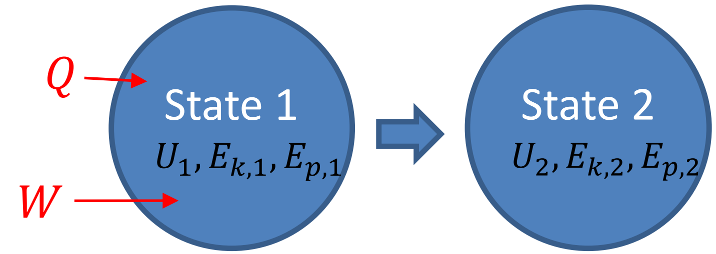
First law

Thermodynamic First Law

- **Energy in the universe is constant**

$$E_{univ,1} = E_{univ,2}$$
$$\Delta E_{univ} = 0\ (\Delta = final - initial)$$
$$\Delta E_{sys} + \Delta E_{surr} = 0$$
$$\Delta E_{sys} = E\ from\ surroundings\ into\ the\ system$$



$$U_1 + E_{k,1} + E_{p,1} + Q + W = U_2 + E_{k,2} + E_{p,2}$$

- **Energy**
  - (1) Kinetic energy, $E_k = \frac{1}{2} m\bar{V}^2$
    - E from the bulk(macroscopic) motion of the system
  - (2) Potential energy, $E_p = mgz$
    - E from the bulk(macroscopic) position of the system
  - (3) Internal energy, U
    - E from the motion, position and interaction of the molecules of the substances within the system

$$\Delta U = U_2 - U_1$$
$$\Delta E_k = E_{k,2} - E_{k,1}$$
$$\Delta E_p = E_{p,2} - E_{p,1}$$

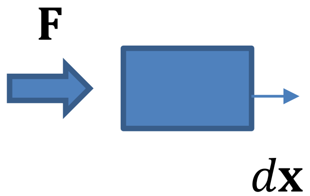
$$\Delta U + \Delta E_k + \Delta E_p = Q + W$$

First law (closed system)

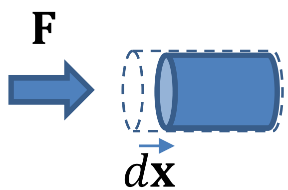
Internal Energy, U

- **There is energy not associated with motion or position of the system.**
  - Changes in temperature
  - Changes in phase
  - Changes in molecular structure (reactions)
- **Internal Energy**
  - (1) Molecular kinetic energy
  - (2) Molecular potential energy
- **For ideal gas, U is a function of T only.**
  - Temperature=Average molecular kinetic energy in the substance

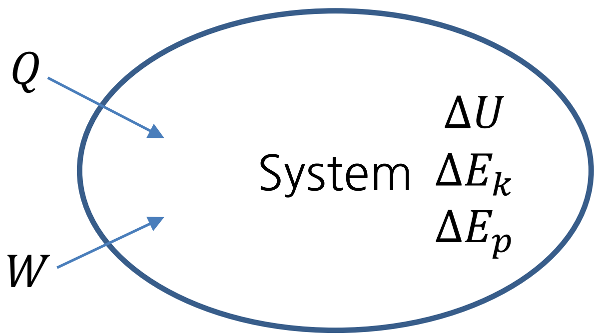
Work



$$W = \int \mathbf{F} \cdot d\mathbf{x}$$



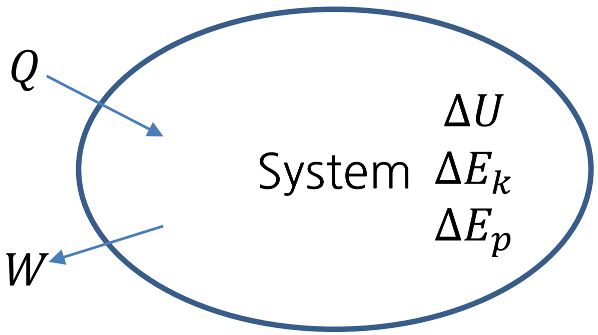
$$W = \int \mathbf{F} \cdot d\mathbf{x} = \int \mathbf{F}/A \cdot A d\mathbf{x} = \int \mathbf{P} \cdot d\mathbf{V}$$



