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Chemical Engineering Thermodynamics

- Chemical Engineering + Thermodynamics
 Chemical L Engineering Thermodynamics
 - Chemical + Engineering Thermodynamics
 - Engineering + Chemical Thermodynamics

- Principles of Chemical Engineering
 + Principles of Thermodynamics
- Text Book:
 - "Chemical, Biochemical, and Engineering Thermodynamics", S.I. Sandler (5th. ed., Wiley, 2017)



Course Outline – Table of Content

- 1. Introduction.
- 2. Conservation of **Mass**.
- 3. Conservation of **Energy**.
- 4. Entropy: An Additional Balance Equation.
- 5. Liquefaction, **Power Cycles**, and Explosions.
- 6. The **Thermodynamic Properties** of Real Substances.
- 7. Equilibrium and Stability in One-Component Systems.
- 1. The Thermodynamics of **Multicomponent Mixtures**.
- 2. The Estimation of the **Gibbs Free Energy and Fugacity** of a Component in a Mixture.
- 1. Vapor-liquid Equilibrium in Mixtures.
- 2. Other types of Phase Equilibria in Fluid Mixtures.
- 3. Mixture Phase Equilibria Involving Solids.
- 4. Chemical Equilibrium.
- 5. The Balance Equations for Chemical Reactors and Electrochemistry.
- 6. Some Biochemical Applications of Thermodynamics.

Fundamental principles, Onecomponent

Multicomponent (mixture)





- Midterm Exam #1 20
- Midterm Exam #2 30
- Final Exam 35

15

• Quiz

Ch.1 Thermodynamics: What Is It?



2. Thermodynamic Systems

3. Principles of Chemical Engineering

4. Units and Dimensions



- Thermodynamics is the study of the changes in the state or condition of a substance when changes in its temperature, state of aggregation, or internal energy are important.
- Thermodynamics is the science of energy. A sound understanding of thermodynamics will allow you to determine how energy is controlled and converted in devises.



- The primary objective is to establish a criterion for determining the feasibility of a spontaneity of a given physical or chemical transformation.
- Once the spontaneous direction of a natural process is determined, we may wish to know how far the process will proceed before reaching equilibrium.
- Thermodynamic methods and concepts provide a powerful approach to the understanding of such problems.

--- Klotz, Rosenburg // p.4



- Scope of classical thermodynamics (A science related to heat in motion)
 - calculate the heat and work associated with processes (1st law)
 - determine the maximum work available from a process or the minimum work required to drive a process (1st law and 2nd law)
 - calculate equilibrium states for systems involving multiple phases and chemical reactions
 - measure, estimate, and correlate the thermodynamic properties

---- Kyle // p.1



- Thermodynamics was then developed to study energy... The first law deals with energy interchanges. *How efficiently can energy be converted from one form to another?* Carnot answered this question, leading to the second law of thermodynamics ...
- When the first and the second laws are combined they lead to relations that tell how much work is available in a given situation, a concept called *availability*, or *exergy*.

--- Levenspiel // p.2



The central problems of thermodynamics

- experimental observations -> principles of thermodynamics
 Jused to study physical and chemical phenomena
- ◆ state 1 (T₁, P₁, H₁, V₁, U₁, ...) → state 2 (T₂, P₂, H₂, V₂, U₂, ...) $\Delta M (\Delta H, \Delta V, \Delta U,)$

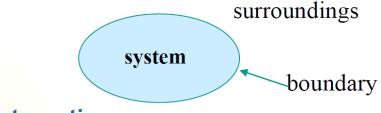
M: macroscopic properties ← average change of the system, not for the detailed changes of individual molecules Temperature : molecular motion Density: How closely the molecules are packed ← intermolecular interactions

 total energy: internal energy (U)-- relative motion of the atoms (electronic, nuclear, vibrational, and rotational contributions)
 external energy- translational contribution (position and motion of the centers of mass of the molecules)



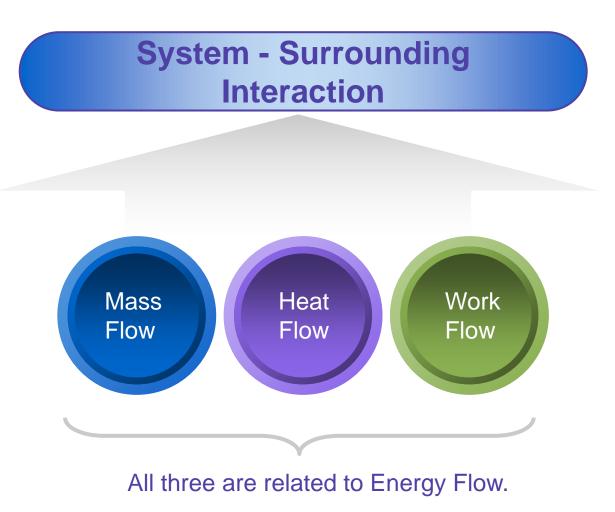
Interactions and Systems in thermodynamics

