KMU220
CHEMICAL ENGINEERING THERMODYNAMICS I

FIRST LAW

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Outline

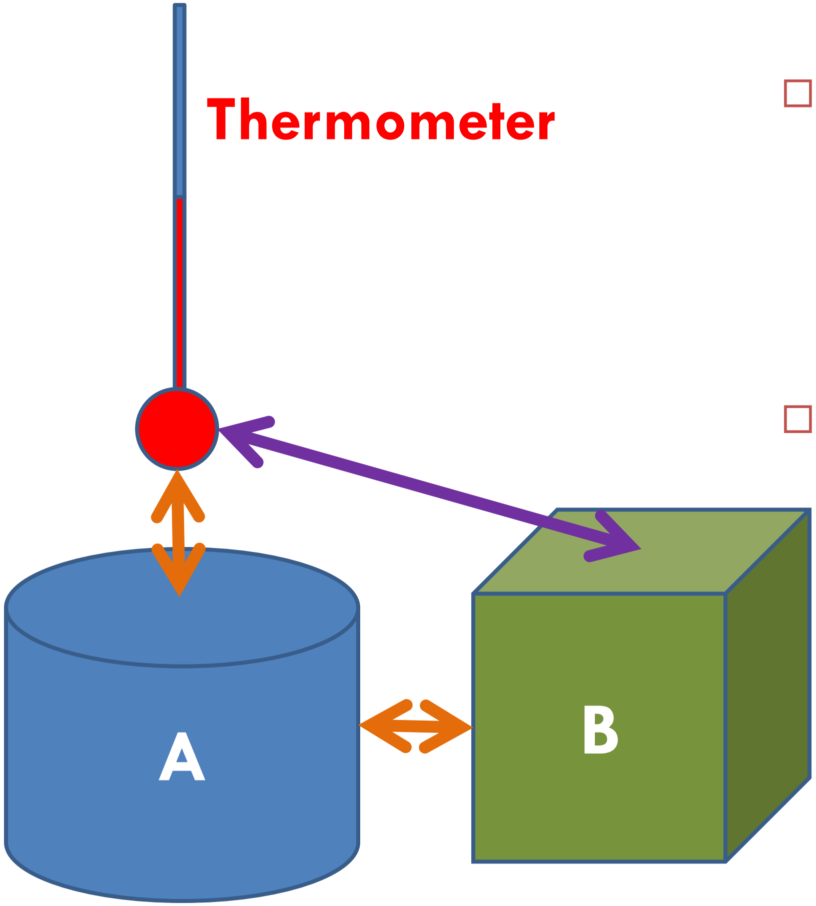
- Zeroth law of thermodynamics
- Conservation of mass
- Conservation of energy: First law of thermodynamics
- Energy balance for closed systems
- Equilibrium and phase rule
- Reversible processes
- P-V systems
- Enthalpy
- Heat capacity

Zeroth law of thermodynamics

Thermal equilibrium → If two bodies are in contact through a thermally-conducting boundary for a sufficiently long time, no further observable changes take place

- Two systems, which are individually in thermal equilibrium with a third are in thermal equilibrium with each other; all three systems have the same value of the property called ***temperature***.

Thermodynamic equilibrium



- Object A is in equilibrium with both the thermometer and object B. Then the thermometer should also be in equilibrium with object B.
- This means all three objects have the same **temperature**

Conservation of mass

Change in total mass is equal to mass exchanged with the surroundings

In a system, we may consider two changes to the mass of species j:

1. internal change $d_{int}m_j$ (due to a reaction)
2. external change with the surrounding $d_{ext}m_j$

$$dm_j = d_{ext}m_j + d_{int}m_j$$

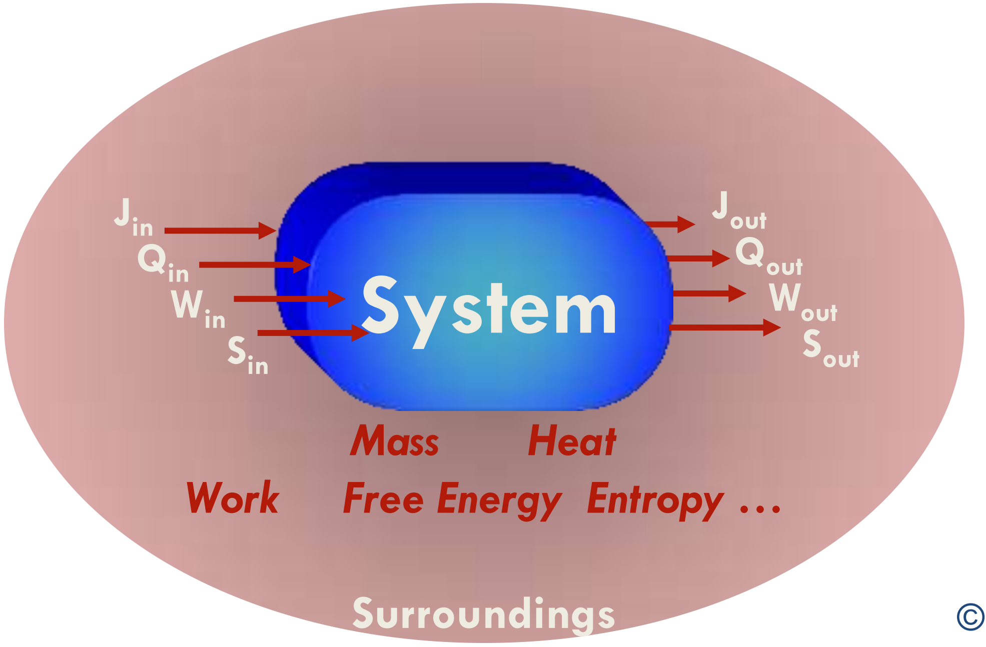
- Closed system → No exchange of matter with surroundings through system boundary, i.e. $d_{ext}m_j = 0$
- Open system→ $d_{ext}m_j \neq 0$

First law of thermodynamics: Conservation of energy

- During a process:

Energy can be transferred and converted from one form to another, while the total energy remains constant

Δ(Energy of the system) + Δ(Energy of the surroundings) = 0



Δ : Finite change in quantity

Remember

Potential, kinetic and internal energy:

External forms of energy related with macroscopic position or motion

Submolecular scale energy associated with atoms, electrons, inter-atomic/molecular forces

