Lecture 3

- 1st law for simple closed system
- Simple processes
    - constant volume
    - isothermal
    - adiabatic: adiabat
    - isobaric (constant pressure) – enthalpy
- Heat capacities
- Carnot cycle
- 1st law for open system
    - different forms (integral, differential, rate-based, steady state)
    - examples with tank filling/emptying

Objectives

- Apply 1st law to simple systems and processes (constant V, constant P, isothermal, adiabatic) using ideal gas EOS
- Understand enthalpy
- Cp, Cv and their relationship
- Understand what each term represents in the open system 1st law
- Know which form (integral, differential, or rate-based, steady state) to use in solving problems.

Read Chs. 3 and 4 Sandler

Systems

- *Open* – exchanges matter with surroundings
- *Closed* – no material exchanges
- *Insulated* (adiabatic) – no thermal interactions (heat)
- *Rigid* – boundary cannot be mechanically deformed
- *Isolated* – independent system with no interactions with surroundings (rigid, adiabatic, impermeable)
- *Semi-open* – open w.r.t. some species but closed to others

Simple System – chemically inert, no internal boundaries (OK to have natural interfaces), not acted on by external (electric, magnetic, gravitational) or inertial forces

Processes

- *Isothermal* – temperature maintained constant by contact with a thermal bath
- *Isobaric* – pressure maintained constant by a pressure reservoir (e.g., constant weight on the piston)
- *Isochoric* – constant volume
- *Cycle* – systems returns to exact initial state
- *Infinitesimal process* – difference between initial and final is infinitesimally small
- *Quasi-static process* – an idealized process in which the net driving force for change is infinitesimal, so process is effected infinitely slowly with no dissipation; reversible

Application of 1ˢᵗ Law to Simple Systems and Processs

Some common simple processes:

- Constant V, no other work

$$dU = \delta Q$$

- Adiabatic

$$dU = \delta W$$

For these two processes, heat and work become path independent

Allows us to define constant-V heat capacity

$$C_v \equiv \left(\frac{\delta Q}{\delta T}\right)_{\mathrm{v}} = \left(\frac{\partial U}{\partial T}\right)_{\mathrm{v}}$$

state function

(amount of heated need for a unit change in T)

Ideal Gas

$$PV = nRT$$

Internal energy: $\qquad U = nu(T) \qquad$ independent of V or P!

(no intermolecular interaction; can prove more formally using ideal gas law)
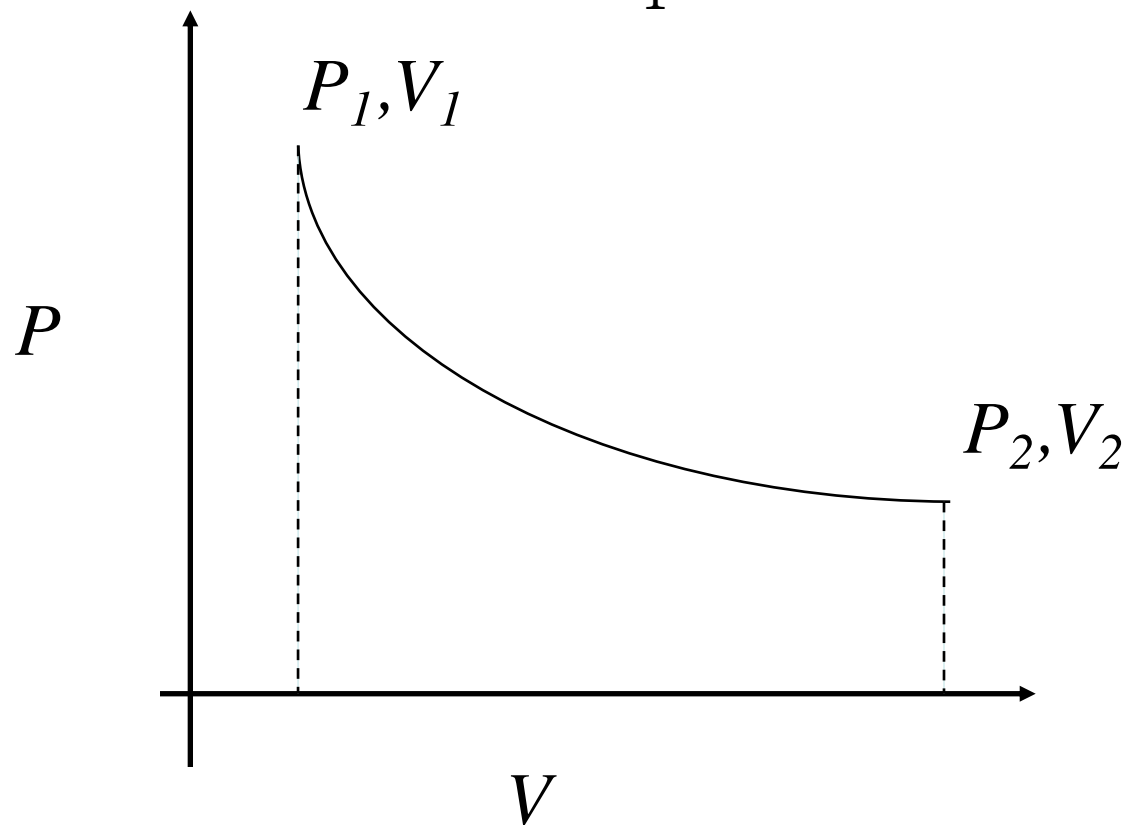
C_V is only function of T