$$\Delta U + \Delta E_k + \Delta E_p = Q + W$$

$$W = -\int P dV$$

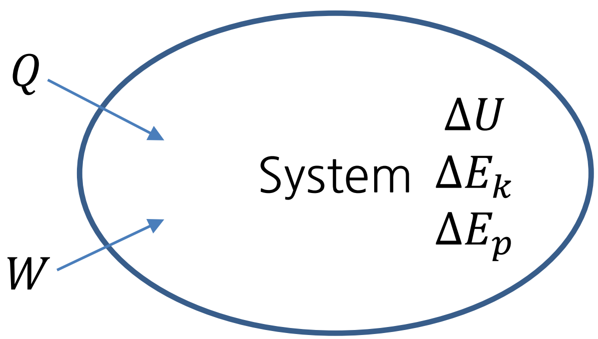
Work



$$\Delta U + \Delta E_k + \Delta E_p = Q - W$$

$$W = \int PdV$$

$$\Delta U + \Delta E_k + \Delta E_p = Q - \int PdV$$

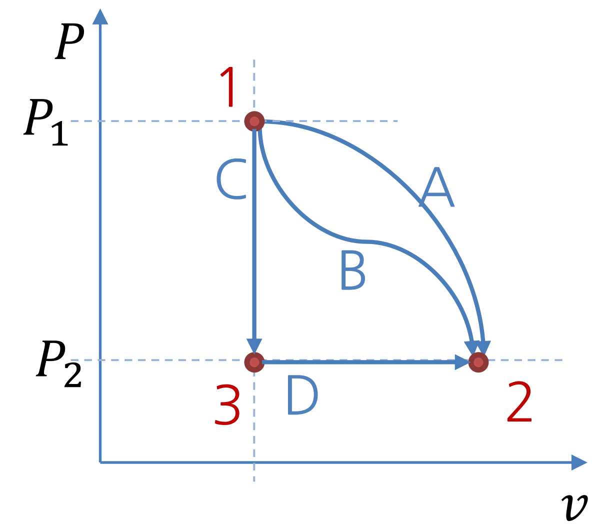


$$\Delta U + \Delta E_k + \Delta E_p = Q + W$$

$$W = -\int PdV$$

Processes

- $\Delta P = 0$: Isobaric
- $\Delta T = 0$: Isothermal
- $\Delta v = 0$: Isochoric
- $Q = 0$: Adiabatic



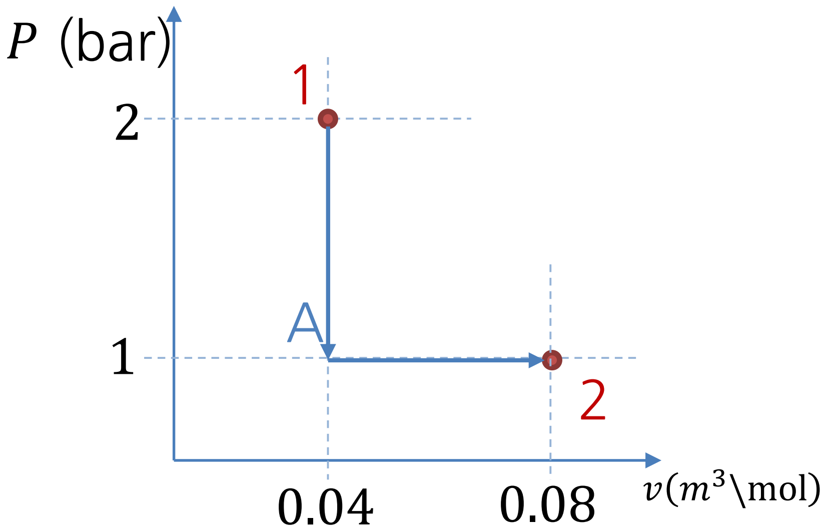
State Function
$$\Delta P_A = \Delta P_B = \Delta P_{CD} = P_2 - P_1$$
$$\Delta U_A = \Delta U_B = \Delta U_{CD} = U_2 - U_1$$

Path Function $W_A \neq W_B \neq W_{CD}$

We do not use ΔQ or ΔW, because we cannot say

$$\Delta W = W_2 - W_1$$

Irreversible process

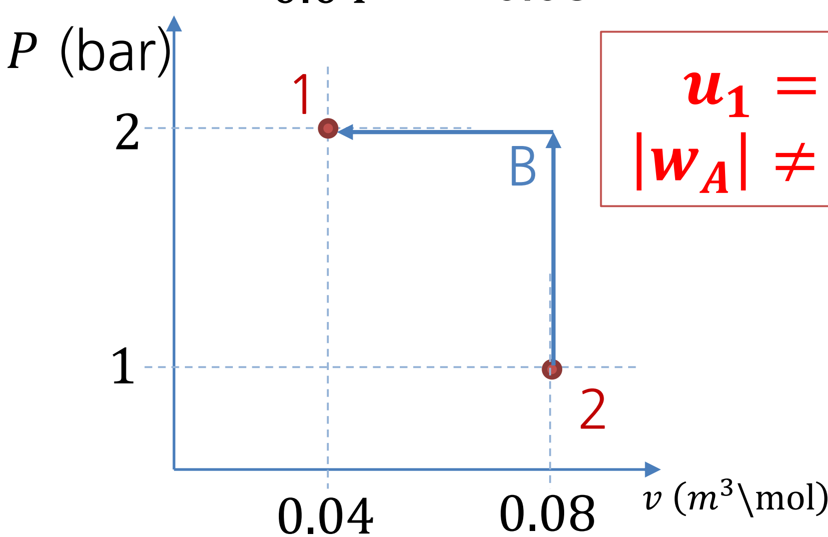


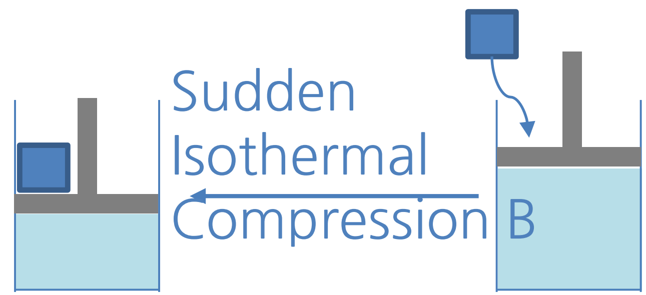
$$w = -\int P dv = -P(v_2 - v_1)$$

$$= -1(bar) \cdot 0.04\ (m^3\backslash \mathrm{mol}) = -4000(\mathrm{J}\backslash \mathrm{mol})$$

