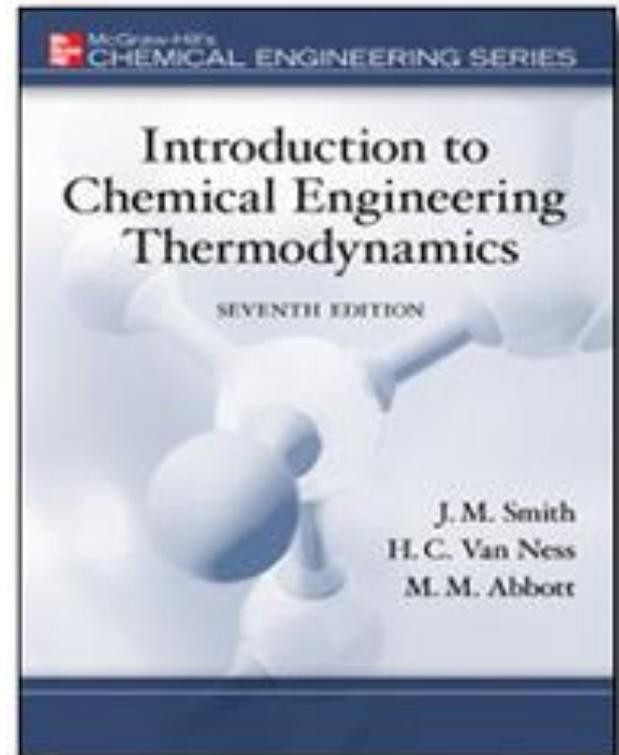


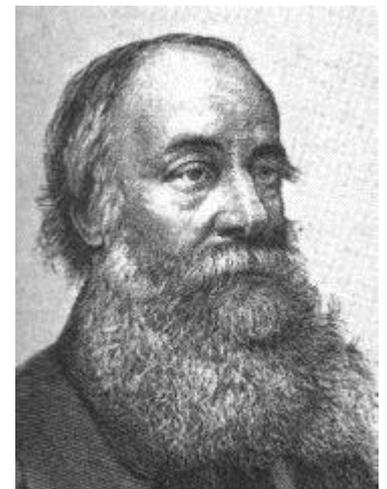
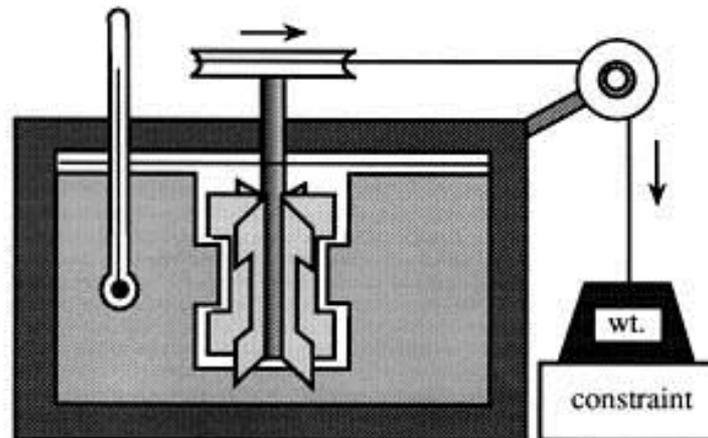
Chapter 2. The First Law and Other Basic Concepts



2.1 Joule's Experiments

□ James P. Joule (1818-1889)

- First experiment to understand the heat and its relation to work and energy (1840)
- Amount of work and temperature changes of the fluid were measured
- Proved that there is a close relationship between heat and energy
- Heat is a form of energy



2.2 Internal Energy

- ❑ **What happened to the energy added to the fluid as work ?**
 - **Contained in another form → internal energy**

- ❑ **Internal Energy**
 - **Do not include the energy due to macroscopic position or movement
→ energy of molecules internal to the substance**

 - **Molecules possess due to ceaseless motion**
 - Kinetic energy of translation
 - Kinetic energy of rotation
 - Kinetic energy of vibration

 - **Internal energy has no concise thermodynamic definition**
 - Cannot be measured directly
 - Only changes are measured and used

2.3 The First Law of Thermodynamics

□ Difference between “Energy” and “Heat and Work”

● Energy

- Can be stored
- Forms : Internal / Potential / Kinetic

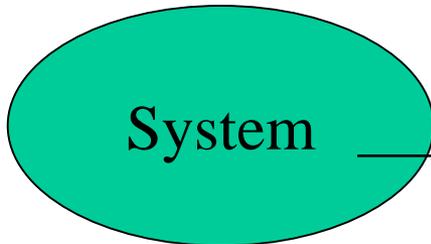
● Heat and Work

- Energy in transit across the boundary
- Never contained in the body or system

The First Law of Thermodynamics

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.