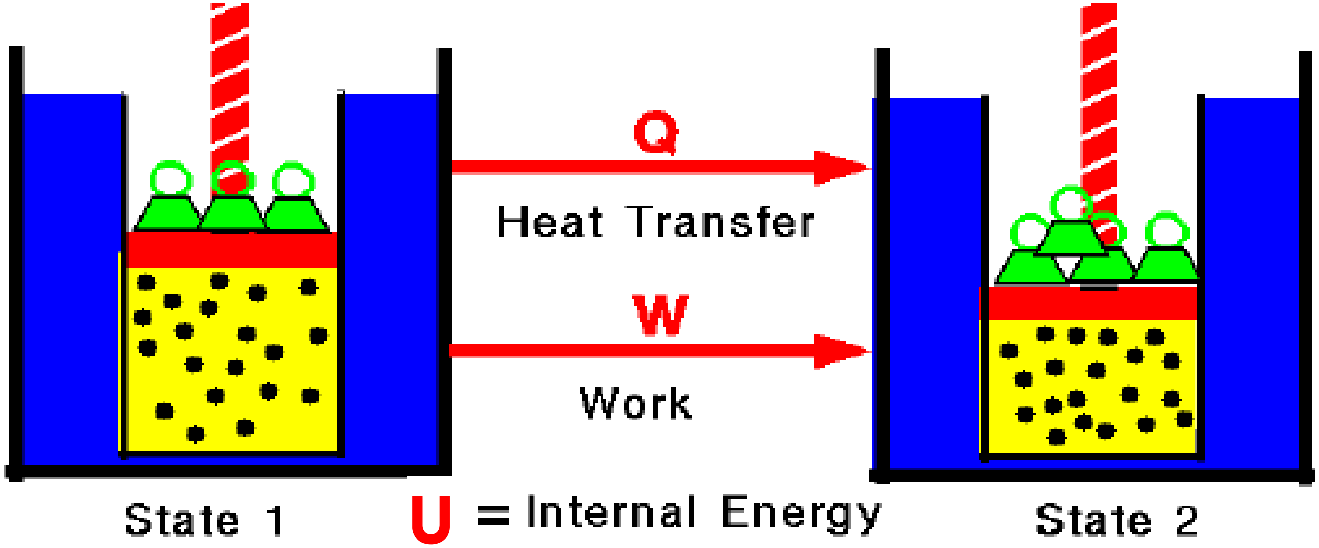
  - Reside with matter
  - Stored in matter
- Heat and work
  - Energy in transit across the boundary
  - Never stored or contained in the system

Internal Energy U

- No concise thermodynamic definition
- Cannot be directly measured
- Only absolute values are known

  (no reference point)
- In thermodynamics, only changes in internal energy are used $\Delta U = U_2 - U_1$

First law of thermodynamics

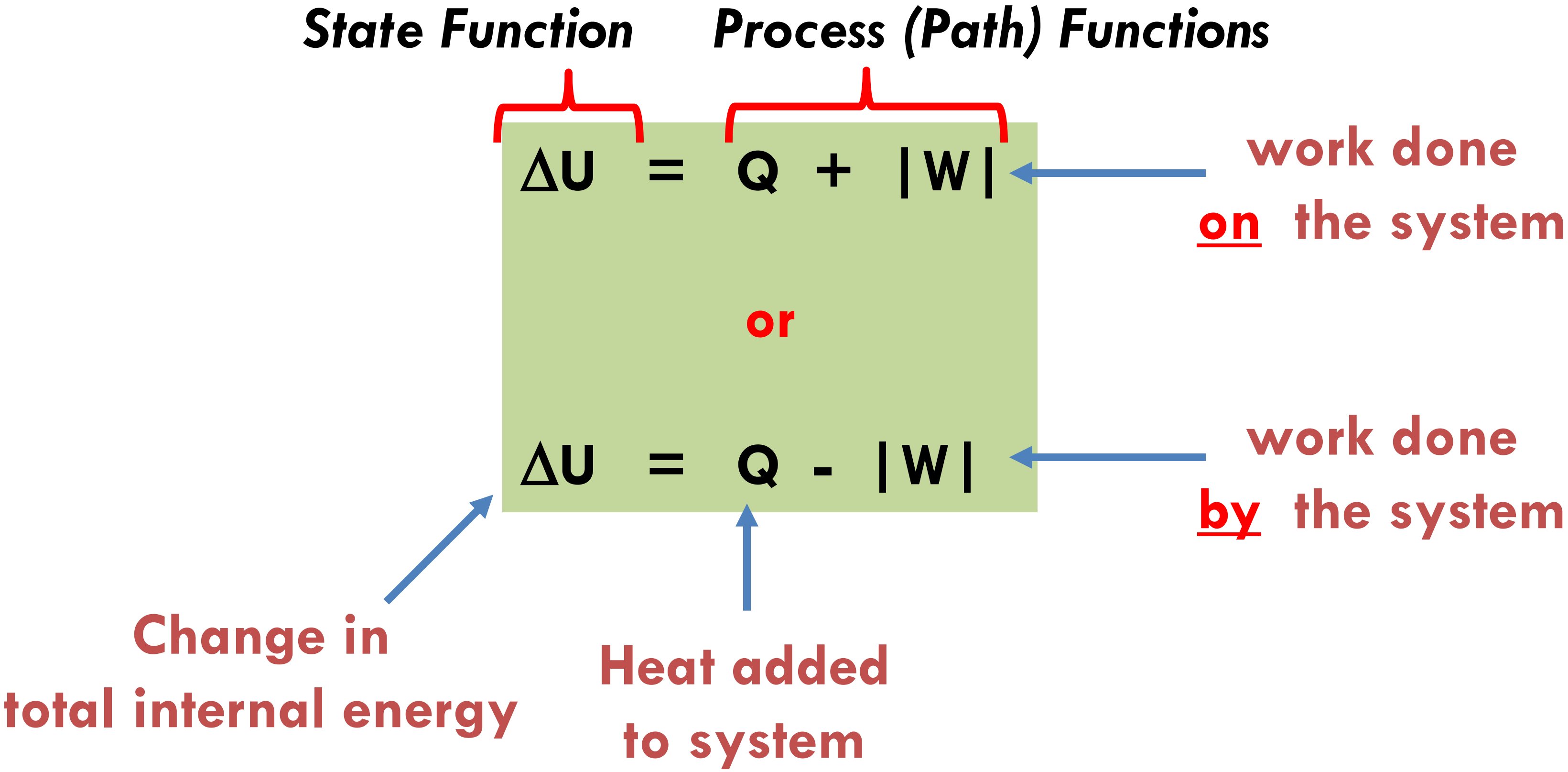


$$U_2 - U_1 = Q - W$$

Any thermodynamic system in an equilibrium state possesses a state variable called the internal energy (U). Between any two equilibrium states, the change in internal energy is equal to the difference of the heat transfer into the system and work done by the system.

Ref: http://www.grc.nasa.gov/WWW/k-12/airplane/thermo1.html

First Law for a closed system



State Function *Process (Path) Functions*

$$\overbrace{\Delta U}^{\text{State Function}} = \overbrace{Q + |W|}^{\text{Process (Path) Functions}}$$

work done **on** the system

or

$$\Delta U = Q - |W|$$

work done **by** the system

Change in total internal energy

Heat added to system

Remember

- Differential of a state function→ infinitesmall change in its value

$$\int_{P_1}^{P_2} dP = P_2 - P_1 = \Delta P \quad \text{and} \quad \int_{V_1}^{V_2} dV = V_2 - V_1 = \Delta V$$

- Differential of heat or work→ NOT a change, but an infinitesmall (finite) amount

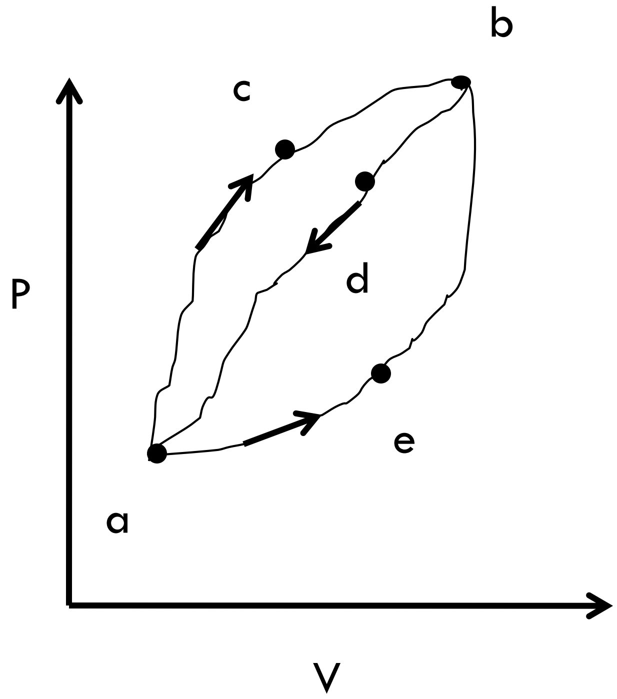
$$\int dQ = Q \quad \text{and} \quad \int dW = W$$

Example 2.4 (Ref: Smith,Van Ness, Abbott, 7th ed, p28)

When a system is taken from state a to state b in Fig. 2.1 along path acb, 100 J of heat flows into the system and the system does 40 J of work.

a) How much heat flows into the system along path aeb if the work done by the system is 20 J?