$$\boldsymbol{u_1 = u_2}$$

$$\boldsymbol{|w_A| \neq |w_B|}$$



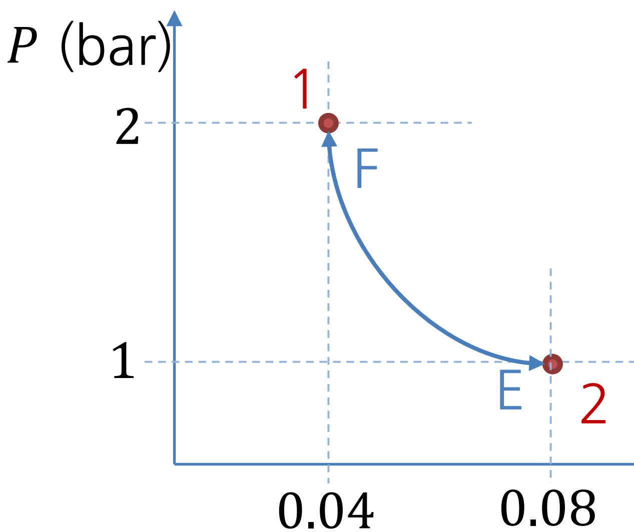


$$w = -\int P dv = -P(v_1 - v_2)$$

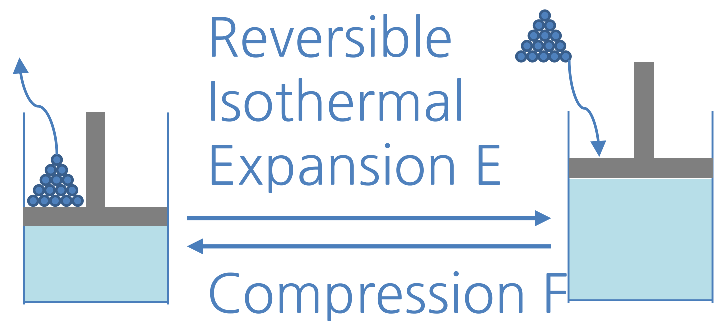
$$= -2(bar) \cdot -0.04(m^3\backslash \mathrm{mol}) = 8000(\mathrm{J}\backslash \mathrm{mol})$$

Reversible process

- For the system to undergo reversible change, it should occur infinitely slowly due to infinitesimal gradient



$$u_1 = u_2$$
$$|w_A| = |w_B|$$



For an isothermal process,
$$P_1 v_1 = P_2 v_2 = Pv$$

$$w_A = -\int P dv = -\int_{v_1}^{v_2} \frac{P_1 v_1}{v} dv$$
$$= -2 \cdot 0.04 [\ln v]_{v_1}^{v_2} = -5545 (\text{J}\backslash\text{mol})$$

$$w_B = -\int P dv = -\int_{v_2}^{v_1} \frac{P_1 v_1}{v} dv$$
$$= -2 \cdot 0.04 [\ln v]_{v_2}^{v_1} = 5545 (\text{J}\backslash\text{mol})$$

