

# Advanced Thermodynamics

## Note 1

The 1st law and other basic concepts

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# Preclassical thermodynamics

(1600s ~ late 1800s)

- Galileo (circa 1600) :
  - thermometry quantification
- Joseph Black (1760s) :
  - the specific heat
- Count Rumford (1780s):
  - mechanical work is an inexhaustible source of **caloric** → 

Heat quantity  
Energy  
Entropy
  - a revival of mechanical concept of heat
- Carnot (1824) :
  - cyclic operation of an engine - conservation of caloric
- Helmholtz (1847) :
  - conservation of energy
- Joule (late 1800s) :
  - equivalence of mechanical, electrical and chemical energy of heat

# Thermodynamics

- Their validity lies in the absence of contrary experience.
  - It shares with mechanics and electromagnetism a basis in primitive laws.
- Useful equations
  - Calculation of heat and work requirements for physical and chemical processes
  - Determination of equilibrium conditions for chemical reactions
  - Determination of equilibrium for the transfer of chemical species between phases.

# Heat and work

- Heat always flows from a higher temperature to a lower one.
  - Temperature as the driving force for the transfer of energy as heat.
  - Heat is never regarded as being stored within a body.
  - Like work, it exists only as energy in transit from one body to another.
  - Unit: calorie is defined as the quantity of heat which when transferred to one gram of water raised its temperature one degree Celsius, or, British thermal unit (BTU) is defined as the quantity of heat which when transferred to one pound mass of water raised its temperature one degree Fahrenheit.

# Thermodynamics

- **Classical thermodynamics**
- natural laws governing the behaviour of macroscopic systems

- First Law

$$\Delta E = Q + W$$

Internal changes =  $\Sigma$  interactions occurring at boundaries  
(T, P, V, ... etc)

- Second Law

- Reversible process
    - Entropy



Boundary

- (1) adiabatic or diathermal
- (2) permeable or impermeable
- (3) rigid or movable

An isolated system: impermeable, rigid, adiabatic and independent of events in the environment

# The 1<sup>st</sup> law of thermodynamics

- It was first a postulate. However, the overwhelming evidence accumulated over time has elevated it to the stature of a law of nature.
- Although energy assumes many forms, the total quantity of energy is constant, and when energy disappears in one form it appears simultaneously in other forms.



$$\Delta(\text{energy of the system}) + \Delta(\text{energy of surroundings}) = 0$$

Total internal energy of the system, depends on the quantity of material in a system, i.e., the extensive property.

c.f. intensive property,  
e.g. temperature and pressure.  
e.g. specific or molar properties

$$\Delta E = Q + W$$

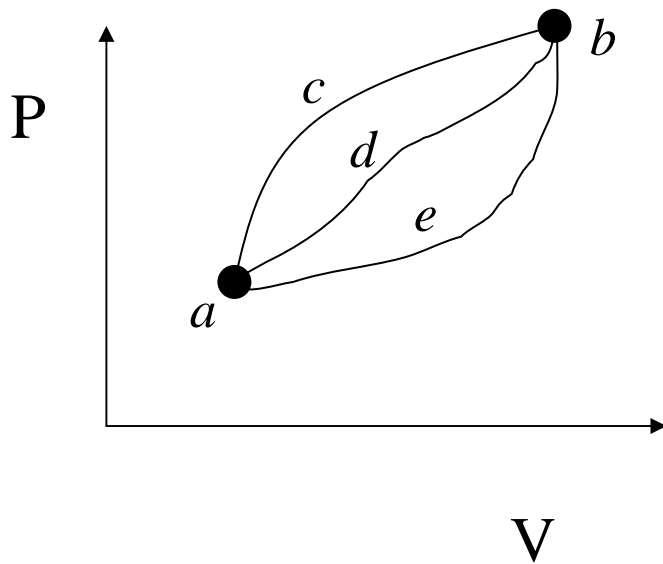



$$\Delta U^t = Q + W$$


- If the gas is heated or cooled, compressed or expanded, and then returned to its initial temperature and pressure, its intensive properties are restored to their initial values.
- Such properties do not depend on the past history of the substance nor on the means by which it reaches a given state. Such quantities are known as **state functions**.
- A state function may therefore be expressed mathematically as a function of other thermodynamic properties. Its values may be identified with points on a graph.