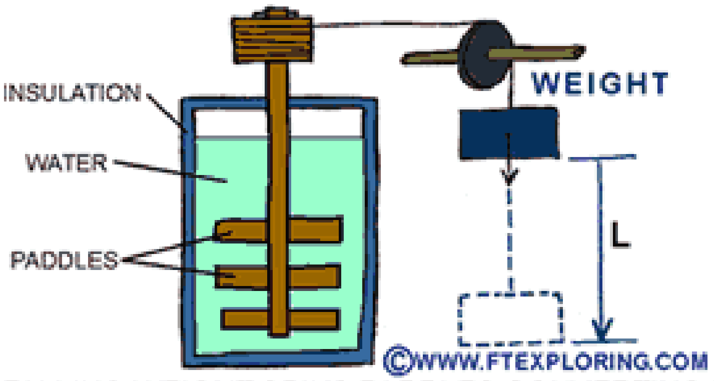
b) The system returns from b to a along path bda. If the work done on the system is 30 J, does the system absorb or liberate heat? How much?



James Prescott Joule’s experiment

- Goal: Use mechanical energy to measure thermal energy (temperature)
- **System:** Thermally insulated container contains a paddle that stirs when the masses at the ends of the ropes spun the device

CONVERSION OF WORK TO THERMAL ENERGY



FALLING WEIGHT SPINS PADDLES CONVERTING MECHANICAL ENERGY TO INTERNAL THERMAL ENERGY IN WATER

http://www.ftexploring.com/energy/first-law_p2.html

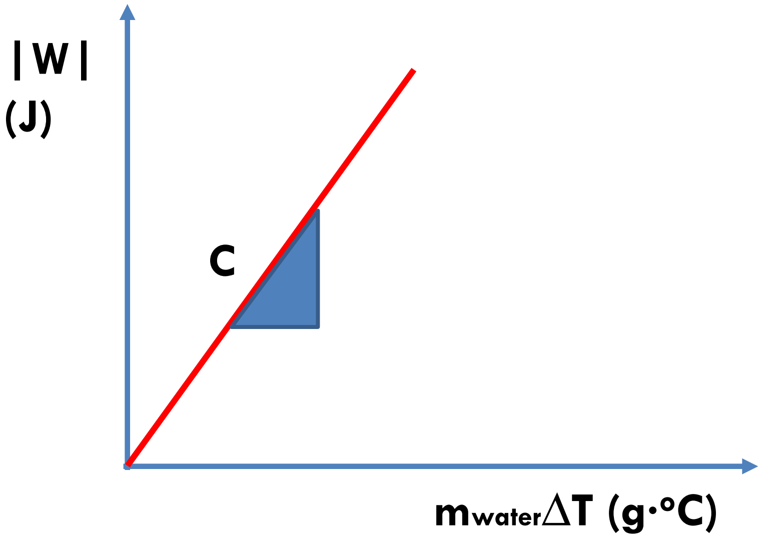
- Temperature of water rises due to stirring , i.e. friction between the water and the paddles.

Mechanical energy = Potential energy of the masses

= Energy that heats water (Heat)

Joule's discovery

- Loss in mechanical energy is proportional to an increase in temperature of the water (ΔT) and the amount of water used (m)
- The constant or proportionality that makes the loss in mechanical energy equal to the increase in temperature of the water = 4.186 J/(g·°C)



$(W = m_{weight} g L) \approx (C m_{water} \Delta T = -Q)$

C: constant → 4.186 J/(g·°C)

$$C = \lim_{\Delta T \to 0} \frac{W}{m_{water} \Delta T} = \frac{1}{m_{water}} \frac{dW}{dT}$$

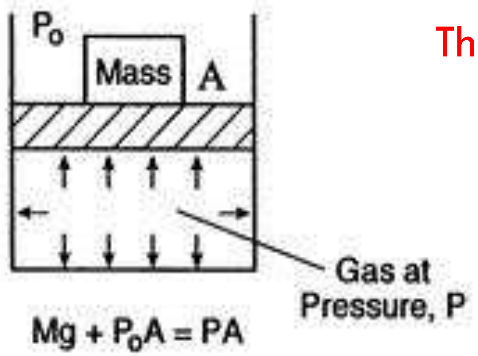
Thermal properties of water

- Maximum density at 4 °C : *1,000 kg/m^3, 1.940 slugs/ft^3*
- Specific Weight *at 4 °C: 9.807 kN/m^3, 62.43 Lbs./Cu.Ft, 8.33 Lbs./Gal., 0.1337 Cu.Ft./Gal.*
- Latent heat of melting: *334 kJ/kg*
- Latent heat of evaporation: *2,270 kJ/kg*
- Critical temperature: *380 °C - 386 °C*
- Critical pressure: *221.2 bar, 22.1 MPa (MN/m^2)*
- **Specific heat water: *4.187 kJ/kgK***
- Specific heat ice: *2.108 kJ/kgK*
- Specific heat water vapor: *1.996 kJ/kgK*
- Thermal expansion from 4 °C to 100 °C: *4.2×10^{-2}*

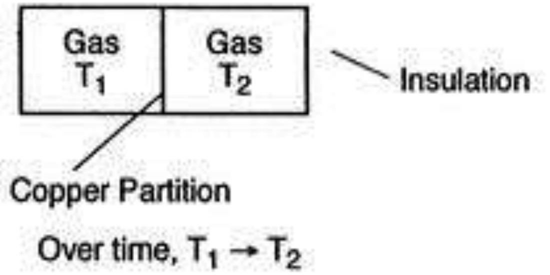
Equilibrium

is the state of a system, in which properties have definite, unchanged values as long as external conditions are unchanged

Mechanical Equilibrium



Thermal Equilibrium



A system in thermodynamic equilibrium satisfies:

- mechanical equilibrium (no unbalanced forces)
- thermal equilibrium (no temperature differences)
- chemical equilibrium (no chemical potential differences)

Gibbs Phase rule: $F = 2 - \pi + N$

How many degrees of freedom does the following systems have?

a) Liquid water in equilibrium with its vapor

b) Liquid water in equilibrium with a mixture of water vapor and nitrogen

c) A liquid solution of alcohol in water in equilibrium with its vapor

Ref: Ex.2.5 Smith, Van Ness, Abbott, 7th ed., p.30

Quiz I

a) List 3 intensive and 3 extensive properties.

b) Phase rule variables are ______________ properties.

c) Various phases can co-exist, but they must be in ______________ for the phase rule to apply.

d) When F=0 the system is ______________, characteristic of a triple point.