Systems, Surroundings, and Boundary



- Interactions
 - Mechanical contact P change
 - ★ Thermal contact T change
- Systems:
 - Isolated: mass flow (no), energy flow (no)
 - Closed: mass flow (no), energy flow (yes)
 - ★ Open: mass flow (yes), energy flow (yes)
 - Adiabatic: mechanical contact (maybe yes), thermal contact (no)
- State: Τ, Ρ, ρ, x,...
- Phase: The state of agglomeration of the system (G, L, S)
- Constraints: e.g., constant V, P, T, …



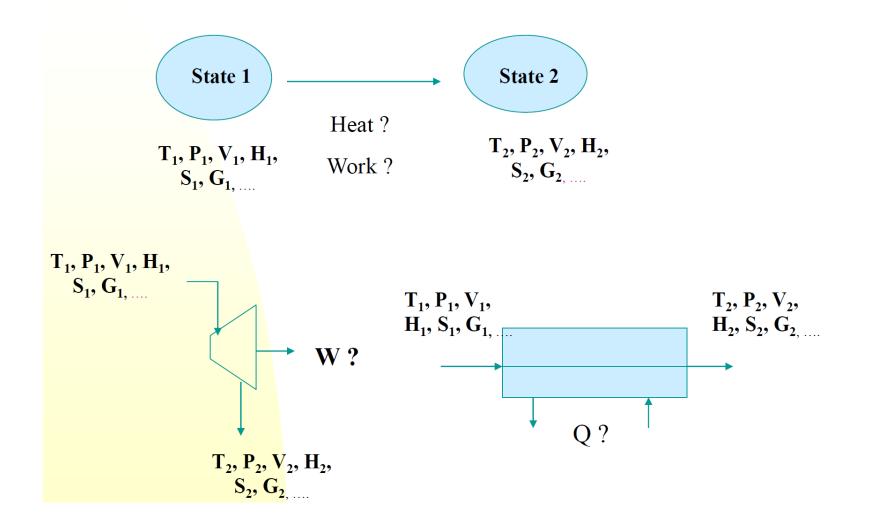


How can we describe the energy associated with matters?

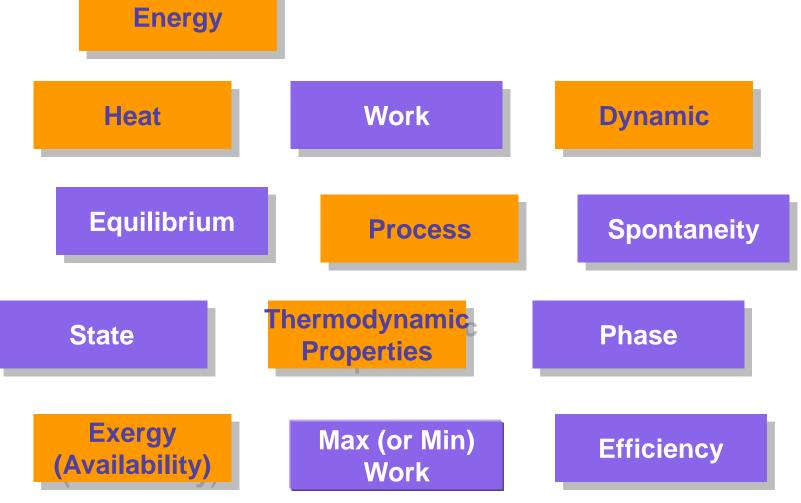


The problems that we are interested in

Energy flow problems









The problems that we are interested in

- Equilibrium problems
 - ♦ Identify or predict → new equilibrium state (physical and chemical equilibria)
 P, V, T, x_i, ... for each phase
 - ♦ pure 1 + pure 2 → mixture at equilibrium state

a single liquid mixture ? or two-liquid-phase mixture ?

Thermodynamics → How far the system to be changed ?
 Kinetics, heat and mass transfer → How fast the system to be changed?



• State of a system

e.g., density, T, P, etc.