Internal energy change: $\qquad \Delta U = \displaystyle\int_{T_1}^{T_2} C_V \, dT$

For constant C_V: $\qquad\qquad \Delta U = C_V(T_2 - T_1)$

Applications to Ideal Gas

Isothermal process: $\Delta U = 0$

$$\Longrightarrow \quad Q = -W = \int_{V_1}^{V_2} P \, dV = nRT \ln \frac{V_2}{V_1}$$

P_1, V_1

P

P_2, V_2

V

Applications to Ideal Gas

Adiabatic process: $\qquad Q = 0$

$\Longrightarrow \qquad dU = \delta W = -PdV$

$\Longrightarrow \qquad C_v dT = -\dfrac{nRT}{V}\, dV$

For constant C_V: $\qquad C_V \ln\dfrac{T_2}{T_1} = -nR \ln\dfrac{V_2}{V_1}$

$\Longrightarrow \qquad \left(\dfrac{T_2}{T_1}\right)^{\frac{C_V}{R}} = \left(\dfrac{V_1}{V_2}\right) \qquad \Longrightarrow \qquad T^{\frac{C_V}{R}} V = const \qquad$ (adiabat)

$\Longrightarrow \qquad PV^{\gamma} = const \qquad\qquad\qquad \gamma \equiv 1 + \dfrac{R}{C_V} = \dfrac{C_P}{C_V} > 1$