Problem Solution Steps

1. Define the problem
2. Draw a diagram to represent the system and its surroundings (show what is going in and out)
3. Write out your goal (what you need to solve for)
4. List given information and parameters
5. List your assumptions (you may have to add to your list of assumptions as you proceed in the problem)
6. Write down your equations and simplify using assumptions
7. Solve your equations using analytical or numerical methods
8. Discuss your result. Does it make sense?

Reversible process

If direction of process can be reversed at any point by an **infinitesimal change** in external conditions → Reversible

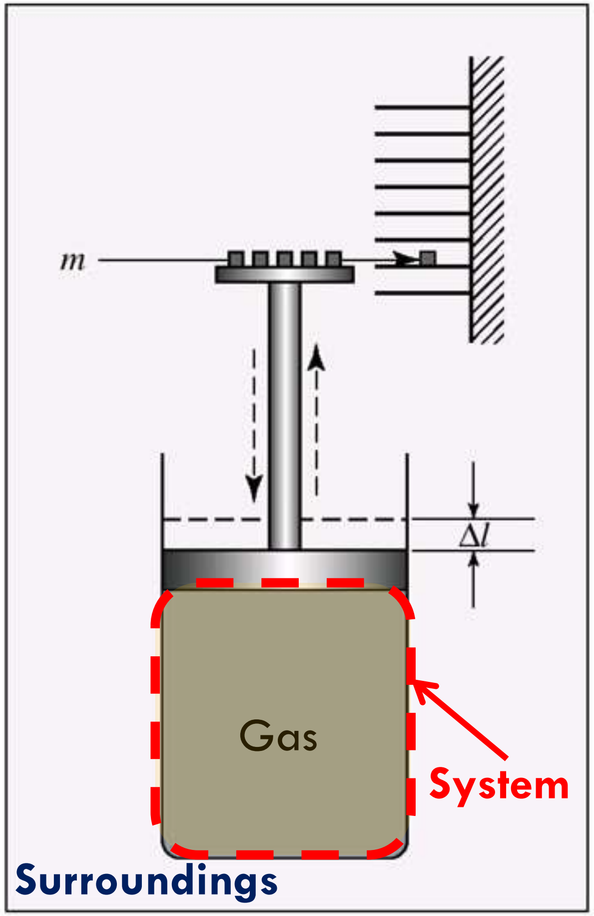
Necessary conditions for Mechanical Reversibility :

- ☐ System is never more than ∞smally displaced from internal eqlb.
  → @ uniform T and P (an equation of state is effective system)
- ☐ $\delta W = PdV$: Internal P is always in virtual balance with forces external to the system
- ☐ If reversed →Follows its forward path

$$W = -\int_{V_1}^{V_2} PdV$$

Restores initial state of system and surroundings

Reversible expansion of gas



System: **Gas in the cylinder**

Assumptions:

-Frictionless piston

-Negligible gas potential energy

(No gravitational forces on the gas)

-Constant temperature

-No dissipative forces acting on the piston due to viccosity of the gas (i.e. Mass is added very slowly and in very small pieces without causing any oscillations of the piston)

Dissipative forces→Irreversible process

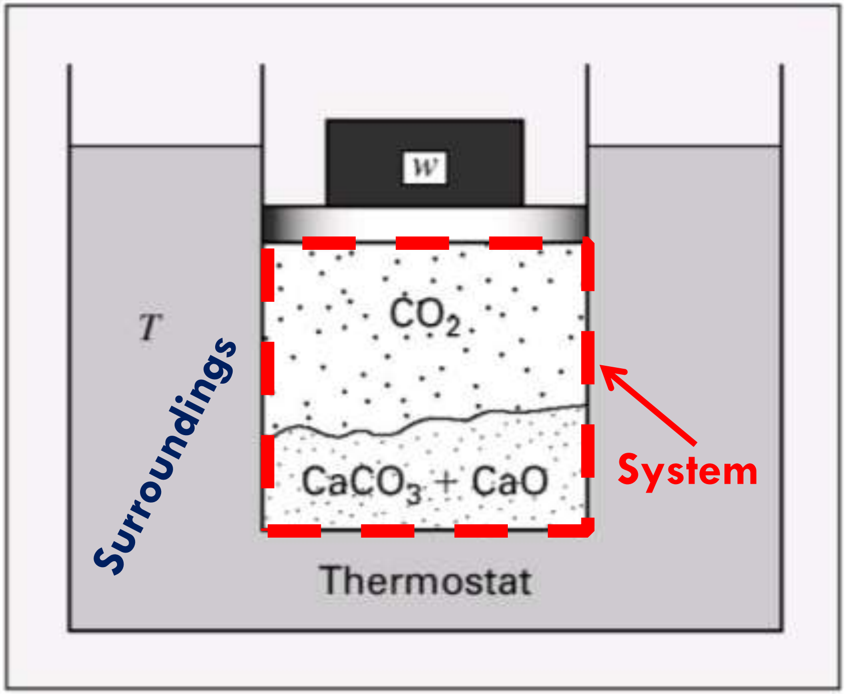
Adapted from Smith, Van Ness and Abbott, Introduction to Chemical Engineering Thermodynamics, 7th Ed, McGraw-Hill, p32

Reversible chemical reaction

T: Constant

If ↓P_{CO_2} ⇨ decomposition of $CaCO_3 \rightarrow CaO + CO_2$

If ↑δw ⇨ ↓dV ⇨ ↑dP_{CO_2} ⇨ ↑dm_{CaCO_3}, $Q=-\Delta H_{rxn}$ and ↑dT_{cyl}



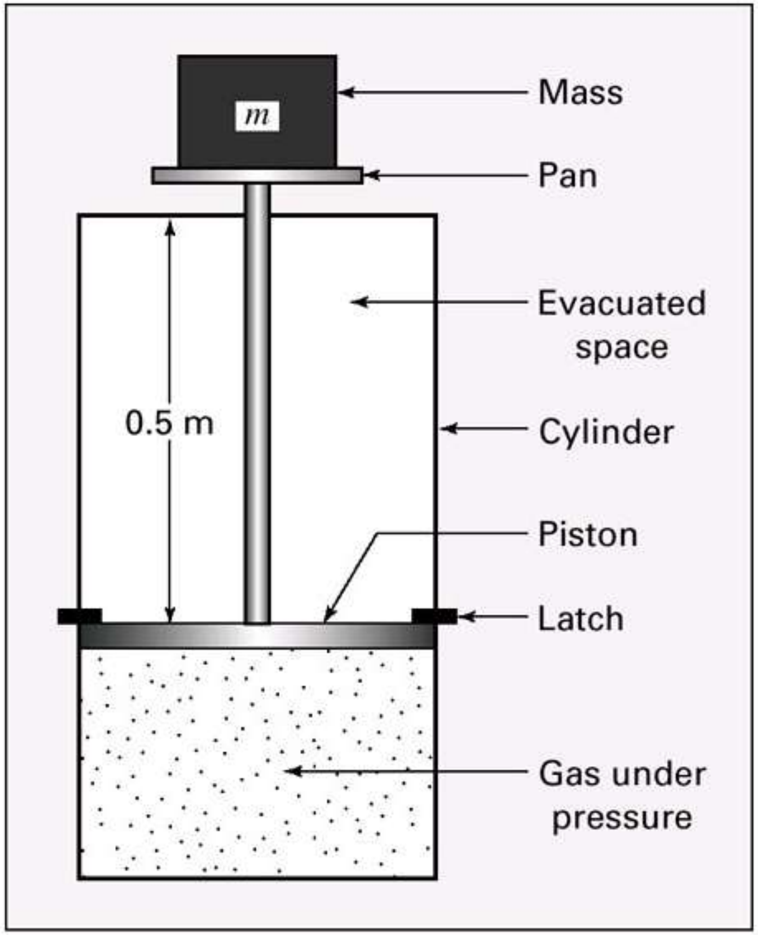
Adapted from Smith, Van Ness and Abbott, Introduction to Chemical Engineering Thermodynamics, 7th Ed, McGraw-Hill, p34

What happens if the bath T is increased or decreased differentially?