Surroundings → Everything with which the system interacts

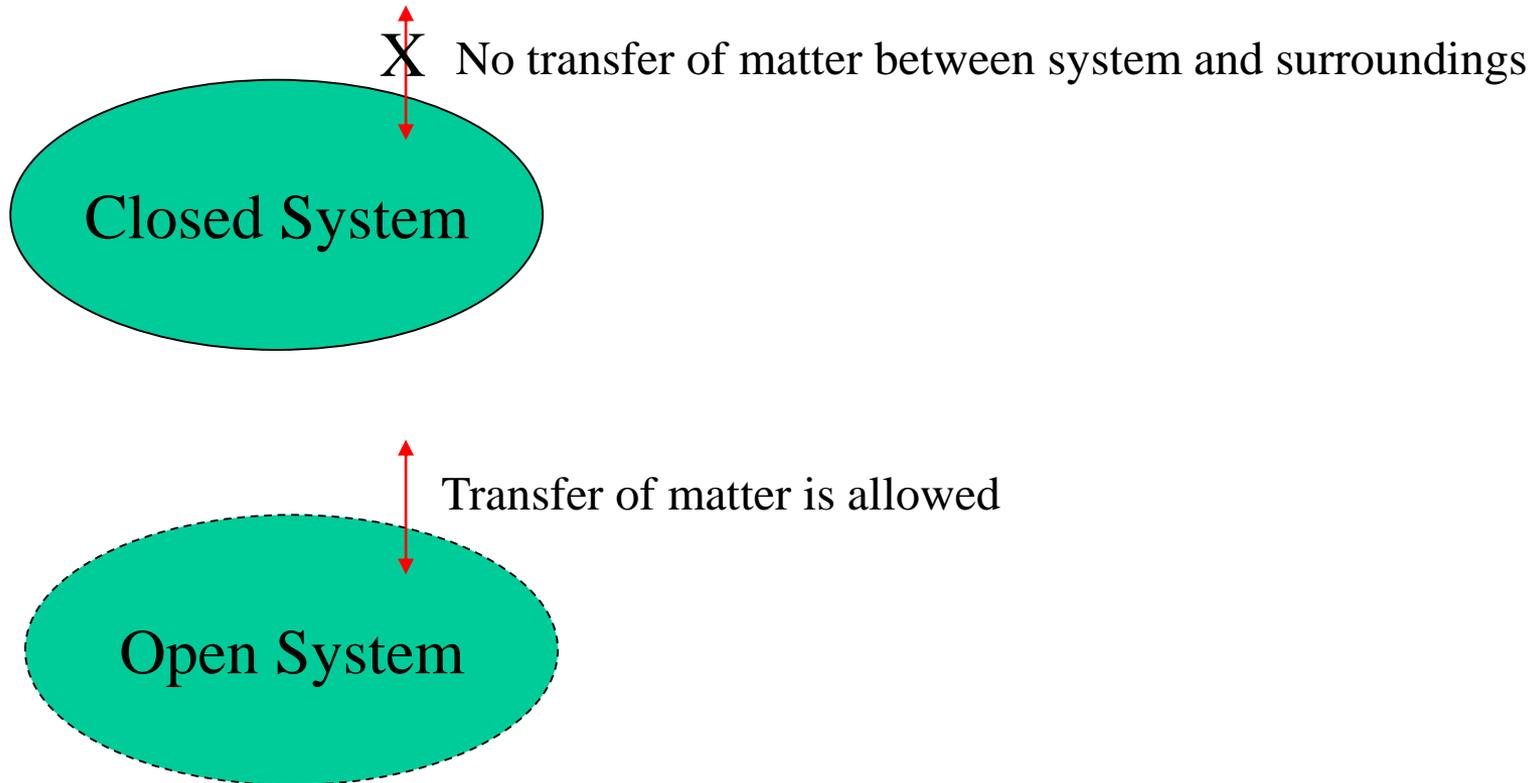


→ The region in which the process occurs

$$\Delta(\text{Energy of the system}) + \Delta(\text{Energy of Surroundings}) = 0$$

2.4 Energy Balance for Closed Systems

□ “Closed System”



Energy Balance for Closed Systems

□ Energy Balance Equation

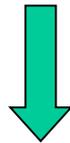
$$\Delta E \text{ (Energy of surroundings)} = \pm Q \pm W$$

□ Convention for W and Q

- When there is an increase in energy then sign is +

$$\Delta E \text{ (Energy of surroundings)} = -Q - W$$

$$\Delta E \text{ (Energy of the system)} = +Q + W$$



*No kinetic and potential energy change
(many cases of closed system)*

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

$$dU^t = dQ + dW$$

Intensive and Extensive Properties

□ Types of Properties

- Extensive Properties : Depends on system size

$$n, m, V^t = nV, U^t = nU, \dots$$

- Intensive Properties : Does not depend on system size

$$T, P, V, U$$

Although V^t and U^t for a homogeneous system of arbitrary size are *extensive properties*, specific and molar volume V and specific and molar internal energy U are *intensive*

The First Law of Thermodynamics

$$\text{For } n = 1 \quad \Delta U = Q + W \quad dU = dQ + dW$$

- **Property Relation** : connects U to measurable properties
 - U : not measurable
 - Q and W : measurable
- **No absolute value for U**
- **The relation provide means to calculate changes in U**

There exists a form of energy, known as **internal energy U , which is an intrinsic property of a system, functionally related to the measurable coordinates which characterize the system. For a closed system, not in motion, the changes in property are given by above equation.**