Meaning of Reversible Work

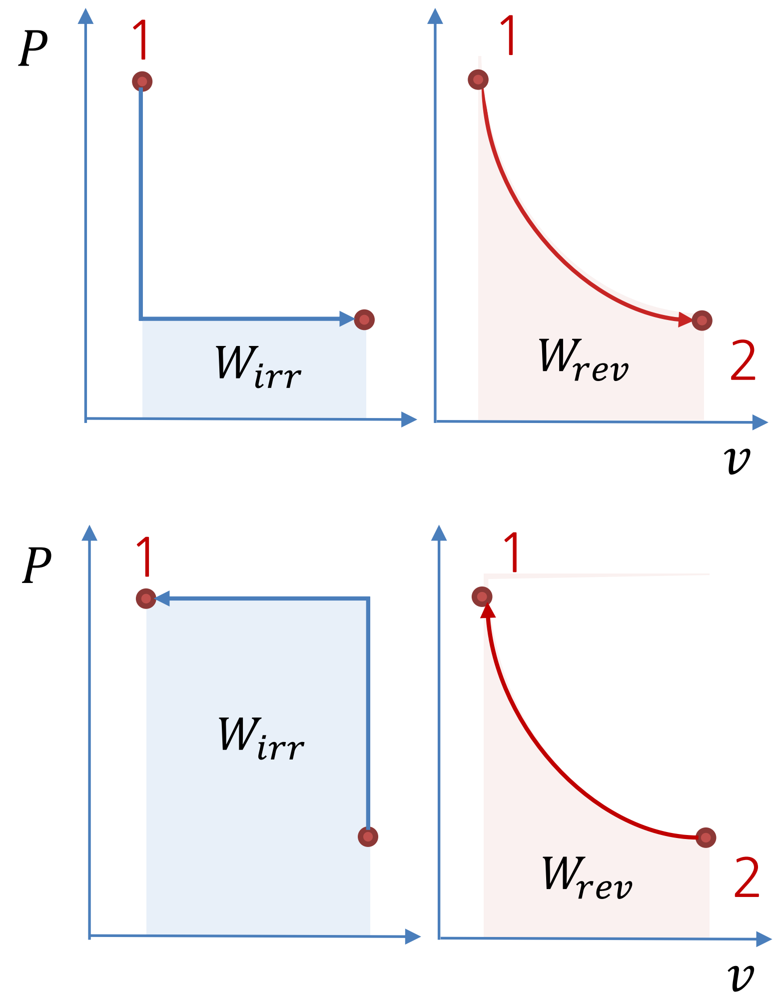
- **Reversible process**

  =Maximum work done by expansion

  =Minimum work required for compression

  =Theoretically the most efficient process

  →Become a theoretical guideline



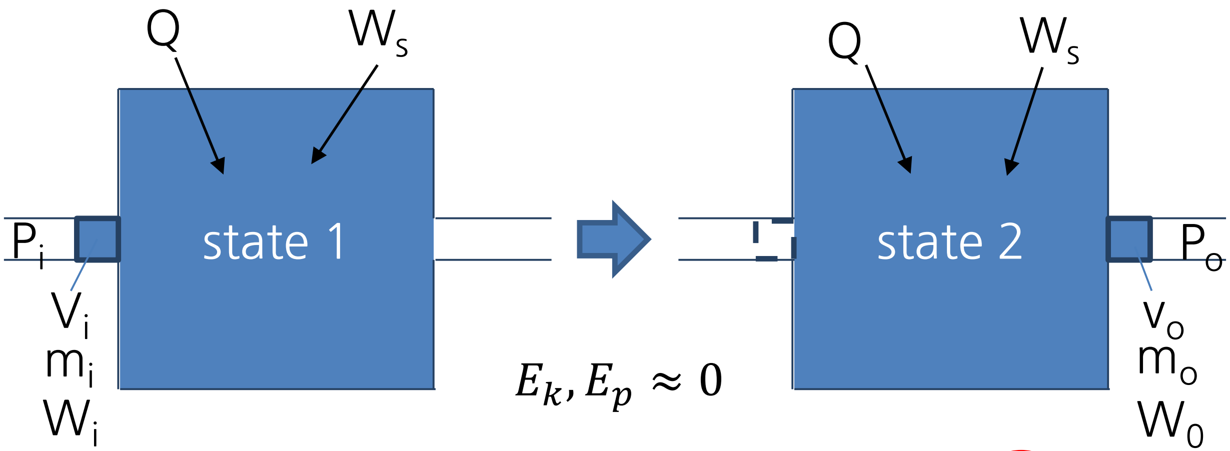
First Law, Closed System

$$\Delta U + \Delta E_k + \Delta E_p = Q + W \qquad \Delta u + \Delta e_k + \Delta e_p = q + w$$

$$dU + dE_k + dE_p = \delta Q + \delta W \qquad du + de_k + de_p = \delta q + \delta w$$

$$\frac{dU}{dt} + \frac{dE_k}{dt} + \frac{dE_p}{dt} = \dot{Q} + \dot{W} \qquad \frac{du}{dt} + \frac{de_k}{dt} + \frac{de_p}{dt} = \dot{q} + \dot{w}$$

First law, open system



$E_k, E_p \approx 0$

Shaft work

Fluid work

$$\Delta E = \Delta U = Q + W$$

$$W = W_s + W_i + W_o$$

$$= W_s - \int_{V_C+V_i}^{V_C} P_i \, dV - \int_{V_C}^{V_C+V_o} P_o \, dV$$

$$= W_s - P_i(-V_i) - P_o(V_o)$$

$$= W_s + P_i V_i - P_o V_o$$

$$\Delta U = U_{sys,2} + U_o - (U_{sys,1} + U_i)$$

$$= \Delta U_{sys} + U_o - U_i$$

$$\Delta U_{sys} + U_o - U_i = Q + W_s + P_i V_i - P_o V_o$$

$$\Delta U_{sys} = Q + W_s + U_i + P_i V_i - U_o - P_o V_o$$

$$\Delta U_{sys} = Q + W_s + H_i - H_o$$

$$H \equiv U + PV$$

Shaft work and Flow work

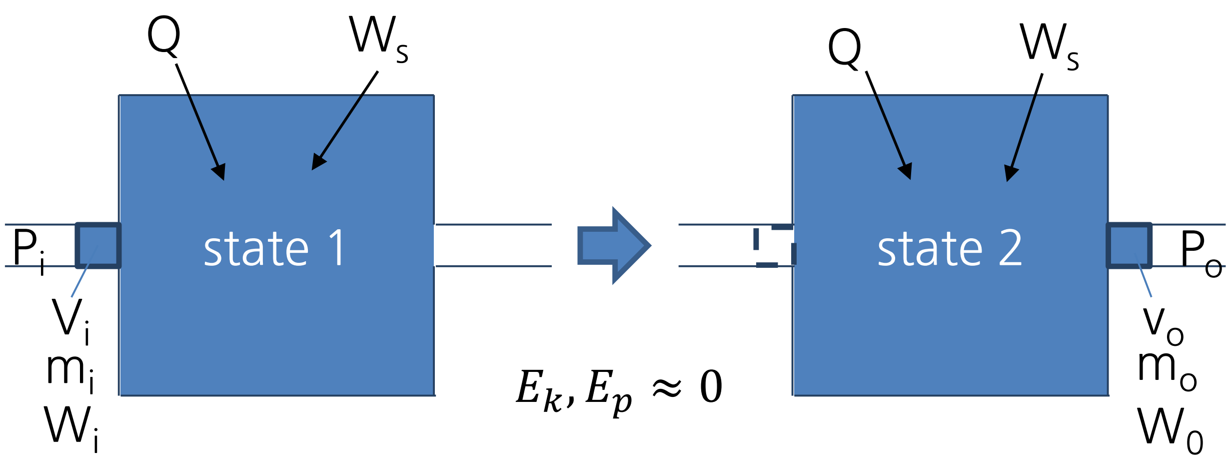
- **Open system has input or output stream and this stream also do "Work"**
- $W = W_F + W_s$
  - Flow work W_F
    - Work due to the inlet and outlet fluid to the system
    - We cannot use this work because this work is related with only fluid inlet and outlet
  - Shaft work W_s
    - Work due to the process fluid within the system
    - This is usable: It can rotate "Shaft"