If ↑T ⇨ decomposition of $CaCO_3$ ⇨?

Process is reversible as long as system is NOT more than differentially displaced from equilibrium

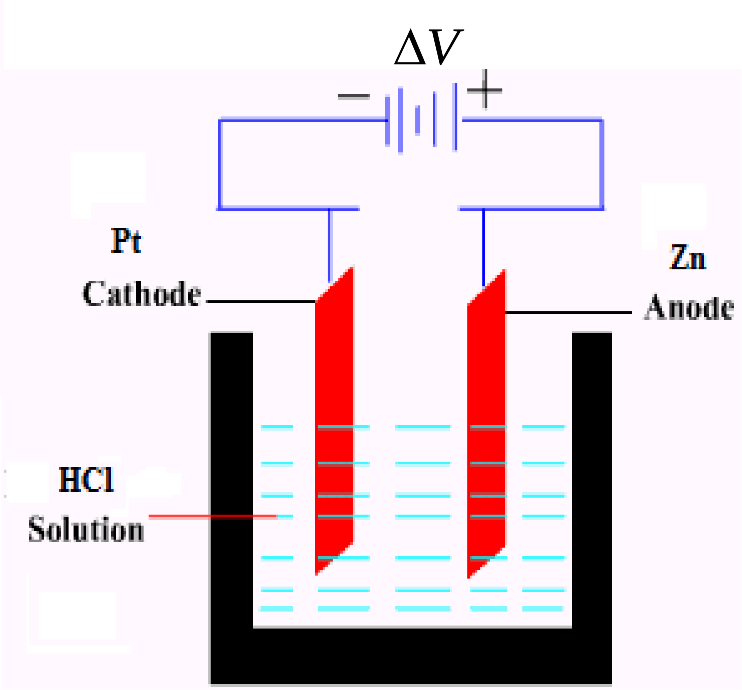
Example 2.7 (Ref: Smith,Van Ness, Abbott, 7th ed, p36)



Piston-cylinder arrangement contains nitrogen gas trapped below the piston at 7 bar. Piston is held in place by latches. Space above the piston is evacuated. A pan is attached to the piston rod and a mass *m* of 45 kg is fastened to the pan. Piston, rod and pan together are 23 kg. Latches holding the piston are released, allowing the piston to rise rapidly 0.5 m until it strikes the top of the cylinder . What are the energy changes ?

Adapted from Smith, Van Ness and Abbott, Introduction to Chemical Engineering Thermodynamics, 7th Ed, McGraw-Hill, p36

Equilibrium: Electrolytic cell



@constant T and P: anodic rxn

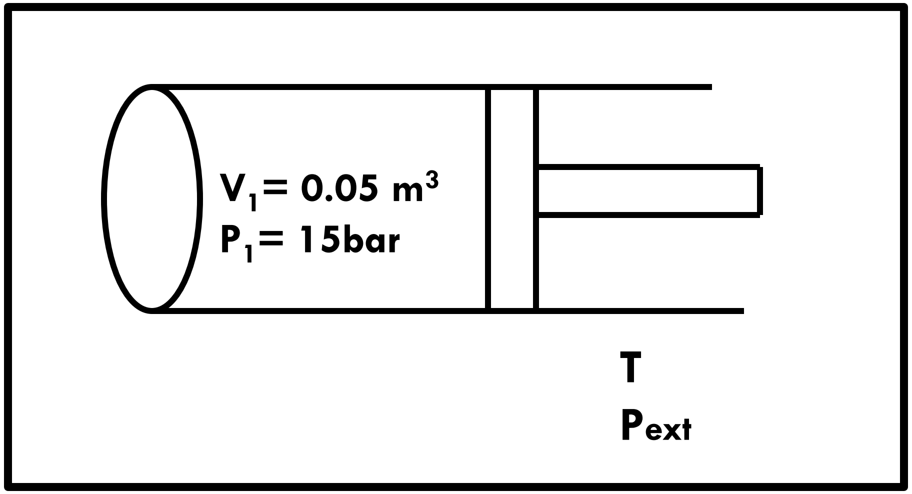
$$Zn+2HCl \rightleftarrows ZnCl_2+H_2$$

Electromotive force produced by cell

↓↑

Electric potential difference (ΔV) (voltage applied)

Example: Horizontal cylinder-piston system



@T: constant

if P$_{ext}$ decreases slowly;

$V_1 \rightarrow V_2=2V_1$ gradually

PV=k=constant, P=k/V

W=?

Assumptions:

- T is constant
- Friction is negligible

Example: Horizontal cylinder-piston system

For a mechanically reversible process:

$$W = -\int_{V_1}^{V_2} PdV = -k\int_{V_1}^{V_2} \frac{dV}{V} = -k\ln\frac{V_2}{V_1}$$

$$k = 15bar \times \frac{10^5\ N/m^2}{1bar} \times 0.05m^3 = 75000\,j$$

$$P_2 = \frac{k}{V_2} = \frac{75000\,j}{0.10m^3} = 75\times10^4\ N/m^2 = 75\times10^4\,Pa = 7.5bar$$

$$W = -75000\ln\frac{0.10}{0.05} = -51986\,j$$

Example: Horizontal cylinder-piston system

$W = ?$ if $P_{ext} \downarrow \Rightarrow P_{ext}/2$ <u>suddenly</u>

For an irreversible process; $V_2 = 2V_1$ sudden expansion

$$\boxed{W = -P\Delta V}$$

Work done aganist external force

=

Final external pressure*volume change

$$W = -(75\times10^4\,Pa)(0.10m^3 - 0.05m^3) = -37500\,j$$

$$\%efficiency = \frac{-37500\,j}{-51986\,j}\times100 = 72.13\%$$

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Problem 2.5 (Ref: Smith,Van Ness, Abbott, 7th ed, p56)

One mole of gas in a closed system undergoes a four-step thermodynamic cycle. Use the data given in the following table to determine numerical values for the missing quantities.