Example 2.1

- Water flows over a waterfall 100 m in height. Take 1 kg of the water as the system, and assume that it does not exchange energy with its surroundings.**
 - (a) What is the potential energy of the water at the top of the falls with respect to the base of the falls?**
 - (b) What is the kinetic energy of the water just before it strikes bottom?**
 - (c) After the 1 kg of water enters the stream below the falls, what change has occurred in its state?**

Example 2.1 - solution

Energy balance become $\Delta(\text{Energy of the system}) = \Delta U + \Delta E_K + \Delta E_P = 0$

2.5 Thermodynamic State and State Function

□ State Functions and Path Functions

● State functions (properties)

- The value itself does not depend on the past history of substances nor means (path).
- Only depends on present condition, however reached
- Changes are represented by difference of two values
- Example) Specific Volume (V) or density, Internal Energy

$$\int_{V_2}^{V_1} dV = V_2 - V_1 = \Delta V \quad \int_{U_2}^{U_1} dU = U_2 - U_1 = \Delta U$$

● Path function (properties)

- Value depend on the nature of the process causing the change
- Represented as area rather than a point
- Example) Heat and Work

$$\int dQ = Q \quad \int dW = W \quad \int \delta Q = Q \quad \int \delta W = W$$

Thermodynamic State and State Function

□ Example of state function and path function

- **Total (or contour) distance from Seoul to Pusan : Path Function**

- Depending on the path taken (which highway?)

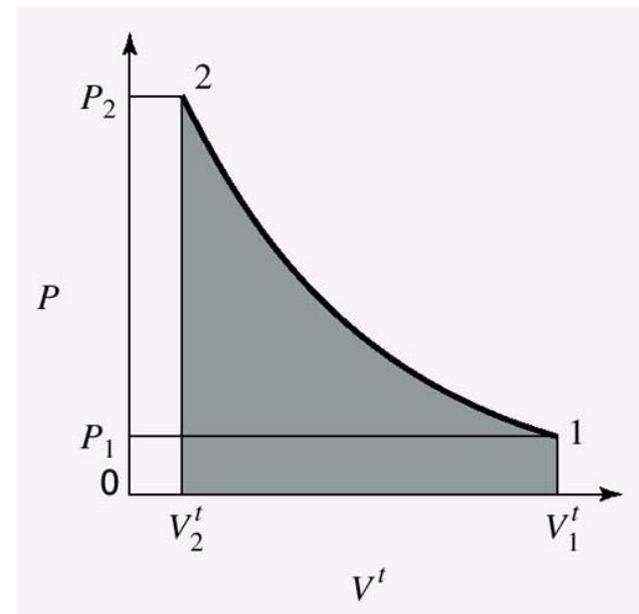
- **Direct distance from Seoul to Pusan : State Function**

- Independent of path

□ Graphical Representation

- **Path Function : Area (Work)**

- **State Function : Point (P and V)**



Notation of Other Books

- ❑ For some books, the first law of thermodynamics is written as;

$$dU = dQ - dW$$

—————> Work is + sign when system does work.

This type of sign convention **is not recommended** by **IUPAC** (International Union of Pure and Applied Chemistry)

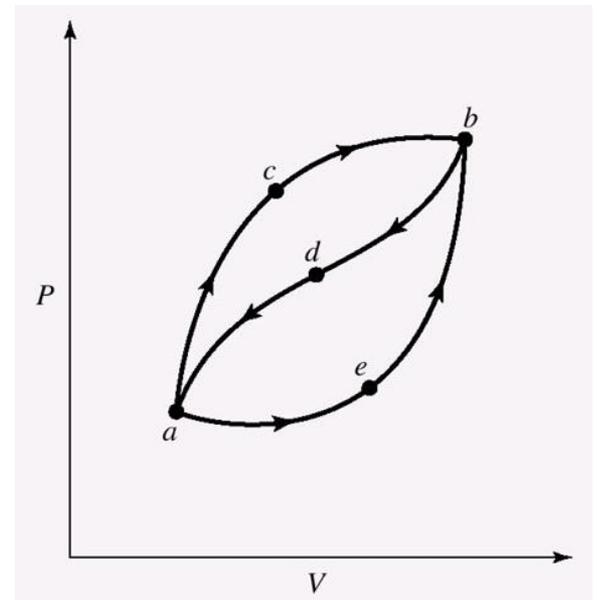
- ❑ To discriminate state function and path function,

$$dU = \delta Q - \delta W$$

δ means integration depends on the path

Example 2.4

- When a system is taken from state a to state b in Figures 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?



Example 2.4 - solution

For path *acb* and any path from *a* to *b*,

$$\Delta U = Q_{acb} + W_{acb} = 100 - 40 = 60 \text{ J}$$

2.6 Equilibrium

□ “Equilibrium”

- Static condition : Absence of change (with time)
- Absence of any tendency toward change on macroscopic scale
- Equivalent to say “**thermodynamically stable**”
- To find the equilibrium property → measure until the property doesn’t change with time

□ Changes are caused by → driving forces

- Imbalance in mechanical forces : energy transfer as work
- Temperature difference : energy transfer as heat
- Gradient in chemical potential : transfer of substance from one phase to another