- Determined by the state of matters constituting the system.
- Gas / liquid / solid state or the coexistence of more than one phases.
- Single component / multi-components.
- Equilibrium / nonequilibrium.
- Process
 - A system changes its state from one to another state.
 - Initial state / path / final state.
 - Reversible / irreversible processes.



- Equilibrium state (of a system):
 - The state does not change with time (time-invariant).
 - The system is uniform.
 - No flow of mass, heat, or work.
 - Net rate of chemical reactions is zero.
 - An undisturbed system will approach an equilibrium state.
- Steady state (of a nonisolated system)
 - Time-invariant state.
 - Contain both inflow and outflow of mass or energy.



- Stable equilibrium state (of a system):
 - The system will return to the same equilibrium state after small disturbance.

 A stable equilibrium state will never spontaneously evolve to a state of nonequilibrium.

(a)

(b)

(c)

• The direction of natural processes : systems evolve toward an equilibrium state, not away from it.



Equilibrium state

Characteristics of the equilibrium state

- Time-invariant
- Uniform
- All flows (of mass, heat, or work) = 0
 - (system ←→surroundings)
- Net rate of chemical reaction = 0
- Equilibrium state Steady state

X ←

- At equilibrium, driving forces = 0

 - Flux of momentum velocity gradient
- Natural flows (spontaneous flows): arise naturally → to equilibrium
- Forced flows: imposed on the system by its surroundings



- The state of a system:
 - Determined by properties of matters within a system, e.g., T, P, composition, density, etc.
 - Can be specified by specifying two independent properties and masses and composition of matters of the system.
 - Some properties are interrelated, e.g., T, P, mass, and V.
 - The equation that correlates T, P, M, V is called *the equation* of state (EOS).
 - The ideal gas law (an EOS) was identified while studying low-density gases.
 - An universal temperature scale, the absolute temperature scale, was defined.



Properties of Matters

- Classification of properties of matters:
 - Intensive / Extensive properties, massdependent or not.
 - Intensive properties: T, P, density, molar volume, refractive index, etc.
 - Extensive properties: mass, volume, etc.
 - Primitive / Derived Properties, directly measurable or not.
 - Primitive properties: color, T, P, etc.
 - Derived Properties:

NOTE: Intensive / Extensive properties, Primitive / Derived Properties



 Properties that are directly observable are called *primitive properties*, e.g., T, P, mass, volume, color, index of refraction, etc.

• Any combination of primitive properties is also a property. Such properties that are indirectly observable are called *derived properties*, e.g., internal energy, heat, etc.



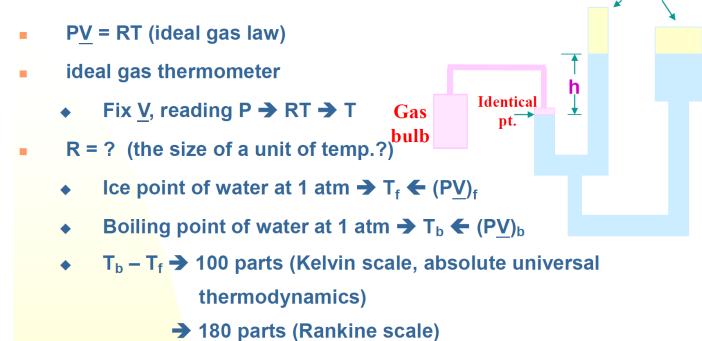
Pressure, temperature and equilibrium

- Pressure: P = F/A
 - ♦ At mechanical equilibrium → no pressure difference
 - Gauge pressure: measured by a pressure gauge
 - Absolute pressure = gauge pressure + atmospheric pressure
- Temperature: a measure of hotness
 - ◆ At thermal equilibrium → no temperature difference
 - Temperature scale:
 - ★ Ideal gas temperature scale
 - <mark>★ Experi</mark>mental results → P<u>V</u> = A + Rτ
 - ★ Let T = τ + A/R \rightarrow PV = RT (ideal gas law)
 - ★ Since P, $\underline{V} > 0 \rightarrow T$ is an absolute scale (≥ 0)
 - **R = ?** (the size of a unit of temperature ?)