Step	ΔU [J]	Q [J]	W [J]
1→2	-200	?	-6 000
2→3	?	-3 800	?
3→4	?	-800	300
4→1	4 700	?	?
12341	?	?	-1 400

Problem 2.5 (Ref: Smith,Van Ness, Abbott, 7th ed, p56)

1→2 ΔU=Q+W =Q+-6000=-200 J Q=5800 J

3→4 ΔU=Q+W =-800+300=-500 J ΔU=-500 J

12341 ΔU=0, Q=-W 4→1 ΔU = 4700 J,

2→3 ΔU=0-(-200+-500+4700)=-4000 J W=-4000--3800=-200 J

Step	ΔU [J]	Q [J]	W [J]
1→2	-200	**5800**	-6 000
2→3	**-4000**	-3 800	**-200**
3→4	**-500**	-800	300
4→1	4 700	**200**	**4500**
12341	**0**	**1400**	-1 400

Constant-V and Constant-P Process

Energy balance for n moles of a homogeneous fluid contained in a closed system:

$$d(nU) = dQ + dW$$

Mechanically reversible, closed system:

$$dW = -Pd(nV)$$

Then

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

@ Constant-V

If V = cnst → $dV = 0$

for closed system $dn = 0$ → $dW = -Pd(nV) = 0$

Then

$$dQ = d(nU)$$

$$\int_1^2 dQ = \int_1^2 d(nU) \quad \rightarrow \quad Q = n\Delta U$$

Mechanically reversible, closed, <u>constant volume</u> system:

Heat transferred = Change in internal energy

@ Constant-P

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

@ cnst. P → $dQ = d(nU) + d(nPV) = d\left[n\left(U + PV\right)\right]$

Enthalpy $H \equiv U + PV$

$$dQ = d\left(nH\right)$$

$$\int_1^2 dQ = \int_1^2 d(nH) \quad \rightarrow \quad Q = n\Delta H$$

Mechanically reversible, closed, constant pressure system:

Heat transferred = Change in enthalpy

Enthalpy

- is used to calculate cooling and heating processes

(heat exchangers, evaporators, distillation columns, pumps, turbines, engines, etc)

- appears in energy balances to calculate Q and W

Enthalpy is a state function as U, P and V: $H \equiv U + PV$

$$dH = dU + d(PV)$$

$$\int_1^2 dH = \int_1^2 d(U) + \int_1^2 d(PV) \Rightarrow \Delta H = \Delta U + \Delta(PV)$$

Ex: Enthalpy of moist and humid air → sensible heat + latent heat

Example 2.8(Ref: Smith,Van Ness, Abbott, 7th ed, p39)

Calculate ΔU and ΔH for 1 kg of water when it is vaporized at 100 °C and 101.33 kPa. Specific volumes of liquid and vapor water at these conditions are 0.00104 and 1.673 m^3/kg.

2256.9 kJ of heat is added to water for it to vaporize.

Solution:

System: 1 kg water @ constant T

Assumption: Mechanically reversible, closed, constant P system

$\Delta H = Q = 2256.9$ kJ

$\Delta H = \Delta U + \Delta(PV) \rightarrow \Delta U = \Delta H - P\Delta V$

$P\Delta V = 101.33\ \text{kPa} * (1.673\text{-}0.00104)\ m^3 = 169.4\ \text{kJ}$

$\Delta U = 2256.9 - 169.4 = 2087.5$ kJ

Heat capacity

- Heat → Energy in transit, so a body has **capacity for heat**
- The smaller the change in T in a body

caused by the transfer of a given quantity of heat, the greater its capacity

$$C \propto \frac{dQ}{dT}$$

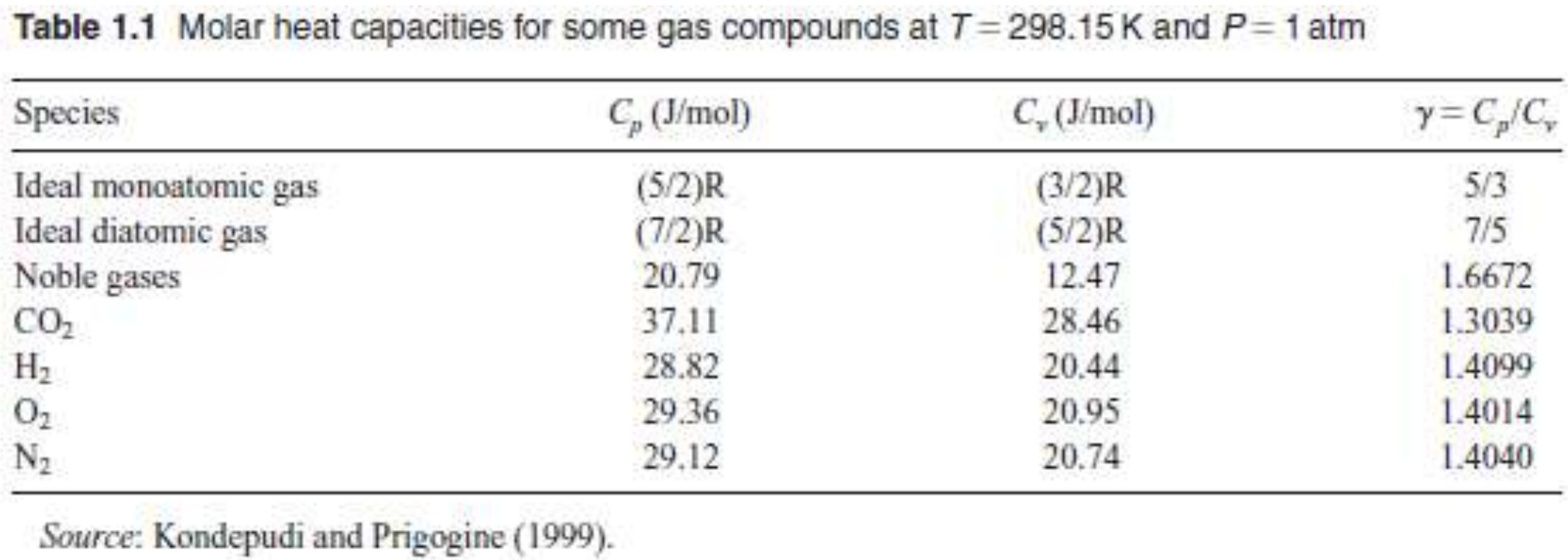


Table 1.1 Molar heat capacities for some gas compounds at $T = 298.15$ K and $P = 1$ atm

Species	C_p (J/mol)	C_v (J/mol)	$\gamma = C_p/C_v$
Ideal monoatomic gas	(5/2)R	(3/2)R	5/3
Ideal diatomic gas	(7/2)R	(5/2)R	7/5
Noble gases	20.79	12.47	1.6672
CO_2	37.11	28.46	1.3039
H_2	28.82	20.44	1.4099
O_2	29.36	20.95	1.4014
N_2	29.12	20.74	1.4040

Source: Kondepudi and Prigogine (1999).

Heat capacity @ constant V

By definition

$$C_v \equiv \left(\frac{\partial U}{\partial T}\right)_v$$

For a constant volume process in a closed system

$$dU = C_v dT \qquad \Delta U = \int_{T_1}^{T_2} C_v dT$$

For a mechanically reversible, constant volume process in a closed system

$$Q = n\Delta U = n\int_{T_1}^{T_2} C_v dT$$

Heat capacity @ constant P

By definition

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

For a constant pressure process in a closed system

$$dH = C_p dT \qquad \Delta H = \int_{T_1}^{T_2} C_p dT$$

For a mechanically reversible, constant pressure process in a closed system

$$Q = n\Delta H = n\int_{T_1}^{T_2} C_p dT$$

Elements of a Thermodynamic Cycle

- Working Substance - medium by which energy is carried through the cycle
- Heat Source - supplies thermal energy to the working substance
- Heat Sink - absorbs heat from the working substance
- Pump - circulates the working substance; acts as a valve between low and high pressure
- Engine - device which converts the thermal energy of the working substance into useful mechanical energy

General mass and energy balances

Open systems: Matter and energy are exchanged through boundary
Most industrial processes → open systems

Mass flow rate	$\dot{m}$	**kg/s or lb/s**	$\dot{m} = M\dot{n}$
Molar flow rate	$\dot{n}$	gmole/s or lbmole/s	$\dot{m} = uA\rho$
Volumetric flowrate	q	m^3/s or ft^3/s	$Q = uA$
Velocity	u	m/s or ft/s	

- Velocity → vectorial quantity
- Speed = Average velocity and a scalar quantity

Control Volume (Open System)

Difference between Control Mass and and Control Volume:

Mass crosses the system boundary of a control volume.