2.7 The Phase Rule

□ Variables

- **Intensive variables : Does not depend on system size**

- $T, P, x, y, H, S, V, \dots$

- **Extensive variables : Depend on system size**

- *Total flow rate (molar, mass), nV, nH, nS, nU, \dots*

□ Degree of Freedom

- **Number of independent variables (variance)**

□ Gibbs Phase Rule : Josiah Willard Gibbs

- **Relation between the number of independent *intensive variables* at equilibrium**

(for multiphase and nonreactive system)

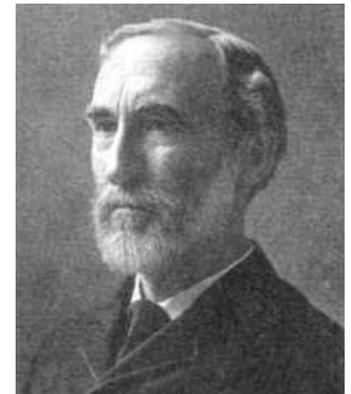
$$F = 2 - \pi + N$$

N : Number of components at equilibrium

π : Number of phases at equilibrium

- **Phase rule for reactive system**

- Page 514 - 515



Derivation of Gibbs Phase Rule

□ Degree of Freedom

- $F = V - E$
- V : number of variables, E : number of equations

□ Number of Variables

- $V = N*\pi + 2$
- Temperature and Pressure (2) + Compositions at Each Phase ($N*\pi$)

□ Number of Equations

- $E = \pi + N(\pi - 1)$
- Sum of mole fractions should be equal to 1 : π
- Equilibrium relation (equality of chemical potential) : $N(\pi - 1)$