Temperature

Scale of temperature



Open to the air

 $(\underline{PV})_{b} - (\underline{PV})_{f} = R (T_{b} - T_{f})$

 $R = [(PV)_b - (PV)_f]/100 = 8.314 J/mol K$

R = [(PV)_b - (PV)_f]/180 = 84.619 J/mol °R

 $T (K) = T (^{\circ}C) + 273.15$ $T(R) = T (^{\circ}F) + 459.67$



Properties of Matters

- Properties whose quantity is proportional to the amount (mass) of matter are called *extrinsic properties*, e.g., volume, gravity force, energy, etc.
- Properties whose quantity is independent of the amount (mass) of matter are called *intrinsic properties*, e.g., density, T, P, color, etc.
 - c.f.: Intensive / Extensive properties Intrinsic / Extrinsic properties

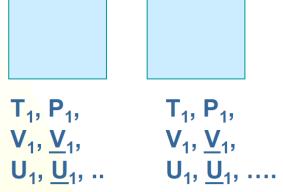


Properties of Matters

- Extrinsic properties divided by the amount of matter become intrinsic properties, e.g.,
 - Molecular weight = mass/mole
 - Density = mass/volume
 - Specific volume = volume/mass
 - Molar volume = volume/mole
 - Energy per unit mass (or per unit mole), e.g., H in steam table

Extensive and intensive properties

 1 kg O_2 1 kg O_2



$$U_2 = 2 U_1 \qquad \Leftrightarrow \qquad \\ V_2 = 2 V_1 \qquad \Leftrightarrow \qquad \\$$

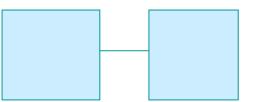
$$T_2 = T_1$$

$$P_{2} = P_{1}$$

$$V_{2} = V_{1}$$

$$U_{2} = U_{1}$$

2 kg O₂

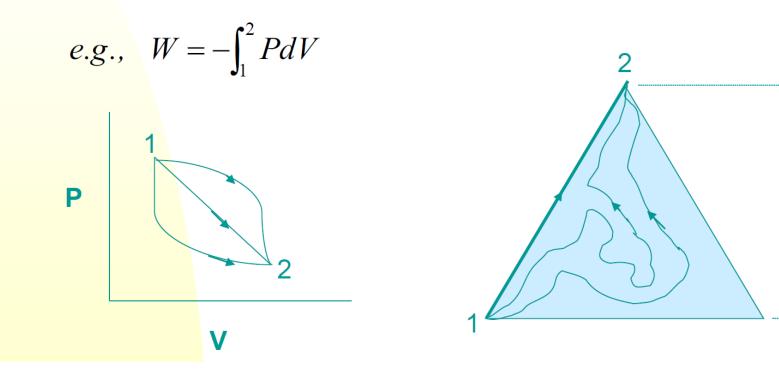


 $\begin{array}{l} \mathsf{T}_2, \, \mathsf{P}_2, \\ \mathsf{V}_2, \, \underline{\mathsf{V}}_2, \\ \mathsf{U}_2, \, \underline{\mathsf{U}}_2, \, \ldots \end{array}$

- size-dependent properties
- extensive properties
- size-independent properties
- intensive properties
- state function, independent of the path or history -> state variables



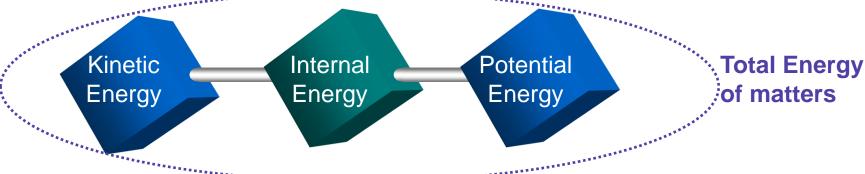
- State variables: the values are independent of the path of change (e.g., intensive property) $\Delta U = U_2 - U_1$
- Path variables: the values are dependent on the path of change





• Properties of matters:

- Energy content of matters:



 Other properties having the same unit as energy

• Enthalpy, Free energy, etc.

NOTE: Heat and Work are energies exchanged between a system and its surrounding, not properties associated with matters.



Properties of Matters

- Energy:
 - Is associated with matters.
 - Has different forms.
 - Can be transferred from one system (matters) to another.
 Q: what can be the driving force for energy transfer?
- For example, internal energy (U) of a singlecomponent, single-phase system
 - $U = \hat{U} \cdot m$
 - $\hat{U} = \hat{U}(T, \hat{V})$
 - Since $P = P(T, \hat{V})$ (EOS)

internal energy can be expressed as $\hat{U} = \hat{U}(T, P)$

or
$$\hat{U} = \hat{U}(P, \hat{V})$$

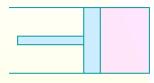


Specifications of the equilibrium state

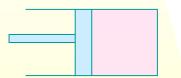
- How to specify a stable equilibrium state ?
- Reproduce the state:
 - ♦ Specify the minimum number of variables →