Control volume: A region in space that may be moving or changing shape.

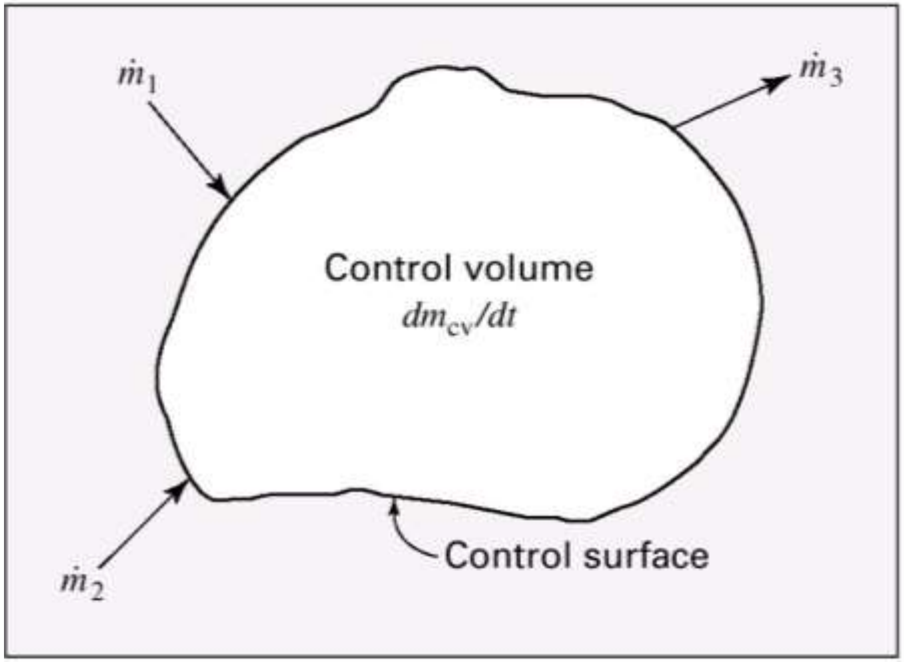
The control volume approach is used for many engineering problems where a mass flow rate is present:

- turbines, pumps and compressors
- heat exchangers
- nozzles and diffusers, etc.

Mass balance for open systems

Control volume (cv) is a region for analysis of an open system

Control surface (cs) separates the control volume from its surroundings



Adapted from Smith, Van Ness and Abbott, Introduction to Chemical Engineering Thermodynamics, 7th Ed, McGraw-Hill, p46

Mass Balance

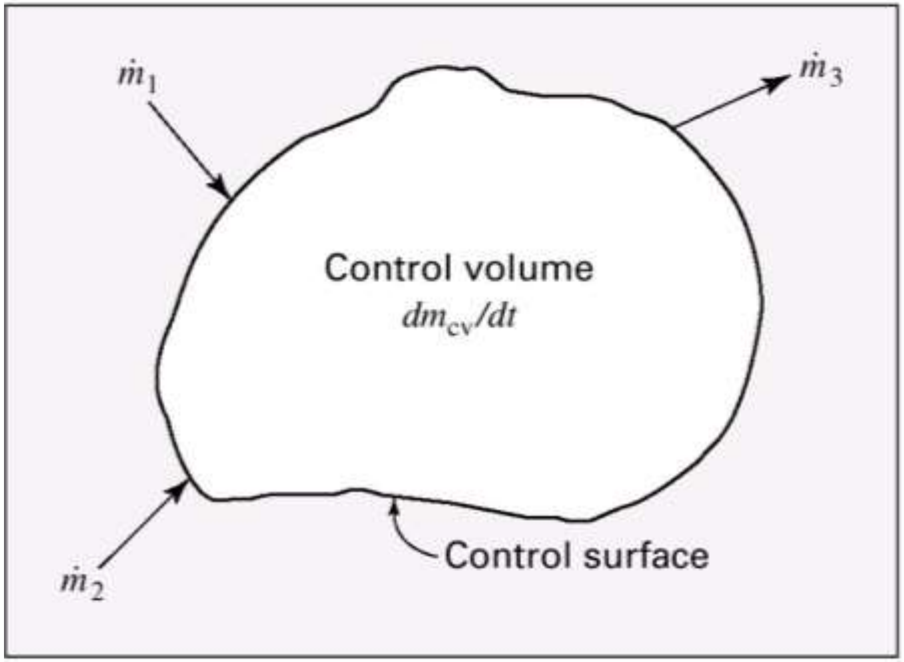
Continuity equation

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

$$\dot{m} = uA\rho$$

$$\frac{dm_{cv}}{dt} + \Delta(\rho uA)_{fs} = 0$$

$$\frac{dm}{dt} + \Delta(\dot{m})_{fs} = 0$$



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Steady flow process: Conditions within control volume do not change with time, there is no accumulation $dm/dt = 0$