P-V Diagram
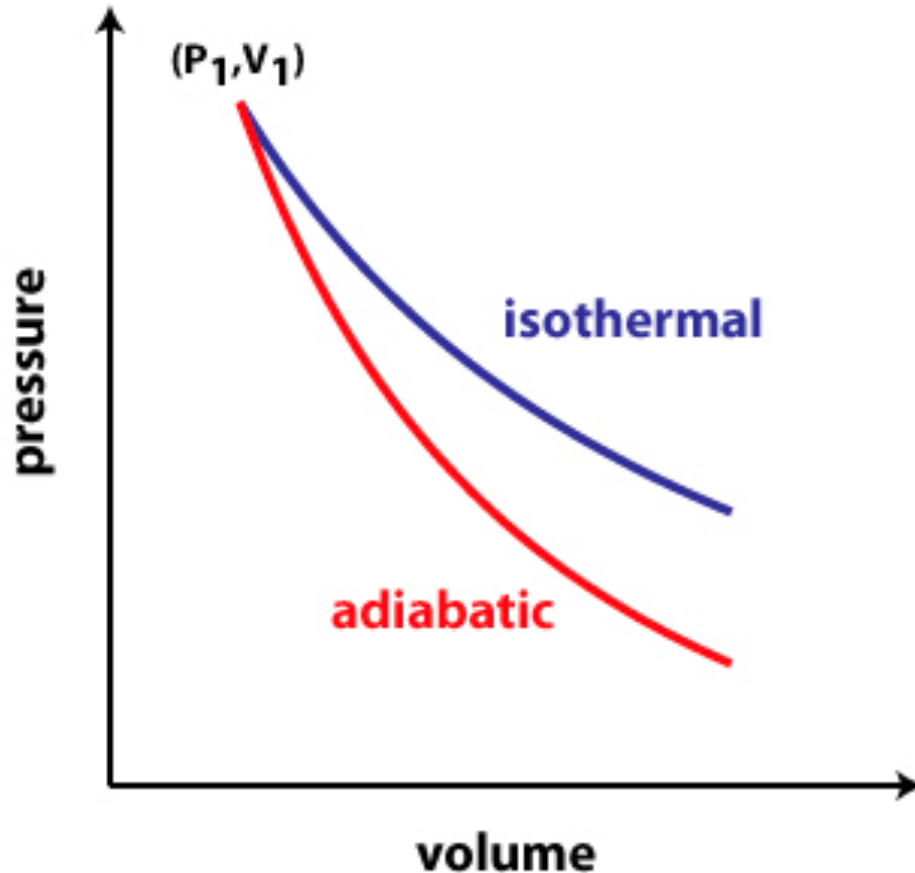
Pressure drop is larger for adiabatic process than for isothermal because the system must expend internal energy in doing expansion work

Adiabatic work

$$W = \Delta U = C_V(T_2 - T_1)$$

Enthalpy

Isobaric (const-P) process: $\quad \Delta U = Q - P\,\Delta V$

Define enthalpy: $\quad H = U + PV$

Then: $\quad Q = \Delta U + P\Delta V = \Delta H \qquad$ (since P is const.)

Differential form: $\quad dH = \delta Q$

Heat directly given by enthalpy change! Independent of path

Const-P heat capacity:

$$C_P \equiv \left(\frac{\delta Q}{\delta T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \text{state function}$$

Ideal gas:
$$PV = nRT$$

$$H = U + PV = U + nRT = n[u(T) + RT]$$

$\implies$ $H = nh(T)$ Enthalpy only function of T
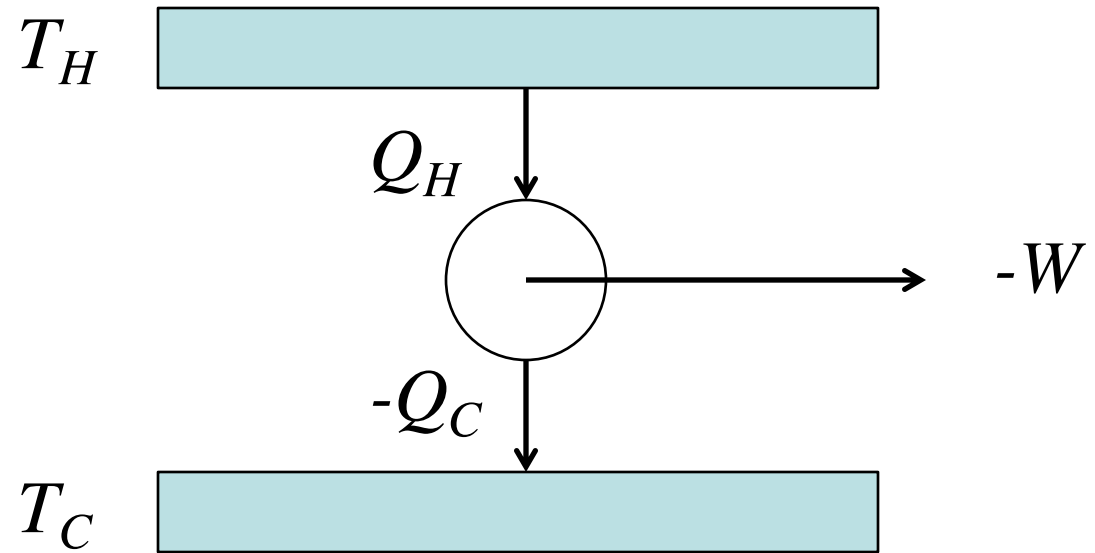
$\implies$ $C_P = C_V + nR$ $\qquad c_P = c_V + R$