Fix the values of all its remaining properties completely

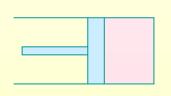
Experiments:



• 1 kg O_2 at T_1 , P_1 , V_1 , U_1 , (refraction index),



1 kg O₂ at T₁ → P₁, V₁, U₁, (refraction index)₁, ?
 <no>



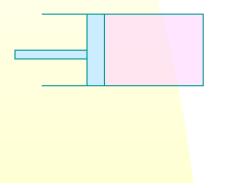
1 kg O₂ at T₁, P₁ → V₁, U₁, (refraction index)₁, ... ?
 <yes>



- For a single-phase, one component system, it is completely specified if two state properties and its mass or an extensive property are given.
- Phase rule: F = 2 + C P

= 2 + 1 - 1 = 2

- Specify other state variables
- Fix the size of the system
- Fix all extensive properties



- 2 kg O₂ at T₁, P₁
- reproduce other intensive properties, V₁, U₁, (refraction index)₁,

$$V_2 = 2 V_1$$



- For each substance, there exists equations relating each state variable to two others.
 - e.g., $P = f(T, V) \leftarrow Volumetric EOS$ $U = f(T, V) \leftarrow Thermal EOS$
- Special cases:
 - Ideal gas: <u>U</u> = f (T) → if fixed T and <u>U</u> →

P = ? (avoid fix T & <u>U</u> for gas)

◆ Solid or impressible fluid: <u>V</u> = f (T) → if fixed T and <u>V</u> →

P = ? (avoid fix T & V for solid)

- - ◆ "Local equilibrium" → non-equilibrium with not very fast system changes



Experiments

 Table 1.5-1 Experiments Designed to Prove the Energy Equivalence of Heat and Work

Form in Which Energy Is Transferred to Water	Mechanism Used	Form of Energy Supplied to Mechanism	Method of Measuring Energy Input	Corrections That Must Be Made to Energy Input Data
(1) Mechanical energy	Stirring: Paddlewheel driven by electric motor	Electrical energy	Product of voltage, current, and time	Electrical energy loss in motor and circuit, temperature rise of paddlewheel
(2) Mechanical energy	Stirring: Paddlewheel driven by pulley and falling weight	Mechanical energy	Change in potential energy of weight: product of mass of weight, change in height, and the gravitational constant g	Temperature rise of paddlewheel
(3) Heat flow	Electrical energy converted to heat in a resistor	Electrical energy	Product of voltage, current, and time	Temperature rise of resistor and electrical losses in circuit
(4) Heat flow	Mechanical energy of falling weight is converted to heat through friction of rubbing two surfaces together, as with a brake on the axle of a pulley	Mechanical energy	Change in potential energy of weight: product of mass of weight, change in height, and g	Temperature rise of mechanical brakes, etc.



Experimental Observations

- 1. In any change of state (except involving nuclear reaction), total mass is conserved.
- 2. In any change of state, total momentum is conserved.
- 3. In any change of state, total energy (including internal, potential, and kinetic energy, heat and work) is conserved.
- 4. Heat flow and work flow are equivalent in that supplying a given amount of energy to a system and either can be made to result in the same increase in its internal energy. Heat (thermal energy) and work (mechanical energy) are not equivalent in the sense that work can be completely converted to heat but heat can be only partially converted to work.



Joule's experiments

- Table 1.5-1: Experimental Designed to Prove the Energy Equivalence of Heat and Work
- A specific amount of energy:
 - mechanical work
 - electrical work
 - heat
 - ➔ produce the same temperature rise.
- Energy conservation principle:
 - In any change of state, the total energy (including U, KE, PE, heat, electrical, and mechanical work) is conserved.
 - Energy is neither created nor destroyed, but may change in form.



Experimental Observations

- 5. A system that is not subjected to forced flows of mass or energy from its surroundings will evolve to the equilibrium state.
- 6. A system in equilibrium with its surrounding will never spontaneously revert to a nonequilibrium state.
- 7. Equilibrium states that arise naturally are stable to small disturbances.
- 8. The stable equilibrium state is completely characterized by values of only equilibrium properties. For a single-component single-phase system, two independent intensive properties are needed to fix the thermodynamic state of an equilibrium system completely; the further specification of one extensive variable of the system fixes its size.