$$\sum_{i=1}^C x_i = 1$$
$$\sum_{i=1}^C y_i = 1$$
$$\vdots$$

$$\mu_i^L = \mu_i^V$$

Examples of Gibbs Phase Rule

□ Pure Water

- $F = 2 + 1 - 1 = 2$

□ Mixture of Ice and Water

- $F = 2 + 1 - 2 = 1$

□ VLE of acetone + nitrogen

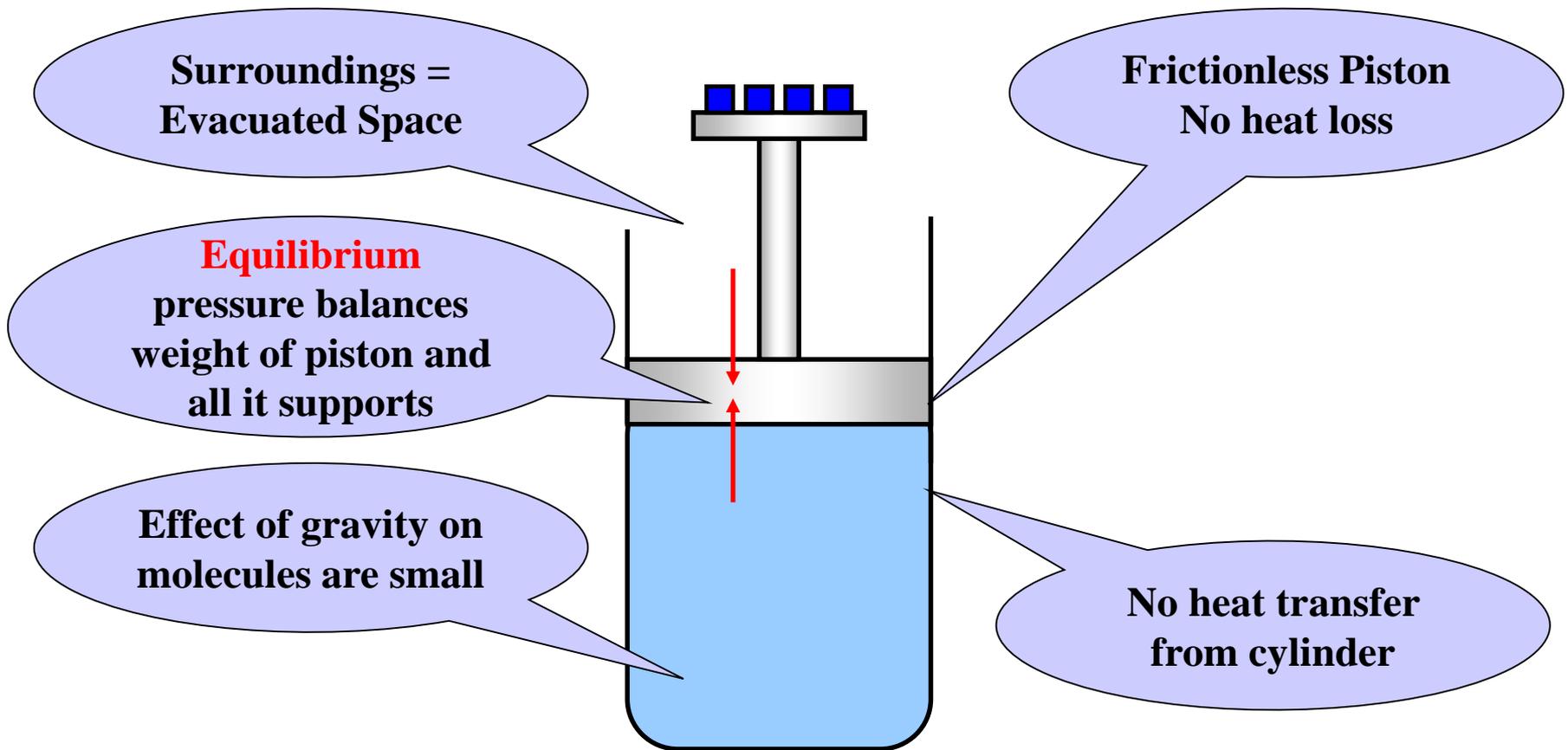
- $F = 2 + 2 - 2 = 2$

2.8 *The Reversible Process*

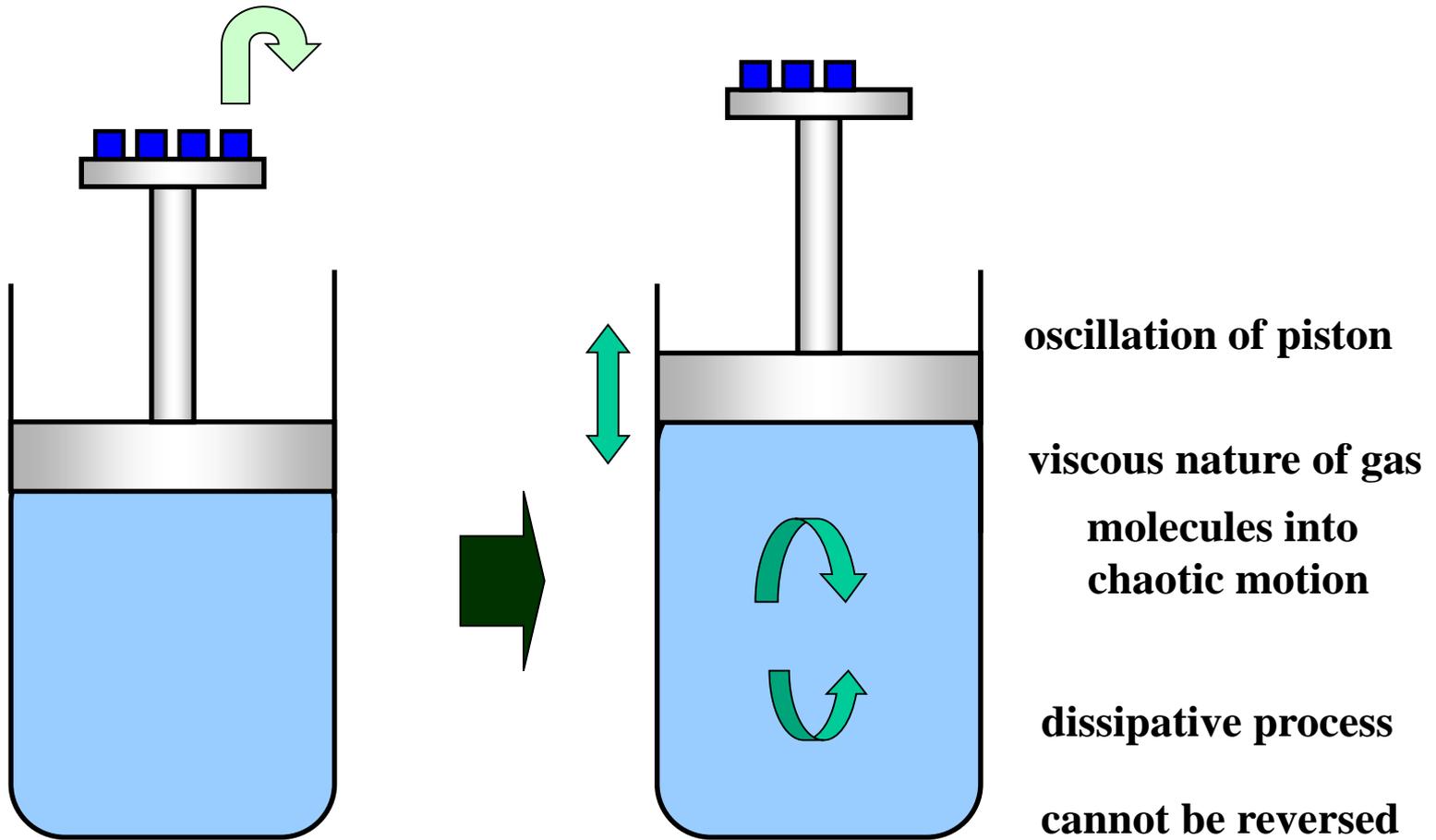
A process is *reversible* when its direction can be reversed at any point by an infinitesimal change in external conditions