Enthalpy

- Internal energy and flow work are always associated and flow work is not usable

  → it's convenient to group theses.

$$H \equiv U + PV \quad \text{or} \quad h \equiv u + Pv$$



First law, open system = Energy Balance

$$\Delta U_{sys} = Q + W_s + H_i - H_o$$

If there are multiple input and output streams

$$\Delta U_{sys} = Q + W_s + \sum H_i - \sum H_o$$

If E_k and E_p is not negligible,

$$\Delta\left(U + E_k + E_p\right)_{sys} = Q + W_s + \sum\left(H_i + E_{k,i} + E_{p,i}\right) - \sum\left(H_o + E_{k,o} + E_{p,o}\right)$$

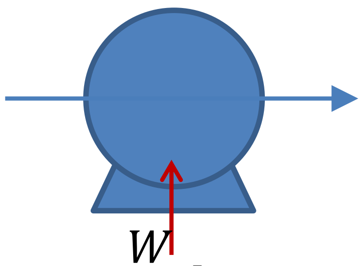
$$\Delta\left(U + E_k + E_p\right)_{sys} = Q + W_s + \sum\left(H_i + m_i\vec{V_i}^2/2 + m_i g z_i\right) - \sum\left(H_o + m_o\vec{V_o}^2/2 + m_o g z_o\right)$$

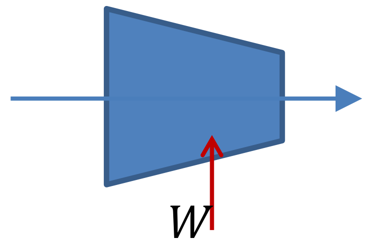
$$\Delta\left(U + E_k + E_p\right)_{sys} = Q + W_s + \sum m_i\left(h_i + \vec{V_i}^2/2 + g z_i\right) - \sum m_o\left(h_o + \vec{V_o}^2/2 + g z_o\right)$$

$$\frac{d\left(U + E_k + E_p\right)_{sys}}{dt} = \dot{Q} + \dot{W}_s + \sum \dot{m}_i\left(h_i + \vec{V_i}^2/2 + g z_i\right) - \sum \dot{m}_o\left(h_o + \vec{V_o}^2/2 + g z_o\right)$$

Open System Equipment

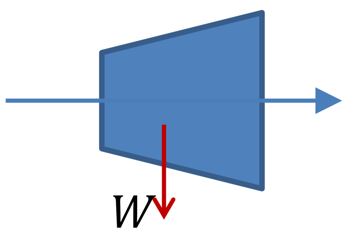
- Pump, Compressor (P1<P2) :





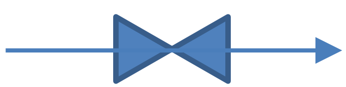
To increase P by consuming W

- Turbine, Expander (P1>P2)



To produce W by expansion

- Valve (P1>P2)



To drop pressure and control flow rate

You can solve these by using energy balance!

Process Equipment - Pump

shaft work consumed to drive rotation

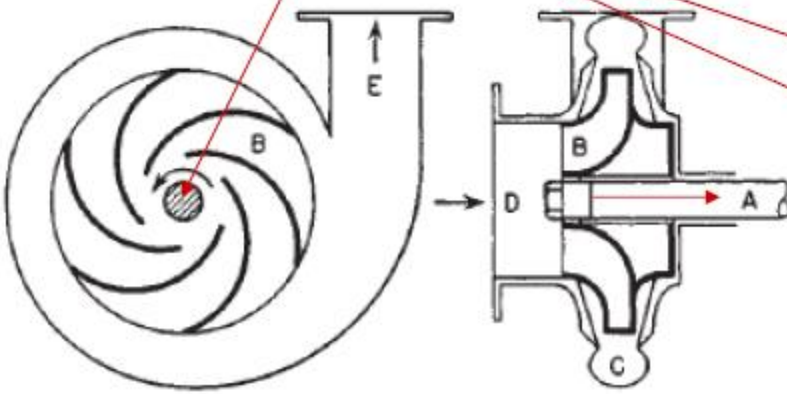


FIG. 10-27 A simple centrifugal pump.