Experimental Observations

- 9. The interrelationships between the thermodynamic state variables for a fluid in equilibrium also apply locally for a system not in equilibrium.
- 10. For nonequilibrium systems, the rate at which natural relaxation processes occur are directly proportional to the magnitude of the driving forces.
 - Heat flow (units of J/s or W) or heat flux (units of J/m²s)

$$\dot{\mathbf{Q}} = -h\Delta T$$
 or $\mathbf{q}_{\mathbf{x}} = -k\frac{\partial T}{\partial \mathbf{x}}$

• Mass flux of species A in the x direction

$$j_{A}\big|_{x} = -\rho D \frac{\partial W_{A}}{\partial x}$$

• The flux of the x-component of momentum in the y-coordinate direction $\partial V_{...}$

$$\tau_{yx} = -\mu \frac{\partial V_x}{\partial y}$$



Summary of experimental observations

- In any change of state (without nuclear reaction), total mass, total momentum, and total energy (U, PE, KE, Q, W) are conserved.
- Thermal energy and mechanical energy are quantitatively equivalent. The quality of mechanical energy > that of thermal energy.
- A time-invariant state with uniform or composed of uniform subsystem is the equilibrium state
- An equilibrium system will never spontaneously revert to a non-equilibrium state
- Equilibrium states that arise naturally are stable to small disturbances.
- For a single-phase, one component system, only two state variables are needed to fix the thermodynamic state of the equilibrium system completely. One extensive property fixes its size.



- Local equilibrium for non-equilibrium process if the internal relaxation processes are rapid w.r.t. the rate change of the system.
- For non-equilibrium processes: (transport processes)

$$\frac{flow \, o}{f} \, heat : \dot{Q} = -h\Delta T$$

heat flux in
$$x - direction: q_x = -k(\partial T / \partial x)$$

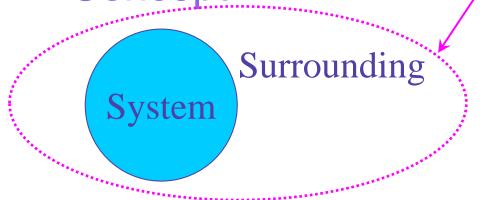
mass flux of $A: j_{A|x} = \rho D(\partial w_A / \partial x)$

flux of the x – component of momentum in y – direction: $\tau_{yx} = -\mu(\partial v_x / \partial y)$



Conservation of Energy

- Though the forms of energy can change, the total energy associated with an isolated system will remain unchanged unless in the presence of nuclear reactions.
- Conservation of energy is obviously true for isolated systems.
- For other systems, apply the Balance Concept