Reversible Expansion of a Gas

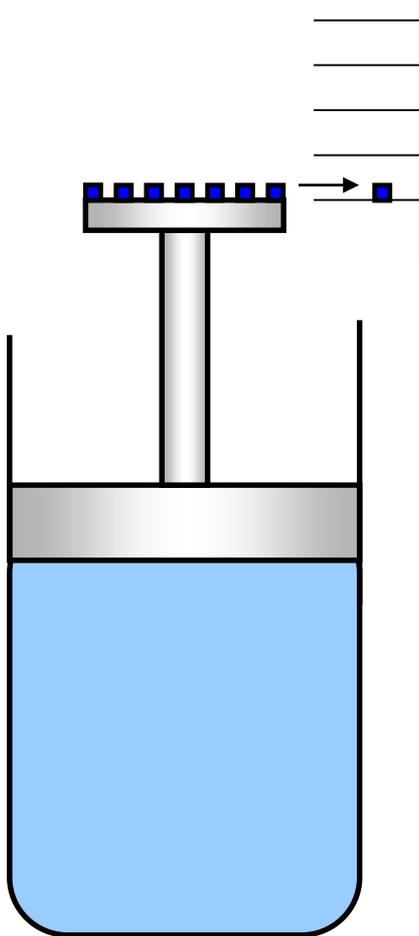
□ Imaginary Piston / Cylinder Assembly



Irreversible Process



Reversible Process



- Imaginary process – free of dissipative effects**
- Mass – infinitesimal**
- Process can be reversed forward and backward**

Reversible Process

- ❑ Is frictionless
- ❑ Is never more than differentially removed from equilibrium
- ❑ Traverses a succession of equilibrium states
- ❑ Is driven by forces whose imbalance is differential in magnitude
- ❑ Can be reversed at any point by differential change in external conditions
- ❑ When reversed, retraces its forward path, and restores initial state of system and surroundings

reversible process

$$dW = -PdV^t \quad \longrightarrow \quad W = -\int_{V_1^t}^{V_2^t} PdV^t$$

Sum of infinitesimal reversible process

Reversible Process

- ❑ In thermodynamics, a reversible process is a process that can be "reversed" by means of infinitesimal changes in some property of the system without loss or dissipation of energy.
- ❑ Due to these infinitesimal changes, the system is at rest throughout the entire process. Since it would take an infinite amount of time for the process to finish, perfectly reversible processes are impossible.

$$dW = -PdV^t \xrightarrow{\text{reversible process}} W = -\int_{V_1^t}^{V_2^t} PdV^t$$

Sum of infinitesimal
reversible process
(Integrable)

(From Wikipedia.com)

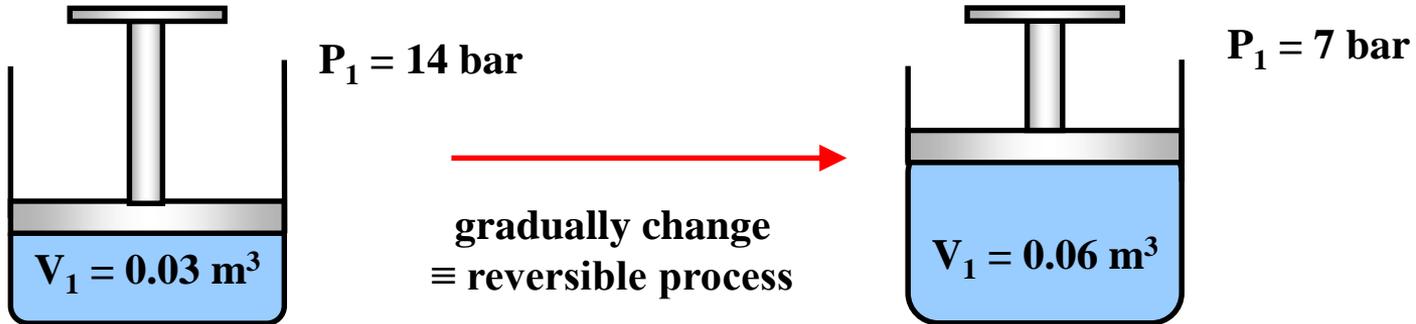
Example 2.6

- **A horizontal piston/cylinder arrangement is placed in a constant T bath. The piston slides in the cylinder with negligible friction, and an external force holds it in place against an initial gas pressure of 14 bar. The initial gas volume is 0.03 m³. The external force on the piston is reduced gradually, and the gas expands isothermally as its volume doubles.**

If the volume of the gas is related to its pressure so that the product PV^t is constant, what is the work done by the gas in moving the external force?

How much work would be done if the external force were suddenly reduced to half its initial value instead of being gradually reduced?

Example 2.6 - solution



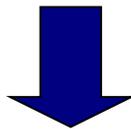
2.9 Constant- V and Constant- P Processes

- Energy balance for a homogeneous closed system of n mole

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

- Mechanically reversible, closed system

$$dW = -pd(nV)$$



$$d(nU) = dQ + dW = dQ - pd(nV)$$

Constant-Volume Process

- No change in total volume ($d(nV) = 0$)

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

$$dQ = d(nU)$$

$$Q = n\Delta U$$

Heat transfer is equal to internal-energy change of the system

Constant-Pressure Process

- For constant-pressure change of state

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

- Definition of Enthalpy

$$H \equiv U + PV$$

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

- For constant P process

$$d(nH) = d(nU) + Pd(nV) + \cancel{nVdP} = d(nU) + Pd(nV)$$

$$dQ = d(nH)$$

$$Q = n\Delta H$$

2.10 Enthalpy

□ Energy balances for industrial applications

- Heat Exchanger/Evaporator/Distillation Column
/Pump/Compressor/Turbine/Engine**
- Require Heat and Work Calculation**
- Constant P process – flow processes**
- Infinite array of possible heat and work is impossible**
- Instead tabulation of enthalpy values can be useful**