When a system is taken from state  $a$  to state  $b$  along path  $acb$ , 100 J of heat flows into the system and the system does 40 J of work. (1) How much heat flows into the system along path  $aeb$  if the work done by the system is 20J? (2) The system returns from  $b$  to  $a$  along path  $bda$ . If the work done on the system is 30J, does the system absorb or liberate heat? How much?



$$\begin{aligned}
 \Delta U_{ab}^t &= Q + W \\
 &= 100 - 40 = 60J \\
 &= Q_{aeb} + W_{aeb} \\
 &= Q_{aeb} - 20
 \end{aligned}$$

$$Q_{aeb} = 80J$$

$$\begin{aligned}
 \Delta U_{ba}^t &= -\Delta U_{ab}^t \\
 &= -60J \\
 &= Q_{bda} + W_{bda} \\
 &= Q_{bda} + 30
 \end{aligned}$$

$$Q_{bda} = -90J$$

# Equilibrium

- In thermodynamics, equilibrium means not only the absence of change but the absence of any tendency toward change on a macroscopic scale.
- Different kinds of driving forces bring about different kinds of change. For example:
  - imbalance of mechanical forces tend to cause energy transfer as a work.
  - temperature differences tend to cause the flow of heat.
  - Gradients in chemical potential tend to cause substance to be transfer from one phase to another.

# Phase rule

- For any system at equilibrium, the number of independent variables that must be arbitrarily fixed to establish its *intensive* state is given by J.W. Gibbs (1875).
- The degrees of freedom of the nonreacting systems:

$$F = 2 - \pi + N$$

- where  $\pi$  is the number of phases,  $N$  is the number of chemical species
- A phase is a homogeneous region of matter. A gas or a mixture of gases, a liquid or a liquid solution, and a crystalline solid are examples of phases. Various phases can coexist, but they must be in equilibrium for the phase rule to apply.
- The minimum number of degrees of freedom for any system is zero:

$$F = 2 - \pi + N = 0$$

- $N = 1$ ,  $\pi = 3$  (i.e. the triple point)

How many degrees of freedom has each of the following systems:

- (1) Liquid water in equilibrium with its vapor.
  - (2) Liquid water in equilibrium with a mixture of water vapor and nitrogen.
  - (3) A liquid solution of alcohol in water in equilibrium with its vapor.
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(1) 1 species, 2 phases

$$F = 2 - \pi + N = 2 - 2 + 1 = 1$$

(2) 2 species, 2 phases

$$F = 2 - \pi + N = 2 - 2 + 2 = 2$$

(3) 2 species, 2 phases

$$F = 2 - \pi + N = 2 - 2 + 2 = 2$$

# The reversible process

- A process is reversible when its direction can be reversed at any point by an infinitesimal change in external conditions.
  - frictionless
  - never more than differentially removed from equilibrium
  - traverses a succession of equilibrium states
  - driven by forces whose imbalance is differential in magnitude
  - can be reversed at any point by a differential change in external conditions
  - when reversed, retraces its forward path, and restores the initial state of system and surroundings
- The reversible process is ideal; it represents a limits to the performance of actual process. Results for reversible processes in combination with appropriate *efficiencies* yield reasonable approximations of the work for actual processes.

# Constant-V and constant-P

- The general 1st law equation for a mechanically reversible, closed-system process:

$$d(nU) = dQ - Pd(nV)$$

- constant total volume:
  - $Q = n\Delta U$
  - the heat transferred is equal to the internal-energy change of the system
- constant pressure:  $dQ = d(nU) + d(nPV) \longrightarrow dQ = d[n(U + PV)]$ 
  - $Q = n\Delta H$
  - the mathematical definition of enthalpy:  $H \equiv U + PV$
  - the heat transferred is equal to the enthalpy change of the system

Calculate  $\Delta U$  and  $\Delta H$  for 1 kg of water when it is vaporized at the constant temperature of 100 °C and the constant pressure of 101.33 kPa. The specific volumes of liquid and vapor water at these conditions are 0.00104 and 1.673 m<sup>3</sup>/kg. For this change, heat in the amount of 2256.9 kJ is added to the water.