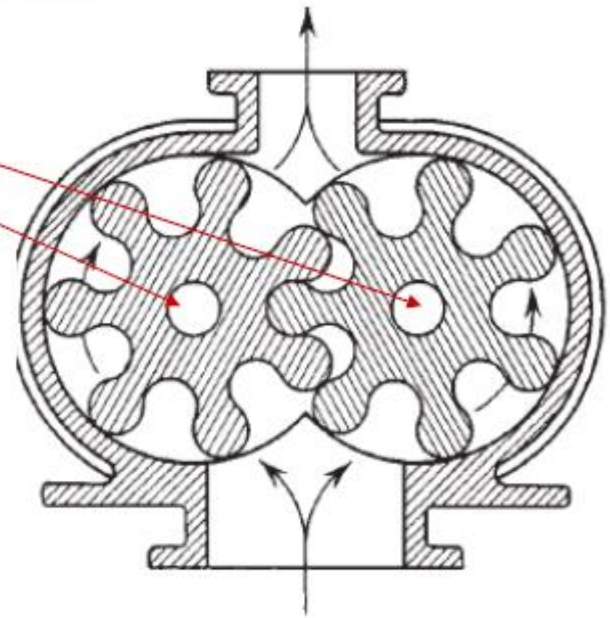


FIG. 10-54 Positive-displacement gear-type rotary pump.

Perry's Chemical Engineers' Handbook (7th Edition)
Edited by: Perry, R.H.; Green, D.W. © 1997; McGraw-Hill
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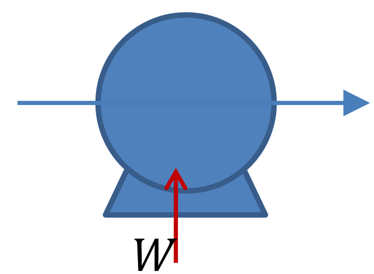
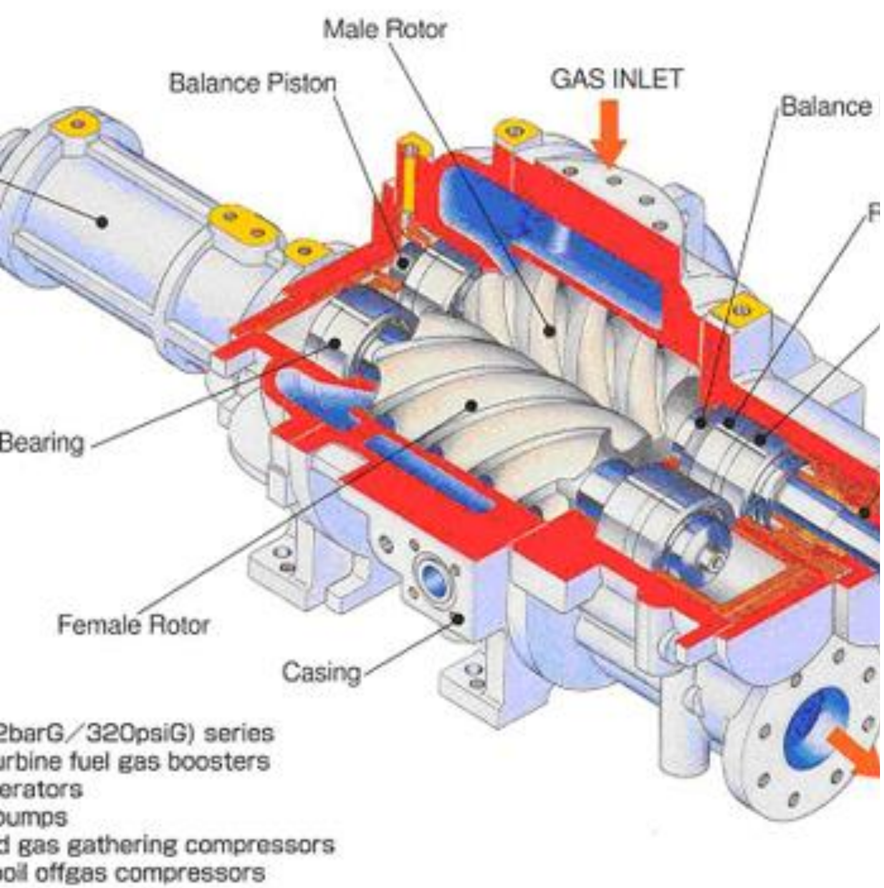
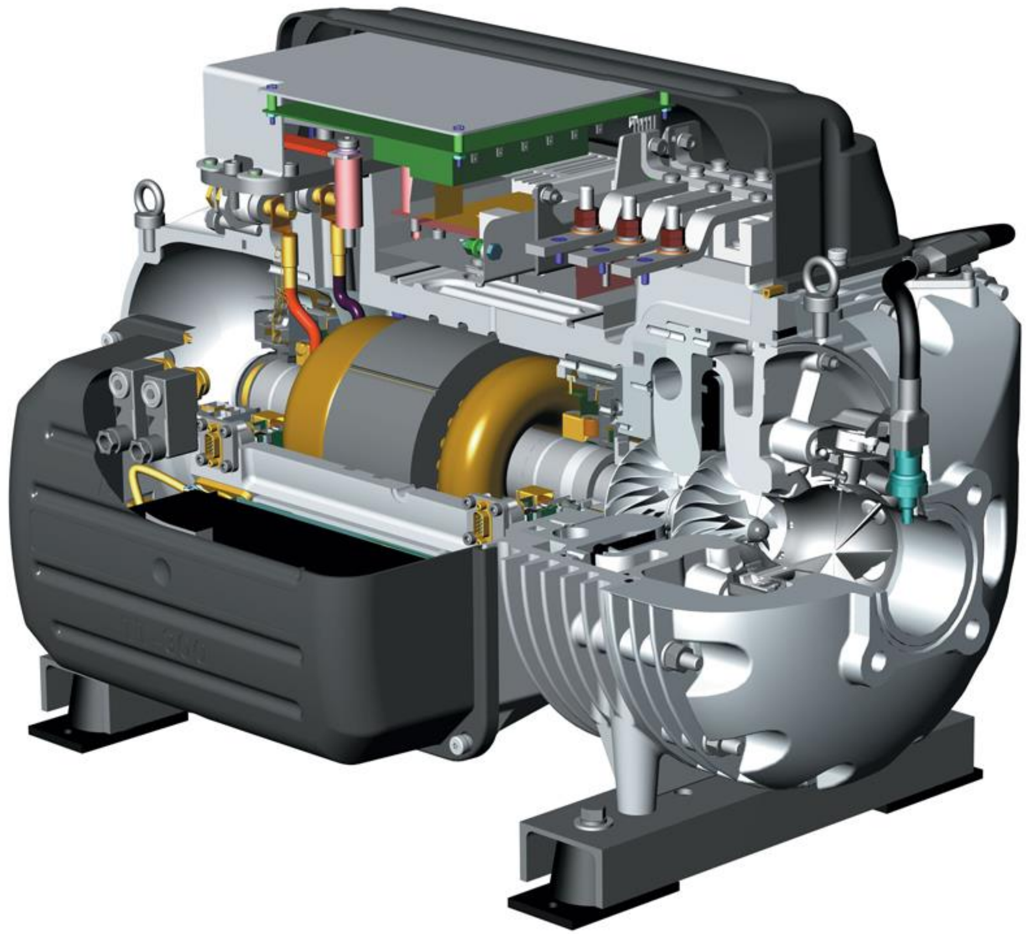