□ Enthalpy is also state function

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

$$\Delta H = \Delta U + \Delta(PV)$$

2.11 Heat Capacity

□ Effect on body when heat is transferred

- Capacity for heat

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

- $Q \rightarrow$ Process dependent quantity
- It is more convenient to use other state function

Heat Capacity at Constant Volume

- The constant-volume heat capacity

$$C_v \equiv \left(\frac{dU}{dT} \right)_v$$

- For constant volume process,

$$dU = C_v dT$$

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

For the calculation of property changes, an actual process may be replaced by any other process which accomplishes the same change in state

Heat Capacity at Constant Pressure

- The constant-pressure heat capacity

$$C_P \equiv \left(\frac{dH}{dT} \right)_P$$

- For constant **pressure** process,

$$dH = C_P dT$$

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

Example 2.9

- Air at 1 bar and 298.15 K (25 °C) is compressed to 5 bar and 298.15 K by two different mechanically reversible processes.
 - (a) Cooling at constant P followed by heating at constant V.
 - (b) Heating at constant V followed by cooling at constant P.
- Calculate the heat and work requirements and ΔU and ΔH of the air for each path.

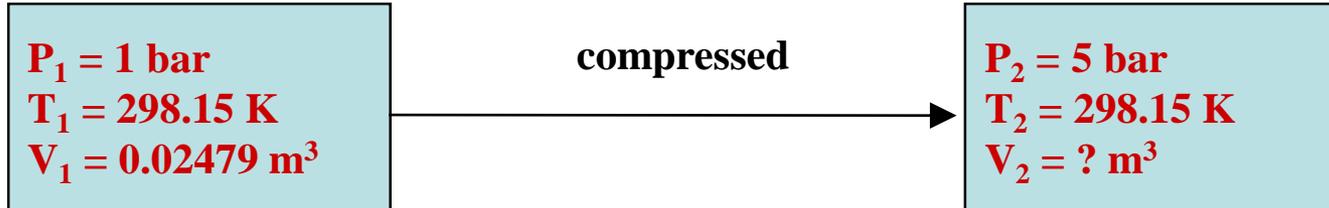
The following heat capacities for air may be assumed independent of temperature

$$C_v = 20.78 \text{ and } C_p = 29.10 \text{ J/mol K}$$

Assume also 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 $0.02479 \text{ m}^3/\text{mol}$.

Example 2.9 - solution



2.12 Mass and Energy Balance for Open Systems

□ Measures of flow

mass flow rate \dot{m}

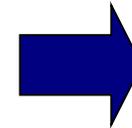
molar flow rate \dot{n}

volumetric flow rate q

velocity u

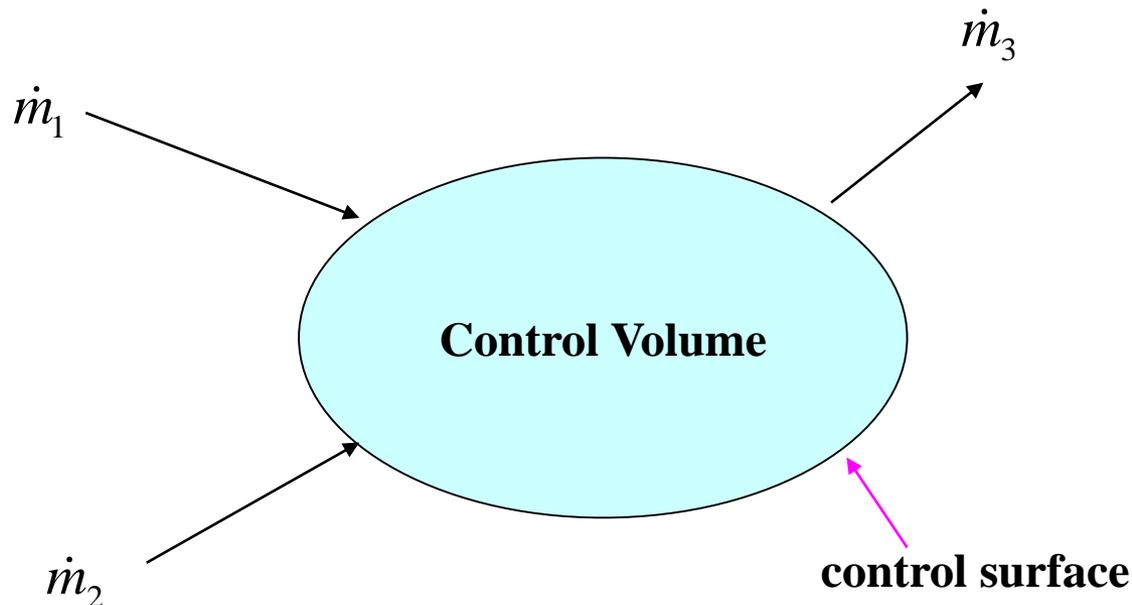
$$\dot{m} = M\dot{n}$$

$$q = uA$$



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

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



Mass Balance for Open Systems

□ Mass balance for open system

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

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

$$\frac{dm_{cv}}{dt} + \Delta(\rho u A)_{fs} = 0 \longrightarrow \text{Often called "Continuity equation"}$$