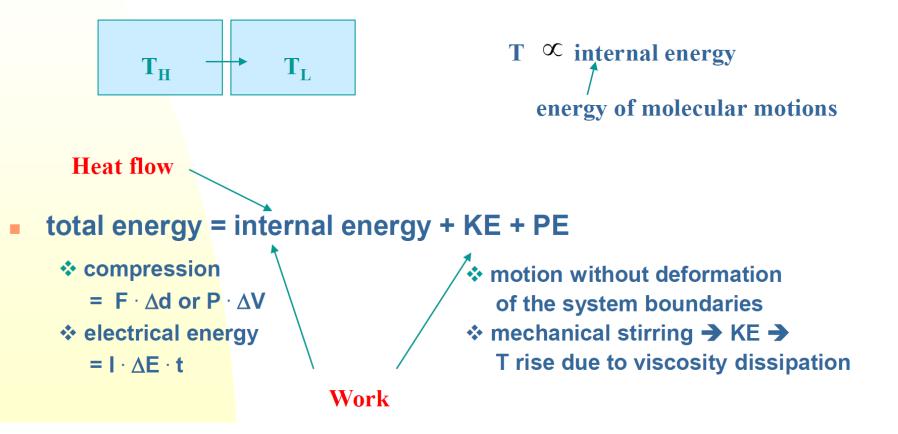


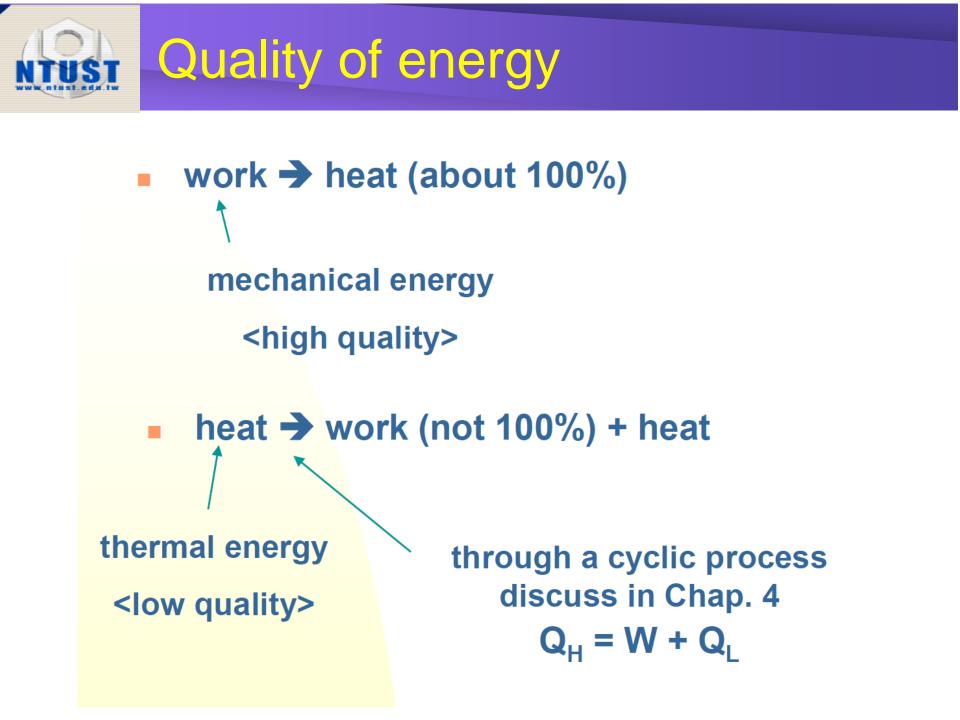
This is an isolated system

The energy of the new isolated system is conserved. The Balance Concept accounts for all the energy interaction between the original system and its surrounding.

Heat, work, and conservation

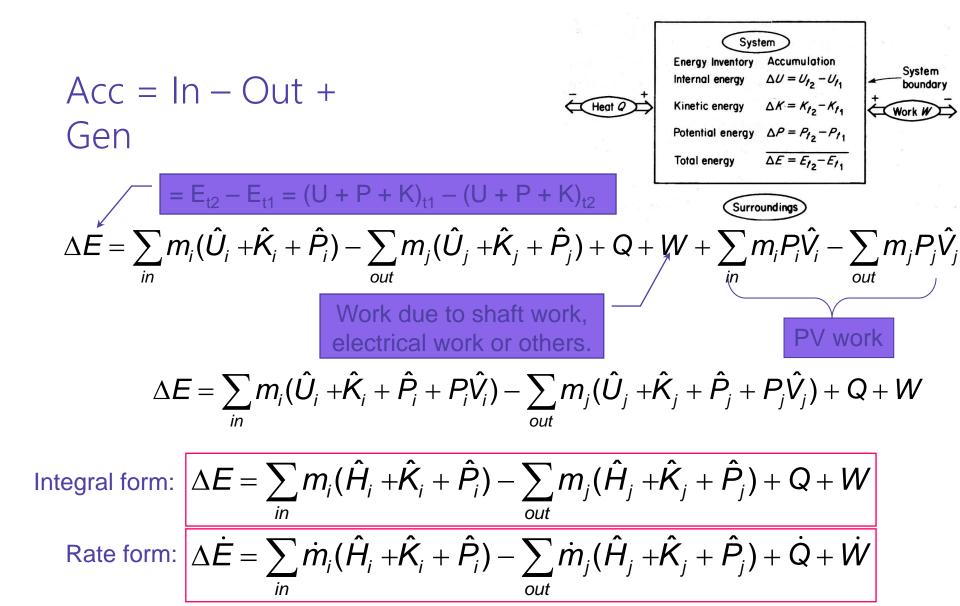
- Heat: energy transfer as a result of only T difference
- Work: energy transfer by any mechanism that involves mechanical motion of or across the system boundaries







Governing Equation for Energy Balance





Unit Systems

(MKS Unit System)

Unit	Name	Abbreviation	Basis of Definition
Length	meter	m	The distance light travels in a vacuum in 1/299792458 second
Mass	kilogram	kg	Platinum-iridium prototype at the International Bureau of Weights and Measures, Sèvres, France
Time	second	S	Proportional to the period of one cesium-133 radiative transition
Electric current	ampere	А	Current that would produce a specified force between two parallel conductors in a specified geometry
Temperature	kelvin	К	1/273.16 of the thermodynamic temperature (to be defined shortly) of water at its triple point (see Chapter 7)
Amount of substance	mole	mol	Amount of a substance that contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12 $(6.022 \times 10^{23}, \text{ which is})$ Avogadro's number)
Luminous intensity	candela	cd	Related to the black-body radiation from freezing platinum (2045 K)