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Imagine the fluid contained in a cylinder by a frictionless piston which exerts a constant pressure of 101.33 kPa. As heat is added, the water expands from its initial to its final volume. For the 1-kg system:

$$\Delta H = Q = 2256.9 \text{ kJ}$$

$$\begin{aligned}\Delta U &= \Delta H - P\Delta(V) \\ &= 2256.9 \text{ J} - 101.33 \text{ kPa} \times (1.673 - 0.001) \text{ m}^3 \\ &= 2256.9 \text{ kJ} - 169.4 \text{ kJ} \\ &= 2087.5 \text{ kJ}\end{aligned}$$

# Heat capacity

- A body has a capacity for heat. The smaller the temperature change in a body caused by the transfer of a given quantity of heat, the greater its capacity.
- A heat capacity:  $C \equiv \frac{dQ}{dT}$ 
  - a process-dependent quantity rather than a state function.
- Two heat capacities,  $C_V$  and  $C_P$ , are in common use for homogeneous fluids; both as state functions, defined unambiguously in relation to other state functions.



# Heat capacities at ...

- At constant volume

$$C_V \equiv \left( \frac{\partial U}{\partial T} \right)_V$$

$$\Delta U = \int_{T_1}^{T_2} C_V dT \quad (\text{const } V)$$

- $C_V$  is a state function and is independent of the process.

- At constant pressure

$$C_P \equiv \left( \frac{\partial H}{\partial T} \right)_P$$

$$\Delta H = \int_{T_1}^{T_2} C_P dT \quad (\text{const } P)$$

- $C_P$  is a state function and is independent of the process.

Air at 1 bar and 298.15K is compressed to 5 bar and 298.15K by two different mechanically reversible processes: (1) cooling at constant pressure followed by heating at constant volume; (2) heating at constant volume followed by cooling at constant pressure. Calculate the heat and work requirements and  $\Delta U$  and  $\Delta H$  of the air for each path.

Information: the following heat capacities for air may be assumed independent of temperature:  $C_V = 20.78$  and  $C_P = 29.10$  J/mol.K. Assuming for air that  $PV/T$  is a constant, regardless of the changes it undergoes. At 298.15 K and 1 bar the molar volume of air is  $0.02479 \text{ m}^3/\text{mol}$ .

The final volume:  $V_2 = V_1 \frac{P_1}{P_2} = 0.004958 \text{ m}^3$

(1) The temperature of the air at the end of the cooling step:  $T' = T_1 \frac{V_2}{V_1} = 59.63 \text{ K}$

$$Q = \Delta H = C_P \Delta T = -6941 \text{ J} \quad \Delta U = \Delta H - P \Delta V = -4958 \text{ J}$$

During the second step:  $\Delta U = Q = C_V \Delta T = 4958 \text{ J}$

The complete process:  $Q = -6941 + 4958 = -1983 \text{ J}$   $\Delta U = 0$   $W = \Delta U - Q = 1983 \text{ J}$   
 $\Delta H = \Delta U + \Delta(PV) = 0$

(2) The temperature of the air at the end of the heating step:  $T' = T_1 \frac{P_2}{P_1} = 1490.75 \text{ K}$

$$Q = \Delta U = C_V \Delta T = 24788 \text{ J}$$

During the second step:  $Q = \Delta H = C_P \Delta T = -34703 \text{ J}$   $\Delta U = \Delta H - P \Delta V = -24788 \text{ J}$

The complete process:  $Q = 24788 - 34703 = -9915 \text{ J}$   $\Delta U = 0$   $W = \Delta U - Q = 9915 \text{ J}$   
 $\Delta H = \Delta U + \Delta(PV) = 0$

Calculate the internal-energy and enthalpy changes that occur when air is changed from an initial state of 40°F and 10 atm, where its molar volume is 36.49 ft<sup>3</sup>/lb-mole, to a final state of 140°F and 1 atm.

Assume for air that  $PV/T$  is constant and that  $C_v = 5$  and  $C_p = 7$  Btu/lb-mol.F.

Independent of paths!  $\longrightarrow$  Two-step process:

- (1) cooled at constant volume to the final pressure;
- (2) heated at constant pressure to the final temperature.

