size or extent of the system. An extensive property is additive in the sense that its value for the whole system is the sum of the values for its parts.



Basic C	oncepts of Thermodynamic	s			
System bound	dary				
$E_1, \tilde{V}_1, T, \tilde{I}$	$\begin{array}{c} E_{system} = \\ \tilde{V}_{system} = \end{array}$	$e_{m} = E_{1} + E_{2}$ $e_{m} = \tilde{V}_{1} + \tilde{V}_{2}$ Extensive Properties			
$E_2, \tilde{V}_2, T, .$	$P \qquad T_{system} = P \\ P_{system} = P$	$T_1 = T_2$ $P_1 = P_2$	} Intens	ive Propertie	es
	Property	Extensive	Intensive		
	Mass	т	ρ		
	Volume	Ñ	V		
	KE	$\frac{1}{2}mV^2$	$\frac{1}{2}V^{2}$		
	PE	mgZ	gΖ		
	Total Energy	Е	е		
	Internal Energy	U	и		
	Enthalpy	Н	h		
	Entropy	S	5		
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Basic Concepts of Thermodynamics

- A system is in stable/equilibrium State when no finite change of state can occur unless there is an interaction between the system and its environment which leaves a finite alteration in environmental state.
- During a Quasi-static Process, system is at all times infinitesimally near a state of thermodynamic equilibrium; hence, the process should be carried out infinitely slowly to allow the system to settle to a stable state at the end of each infinitesimal step.
- Theoretical calculations must relate to Stable states, since it is only for these we have thermodynamic data.



Basic Concepts of Thermodynamics

Categories of Thermodynamics Quantities

- **9** State functions: all properties are state functions.
- Process or Path functions: quantities whose values depend on the path of the process.



Work & Heat Transfer

Thermodynamic Work & Heat

Work

is performed by a system on its surroundings during a process if the only effect external to the system could be the raising of a weight.

Heat

is energy in transition from one body or system to another solely because of a temperature difference between the systems.

- The magnitudes of heat and work depend on the arbitrary selection of boundaries between interacting systems. These are not properties, and it is improper to speak of heat or work 'contained' in a system.
- Heat and work transfers are the only mechanisms by which energy can be transferred across the boundary of a closed system.

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at the boundary of the system, and both represent energy crossing the boundary.

ME 6101 (2024)

12/25

• Both heat and work are path functions and inexact differentials.

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Energy Transfer as Heat

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Work & Heat Transfer Thermodynamic Work

General Work Expressions

• Thermodynamic work is generalized to include all forms of work, and a generalized force F_k and generalized displacement $d\delta_k$ can be identified:

$$W_k = \int F_k d\delta_k$$

• A general system could have many possible work modes, so a general work expression is:

$$W = W_s + W_b + W_f + \dots = \sum W_k$$

- $W_s \equiv$ shaft work: rotary useful work
- \blacktriangleright $W_b \equiv$ boundary work: due to expansion/compression of system
- $W_f \equiv$ flow work: interaction required for the mass to cross CS
- $W_l \equiv$ electrical work

. . .

macroscopic representation Energy transfer as heat refers to that energy transfer, across a system boundary, associated with microscopic displacements that are not observable macroscopically. Heat transfer results in microscopic vibrations of the wall atoms, but not in macroscopically observable motion, so we

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15 / 25

cannot compute it as a force times an observable displacement.

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ME 6101 (2024) 16/25









20 / 25

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