Enthalpy change:
$$\Delta H = \int_{T_1}^{T_2} C_P \, dT$$
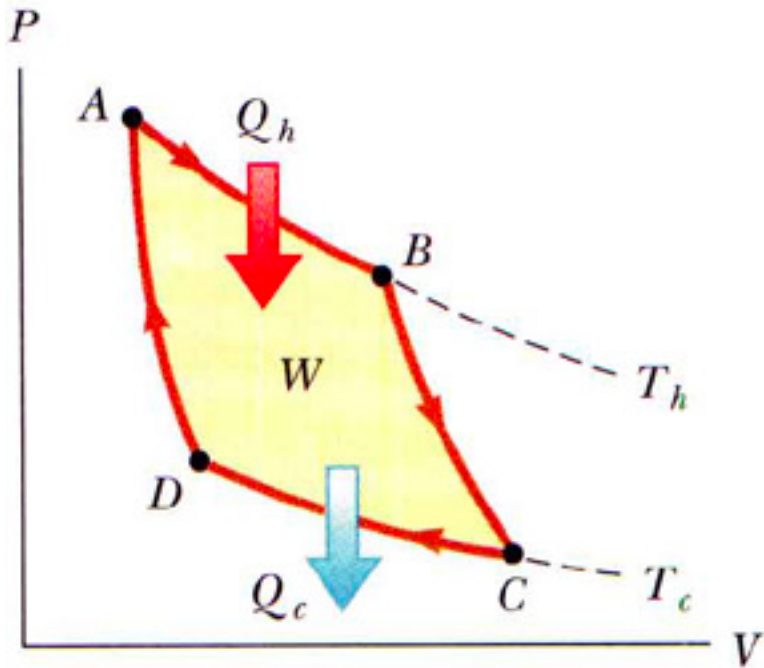
For constant C_v:
$$\Delta H = C_P(T_2 - T_1)$$