$$T_1 = 40 + 459.67 = 499.67 \text{ R}$$

$$T_2 = 140 + 459.67 = 599.67 \text{ R}$$

Constant volume

$$T' = T_1 \frac{P_1}{P_2} = 49.97 \text{ R}$$

$$\Delta U = C_v \Delta T = -2248.5 \text{ Btu}$$

$$\Delta H = \Delta U + \Delta(PV) = -3141.6 \text{ Btu}$$

Intermediate state

Constant pressure

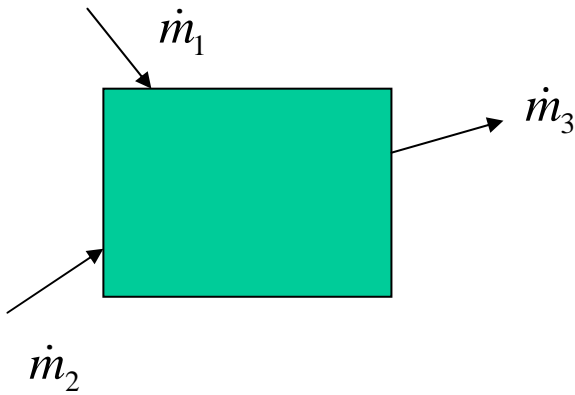
$$V_2 = V_1 \frac{P_1 T_2}{P_2 T_1} = 437.93 \text{ ft}^3$$

$$\Delta H = C_p \Delta T = 3847.9 \text{ Btu}$$

$$\Delta U = \Delta H - P \Delta V = 2756.2 \text{ Btu}$$

$$\Delta H = \Delta H_1 + \Delta H_2 = 507.7 \text{ Btu}$$

$$\Delta U = \Delta U_1 + \Delta U_2 = 706.3 \text{ Btu}$$



# Open systems

- Mass balance for open systems:

$$\frac{dm_{cv}}{dt} = -\Delta(\dot{m})_{fs} = -\Delta(\rho u A)_{fs}$$

$$\Delta(\dot{m})_{fs} = \dot{m}_3 - \dot{m}_1 - \dot{m}_2$$

- energy balance for open systems:

$$\frac{d(mU)_{cv}}{dt} = -\Delta \left[ \left( U + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} + \dot{Q} + \text{work rate}$$



$$\text{PV work} + \text{shaft work} + \dots \text{ etc.} \\ -\Delta[(PV)\dot{m}]_{fs} + \dot{W}$$

$$\frac{d(mU)_{cv}}{dt} = -\Delta \left[ \left( U + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} + \dot{Q} - \Delta[(PV)\dot{m}]_{fs} + \dot{W}$$

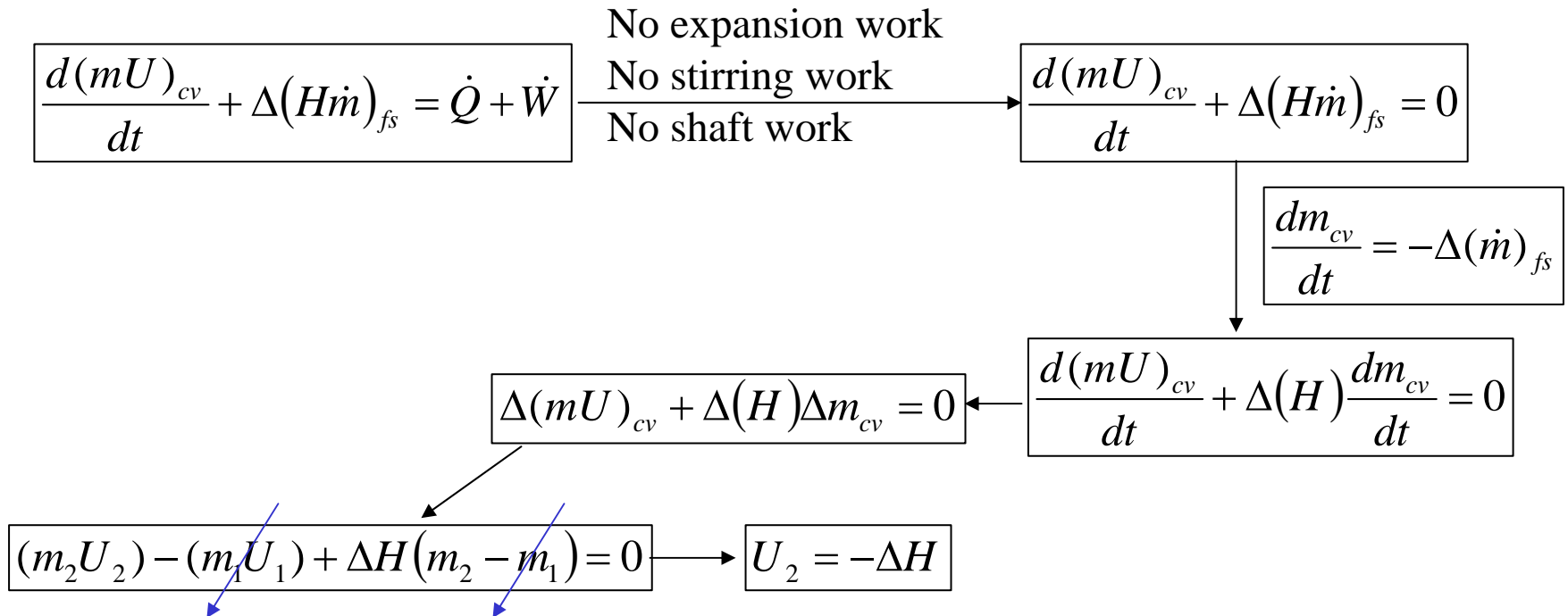
$$\frac{d(mU)_{cv}}{dt} + \Delta \left[ \left( H + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}$$