□ **Steady State** : no accumulation term

$$\Delta(\rho u A)_{fs} = 0$$

□ Only single entrance and single exit stream

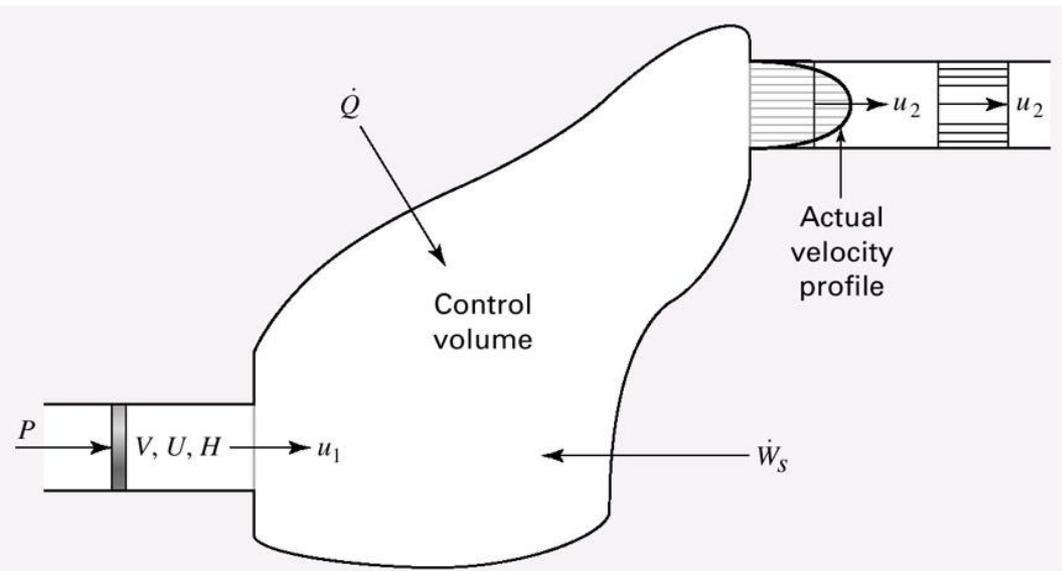
$$(\rho u A)_2 - (\rho u A)_1 = 0$$

$$\dot{m} = (\rho u A)_2 = (\rho u A)_1 = \text{const}$$

The General Energy Balance

- Net rate of change of energy within control volume equals the net rate of energy transfer into control volume

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



PV work

**Stirring work
Shaft work**

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

$$\frac{d(mU)_{cv}}{dt} + \Delta \left[\left(H + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W} \quad (2.28)$$

The velocity u in the kinetic-energy terms of energy balances is the bulk-mean velocity as defined by the equation, $u = \dot{m}/\rho A$. Fluids flowing in pipes exhibit a velocity profile, as shown in Fig. 2.6, which rises from zero at the wall (the no-slip condition) to a maximum at the center of the pipe. The kinetic energy of a fluid in a pipe depends on its velocity profile. For the case of laminar flow, the profile is parabolic, and integration across the pipe shows that the kinetic-energy term should properly be u^2 . In fully developed turbulent flow, the more common case in practice, the velocity across the major portion of the pipe is not far from uniform, and the expression $u^2/2$, as used in the energy equations, is more nearly correct.

The General Energy Balance

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

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



**kinetic and potential energy
changes are negligible**

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

W_s – Shaft work?

- **Shaft work : work done on the system by a moving part within the system**
 - **Components such as turbines, pumps, and compressors – all operate by energy transfer to or from the working-fluid**
 - **Energy transfer usually through blades rotating on a shaft**
 - **Also fluid dynamics problem...**



Energy Balances for Steady-State Flow Processes

□ **Steady state : no accumulation term**

$$\Delta \left[\left(H + \frac{1}{2} u^2 + z g \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}_s$$

Only shaft work
No stirring work for steady-state

$$\Delta \left(H + \frac{1}{2} u^2 + z g \right) = Q + W_s$$



**kinetic and potential energy
changes are negligible**

$$\Delta H = Q + W_s$$

Example 2.14

- 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 $m = 0.2$ kg/s, how long will it take for the temperature of the water in the tank to drop from 60 to 35 °C? Assume cold water enters the tank at 10 °C, and negligible heat losses from the tank. For liquid water let $C_v = C_p = C$, independent of T and P.

Example 2.14 - solution

Energy balance become

$$\frac{d(mU)_{cv}}{dt} + \Delta(H\dot{m})_{fs} = \dot{Q} + \dot{W} \longrightarrow m \frac{dU}{dt} + \dot{m}(H - H_1) = 0$$

Example 2.16

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

Example 2.16 - solution

Energy balance

$$\Delta \left(H + \frac{1}{2} u^2 + zg \right) = Q + W_s \quad \longrightarrow \quad Q = \frac{1}{2} u_2^2 - W_s$$

Homework

Problems

- 2.1, 2.6, 2.12, 2.28, 2.31, 2.32, 2.34

- Due:

Recommend Problems

- 2.5, 2.10, 2.18, 2.24, 2.25, 2.27, 2.30, 2.36, 2.42