General Energy Balance

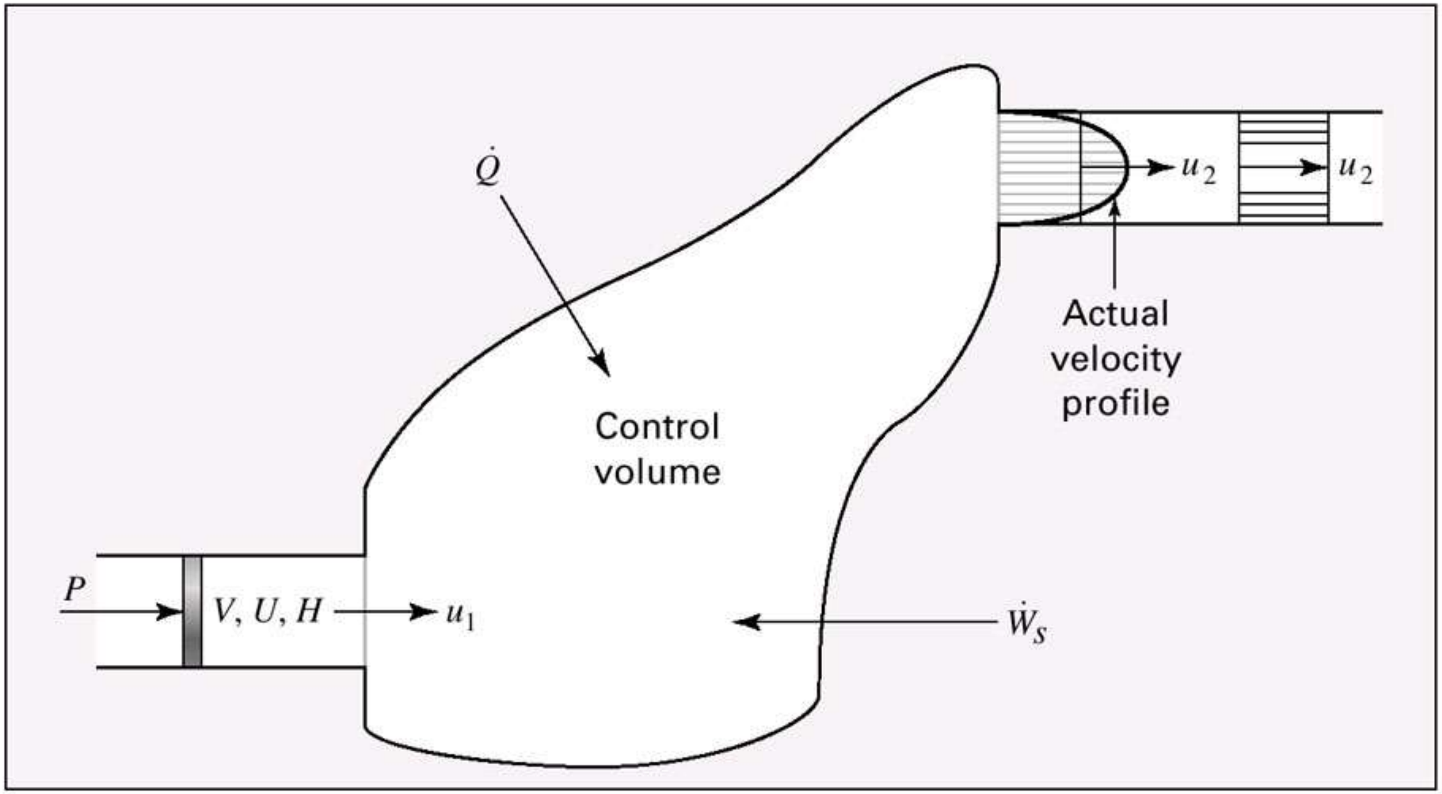
$$\Delta(\rho u A)_{fs} = 0, \quad u_2 A_2 \rho_2 - u_1 A_1 \rho_1 = 0, \quad \dot{m} = \frac{u_1 A_1}{V_1} = \frac{u_2 A_2}{V_2} = \frac{uA}{V}$$

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

Work may be in several forms:

- ☐ Flow work or Boundary work : $\Delta\left[(PV)\dot{m}\right]_{fs}$
- ☐ Shaft work: $\dot{W}_s$

Control volume with one entrance-exit



Adapted from Smith, Van Ness and Abbott, Introduction to Chemical Engineering Thermodynamics, 7th Ed, McGraw-Hill, p47

Control volume with one entrance-exit

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

or in terms of enthalpy H; $H = U + PV$

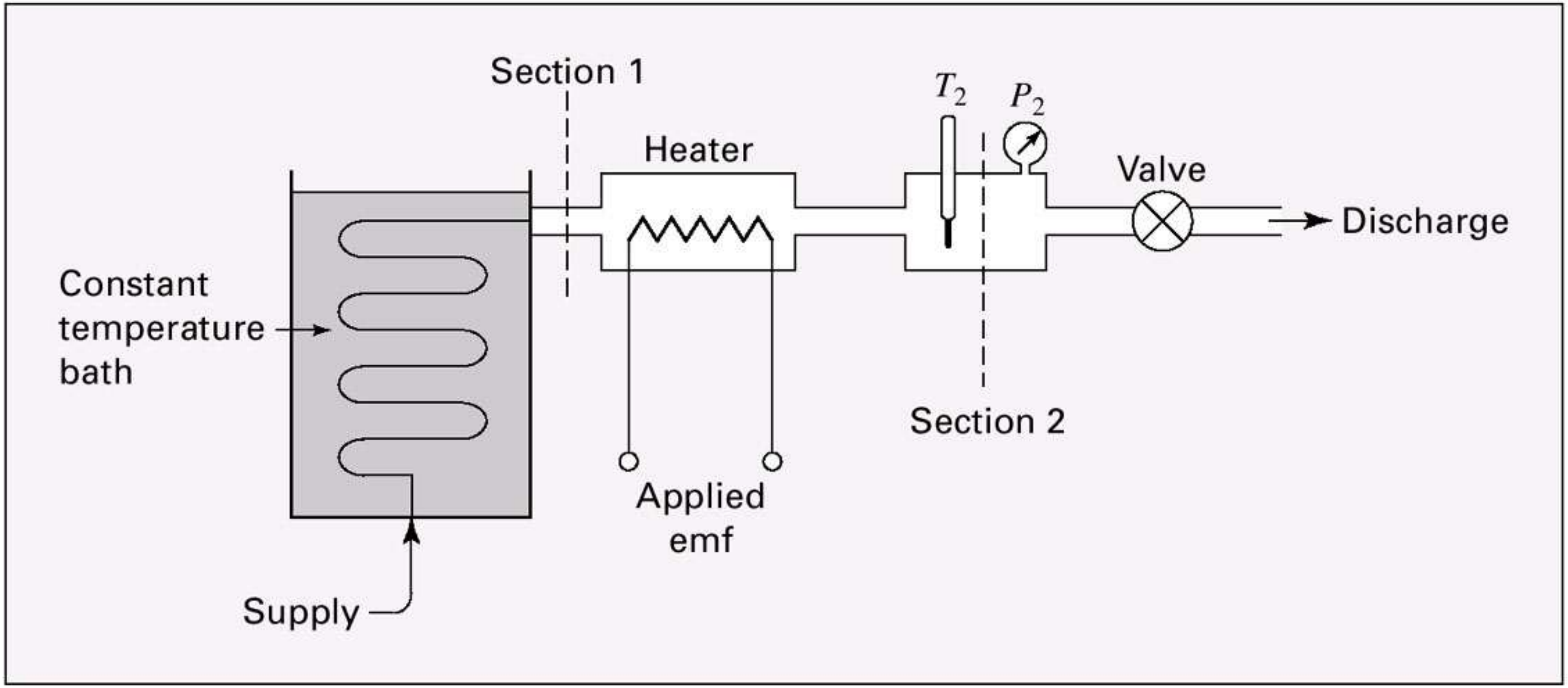
$$\frac{d(mU)_{cv}}{dt} = -\Delta\left[\left(H+\frac{1}{2}u^2+zg\right)\dot{m}\right]_{fs} + \dot{Q} + \dot{W}_s$$

For most chemical engineering operations:

kinetic energy KE and potential energy PE are negligible, then

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

Flow Calorimeter for Enthalpy Measurements



Adapted from Smith, Van Ness and Abbott, Introduction to Chemical Engineering Thermodynamics, 7th Ed, McGraw-Hill, p52

Entropy

- Entropy change

$$dS = \frac{\delta q_{\mathrm{rev}}}{T}$$

δq_{rev} : Reversible heat flow

- When a fluid system changes from state A to state B by an irreversible process:
- Change of its entropy is $\Delta S = S_B - S_A$

Entropy is a state function and an extensive property

Properties of entropy

- To determine entropy, we need to know the measured enthalpy
- Then use the relation:

$$T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P = C_p$$

- For a single phase, $dS \geq q/T$
  - inequality is for a natural change
  - equality is for a reversible change
- Change of entropy is expressed as $dS = d_eS + d_iS$ where $d_eS = q/T$ is the change due to the interaction of a system with its surroundings
  - d_iS is the increase due to a natural change (ex: a chemical reaction) within the system
  - d_iS is always positive for irreversible changes ($d_iS > 0$) and zero at equilibrium ($d_iS = 0$).