Process Equipment - Compressor





http://www.energy.siemens.com/hq/en/compression-expansion/compressor-packages/smcp.htm#content=Technical%20Data
http://www.thermalcare.com/central-chillers/tc-series-central-chillers.php

Process Equipment - Turbine

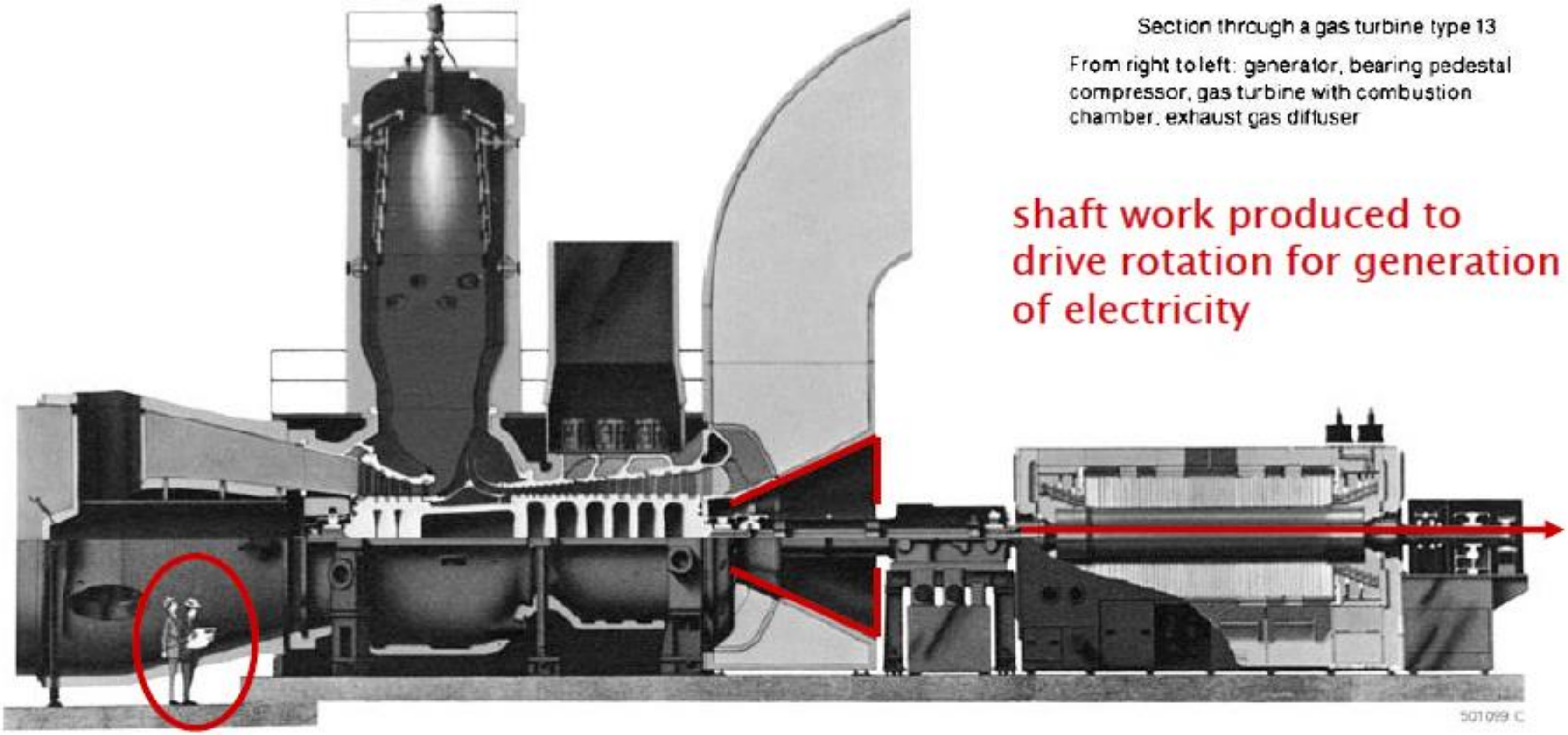


FIG. 29-25 Section through a Brown-Boveri gas turbine (with permission of Asea-Brown Boveri).