$$\frac{d(mU)_{cv}}{dt} + \Delta(H\dot{m})_{fs} = \dot{Q} + \dot{W}$$


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An evacuated tank is filled with gas from a constant-pressure line. What is the relation between the enthalpy of the gas in the entrance line and the internal energy of the gas in the tank? Neglect heat transfer between the gas and the tank.



An insulated, electrically heated tank for hot water contains 190 kg of liquid water at 60 °C when a power outage occurs. If water is withdrawn from the tank at a steady rate of 0.2 kg/s, how long will it take for the temperature of the water in the tank to drop from 60 to 35 °C? Assume that cold water enters the tank at 10 °C and that heat losses from the tank are negligible. For liquid water let  $C_v = C_p = C$ , independent of  $T$  and  $P$ .

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$$\begin{aligned}
 &\boxed{\frac{d(mU)_{cv}}{dt} + \Delta(H\dot{m})_{fs} = \dot{Q} + \dot{W}} \longrightarrow \boxed{m \frac{dU}{dt} + \dot{m}(H - H_1) = 0} \\
 &\quad \downarrow \quad \boxed{\frac{dU}{dt} = C \frac{dT}{dt}} \quad \boxed{(H - H_1) = C(T - T_1)} \\
 &\quad \downarrow \quad \boxed{dt = -\frac{m}{\dot{m}} \frac{dT}{T - T_1}} \\
 &\quad \downarrow \quad \boxed{t = -\frac{m}{\dot{m}} \ln\left(\frac{T - T_1}{T_0 - T_1}\right)} \\
 &\quad \downarrow \quad \boxed{t = -\frac{190}{0.2} \ln\left(\frac{35 - 10}{60 - 10}\right) = 658.5 \text{ s}}
 \end{aligned}$$

Air at 1 bar and 25 °C enters a compressor at low velocity, discharge at 3 bar, and enters a nozzle in which it expands to a final velocity of 600 m/s at the initial conditions of pressure and temperature. If the work of compression is 240 kJ/kg of air, how much heat must be removed during the compression?

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$$\frac{d(mU)_{cv}}{dt} + \Delta \left[ \left( H + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}$$

Steady state flow process

Return to initial pressure and temperature, no enthalpy change

No potential energy change

Initial kinetic energy is negligible

$$\frac{u_2^2}{2} = Q + W_s$$

$$Q = \frac{1}{2}(600)^2 - 240 = -60 \text{ kJ / kg}$$

Heat must be removed in the amount of 60 kJ for each kilogram of air compressed.

Water at 200 °F is pumped from a storage tank at the rate of 50 gal/min. The motor for the pump supplies work at the rate of 2 (hp). The water goes through a heat exchanger, giving up heat at the rate of 40000 Btu/min. and is delivered to a second storage tank at an elevation 50 ft above the first tank. What is the temperature of the water delivered to the second tank?

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$$\frac{d(mU)_{cv}}{dt} + \Delta \left[ \left( H + \frac{1}{2} u^2 + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}$$

Steady state flow process  
Kinetic energy is negligible

$$\Delta[(H + zg)\dot{m}] = \dot{Q} + \dot{W}_s$$

$$\Delta H = Q + W_s - \frac{g}{g_c} \Delta z = -99.35 \text{ Btu} / \text{lb}_m$$

From steam table,  $H_1 = 168.09 \text{ Btu/lbm}$

$$H_2 = \Delta H + H_1 = -99.35 + 168.09 = 68.74 \text{ Btu} / \text{lb}_m$$

From steam table

$$t = 100.74 \text{ } ^\circ F$$