Table 1.2-1The SI Unit System



			Expression in	
Quantity	Name	Symbol	SI Units	Derived Units
Force	newton	Ν	m kg s ^{-2}	$J m^{-1}$
Energy, work, or quantity of heat	joule	J	$m^2 kg s^{-2}$	N m
Pressure or stress	pascal	Pa	$m^{-1} kg s^{-2}$	N/m^2
Power	watt	W	$m^2 kg s^{-3}$	J/s
Frequency	hertz	Hz	s^{-1}	

Table 1.2-2 Derived Units with Special Names and Symbols Acceptable in SI Units

Quantity	Expression in SI Units	Symbol
Concentration of substance	$mol m^{-3}$	mol/m ³
Mass density ($\rho = m/V$)	kg m ⁻³	kg/m^3
Heat capacity or entropy	$m^2 kg s^{-1} K^{-1}$	J/K
Heat flow rate (\dot{Q})	$m^2 kg s^{-3}$	W or J/s
Molar energy	$m^2 kg s^{-2} mol^{-1}$	J/mol
Specific energy	$m^2 s^{-2}$	J/kg
Specific heat capacity or specific entropy	$m^2 s^{-2} K^{-1}$	J/(kg K)
Specific volume	$m^3 kg^{-1}$	m^3/kg
Viscosity (absolute or dynamic)	$m^{-1} kg s^{-1}$	Pa s
Volume	m ³	m ³
Work, energy (W)	$m^2 kg s^{-2}$	J or N m

 Table 1.2-3
 Other Derived Units in Terms of Acceptable SI Units



Unit Systems

Table 1.2-4 Prefixes for SI Units				
Multiplication Factor	Prefix	Symbol		
$ \begin{array}{r} 10^{12} \\ 10^9 \\ 10^6 \\ 10^3 \\ 10^2 \\ 10 \end{array} $	tera giga mega kilo hecto deka	T G M k (e.g., kilogram) h da		
$ \begin{array}{r} 10^{-1} \\ 10^{-2} \\ 10^{-3} \\ 10^{-6} \\ 10^{-9} \\ 10^{-12} \\ 10^{-15} \end{array} $	deci centi milli micro nano pico femto	d c (e.g., centimeter) m μ n p f		



Other Unit Systems

- cgs unit system:
 - "cm", "gram", and "sec" as the three fundamental units.
- fps (British Engineering) unit system:
 - "ft", "lb_f (pound force)", and "sec" as the three fundamental units.
 - Need to note the difference between "pound mass (lb_m)" and "pound force (lb_f)".



- Dimension: measure of property
- Dimensional consistency:

-5 kg + 100 m = ?

- " a + b = c" \rightarrow a, b and c must have the same unit for the equation to be meaningful.



- Classical Thermodynamics / Statistical Thermodynamics / Molecular Thermodynamics / Modern Thermodynamics
- **Classical thermodynamics** presents broad relationships between macroscopic properties, but it is not concerned with quantitative prediction of these properties.
- **Statistical thermodynamics** seeks to establish relationships between macroscopic properties and intermolecular forces through partition functions; it is very much concerned with quantitative prediction of bulk properties.
- *Molecular thermodynamics* presents methods for quantitative prediction of these properties.

----- Prausnitz, Lichtenthaler, Gomes de Azevedo // p.xix



Principles of Chemical Engineering

- HW1 (from Himmelblau,"Basic Principles and Calculations in Chemical Engineering", p.520, 6th ed., 1996.)
 - **5.78.** A turbine is installed between the supply stream at 1800 psia and 250°F and the outlet stream. The exit stream from the turbine is at 800 psia and 80°F, and 25 Btu/lb of fluid are lost from the poorly insulated turbine. Indicate the outlet states from the turbine and the throttling valve as points on the CO₂ chart. See Figure P5.78.
 - (a) How much useful work is extracted in the turbine?
 - (b) The exhaust from the turbine enters a throttling valve and leaves at 140 psia and 30% liquid, but the valve is not perfectly insulated. What is the temperature of the exhaust stream at 140 psia?
 - (c) How much heat is lost from the poorly insulated valve?
 - 1. 寫下此問題求解的governing equation
 - 2. 寫下合理的assumptions (idealization) CO2 in @ 250°F
 - 3. 寫下求解時需要的properties有哪些