Perry's Chemical Engineers' Handbook (7th Edition)
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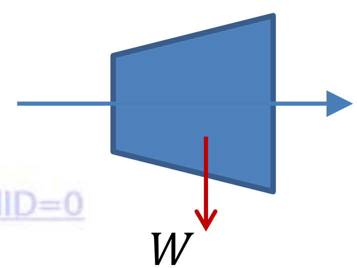
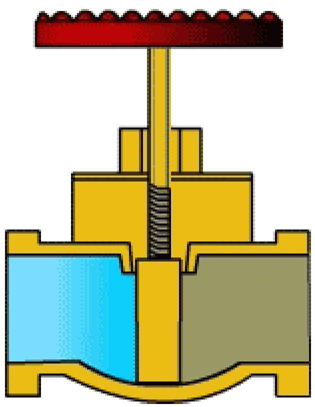


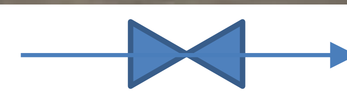
Process Equipment - Valve

- **Valves**
  - Ball valve
  - Gate valve…



Gate Valve Closed

Gate Valve Opened

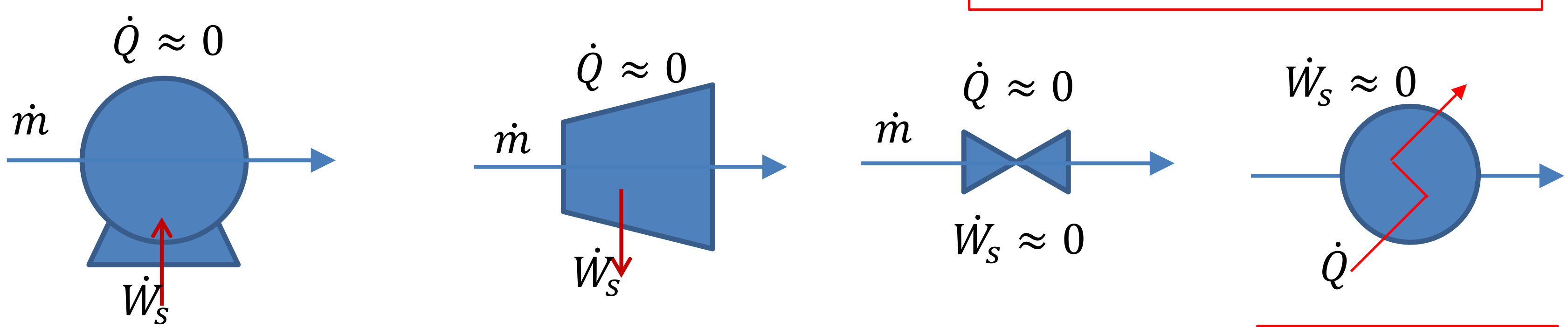


Energy balance and enthalpy

- Energy balance with Steady-state, 1 inlet, 1 outlet, and negligible KE/PE difference

$$\frac{d\left(U+E_k+E_p\right)_{sys}}{dt}=\dot{Q}+\dot{W}_s+\sum\dot{m}_i\left(h_i+\vec{V}_i^{\,2}/2+gz_i\right)-\sum\dot{m}_o\left(h_o+\vec{V}_o^{\,2}/2+gz_o\right)$$

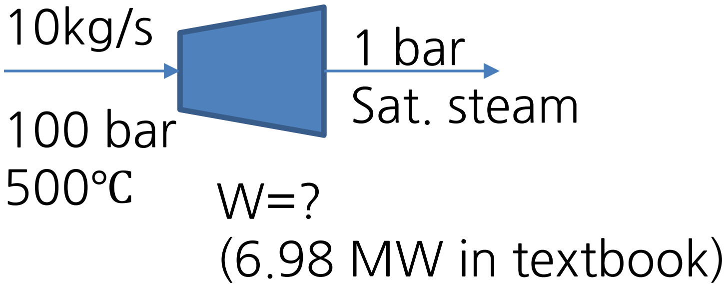
$$\Rightarrow 0=\dot{Q}+\dot{W}_s+\dot{m}(h_i-h_o) \Rightarrow \boldsymbol{0=\dot{Q}+\dot{W}_s-\dot{m}\Delta h}$$



$\dot{W}_s=\dot{m}\Delta h$ $w=\Delta h$	$\dot{W}_s=\dot{m}\Delta h$ $w=\Delta h$	$\Delta h=0$	$\dot{Q}=\dot{m}\Delta h$ $q=\Delta h$

You can solve EB simply from Enthalpy difference!

Example 2.5



18							

Example 2.7

- 2 moles of steam from 200℃, 1MPa to 500℃, 1 Mpa
- Q=? (23.4kJ in textbook)

18ASME	18NBS						