Carnot Cycle

T_H

Q_H

$-W$

$-Q_C$

T_C

Since it's a cycle: $\Delta U = 0$

$$-W = Q = Q_H + Q_C$$

Carnot Cycle – Ideal Gas

$A \rightarrow B$:   isothermal expansion

$B \rightarrow C$:   adiabatic expansion

$C \rightarrow D$:   isothermal compression

$D \rightarrow A$:   adiabatic compression

$$-W = Q = Q_H + Q_C$$

Work only involves isothermal steps

$$Q_H = RT_H \ln \frac{V_B}{V_A} \qquad Q_C = RT_C \ln \frac{V_D}{V_C}$$

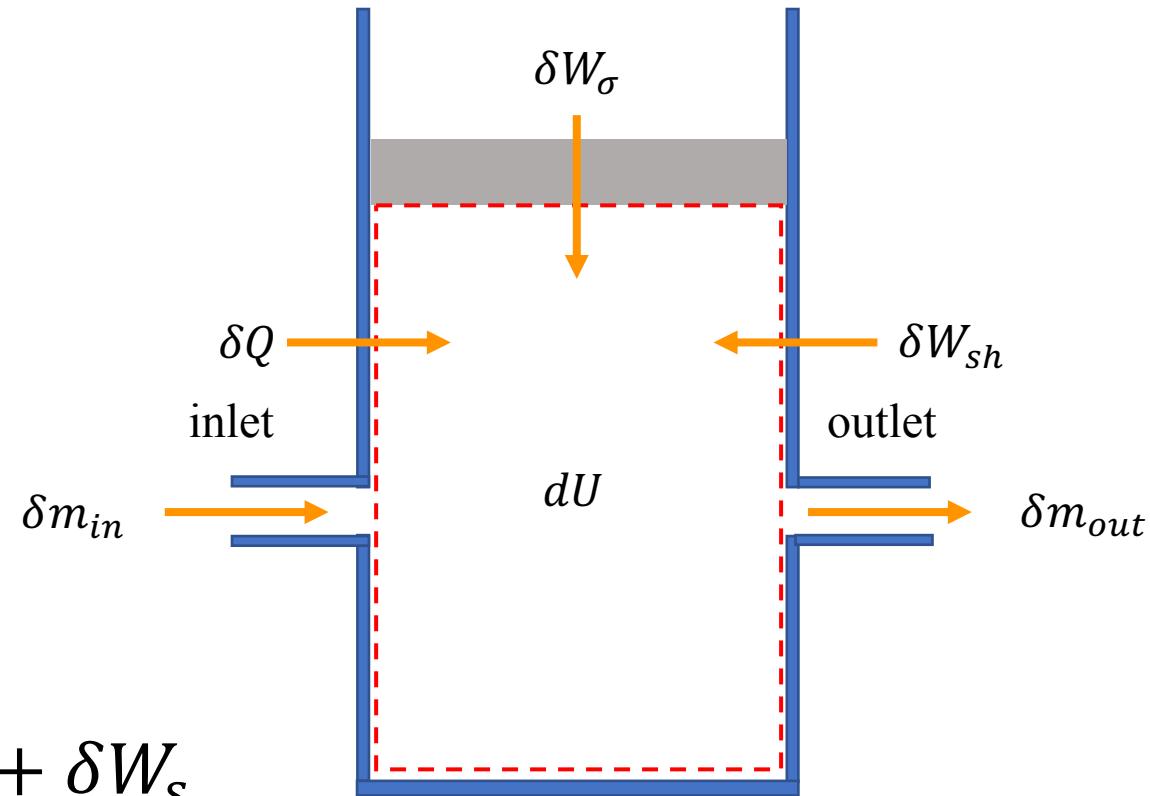Show $\dfrac{Q_H}{T_H} + \dfrac{Q_c}{T_c} = 0$ efficiency $\eta = \dfrac{-W}{Q_H} = 1 - \dfrac{T_C}{T_H}$

First Law for Open System

General conservation law

$$dE$$
$$= \tilde{e}_{in}\delta m_{in} - \tilde{e}_{out}\delta m_{out} + \delta Q + \delta W_\sigma + \delta W_s$$
$$+ (p\tilde{v})_{in}\delta m_{in} - (p\tilde{v})_{out}\delta m_{out}$$
$$= \tilde{h}_{in}\delta m_{in} - \tilde{h}_{out}\delta m_{out} + \delta Q + \delta W_\sigma + \delta W_s$$

δW_σ

δQ

inlet

δW_{sh}

outlet

δm_{in}

dU

δm_{out}

control volume
(volume enclosed by
dashed boundaries)

Common Forms of First Law for Open System

For simple system, single component:

$$dU = h_{in}\delta n_{in} - h_{out}\delta n_{out} + \delta Q + \delta W_\sigma + \delta W_s$$

Constant incoming/outgoing properties:

$$\Delta U = h_{in}n_{in} - h_{out}n_{out} + Q + W_\sigma + W_s$$

Steady-state:

$$0 = (h_{in} - h_{out})\delta n + \delta Q + \delta W_s$$

All differential forms can turn into rate based

Examples

Tank filling: determine final temperature
Constant incoming stream, use integral form

$$\Delta U = h_{in}(T_{in})n_{in}$$

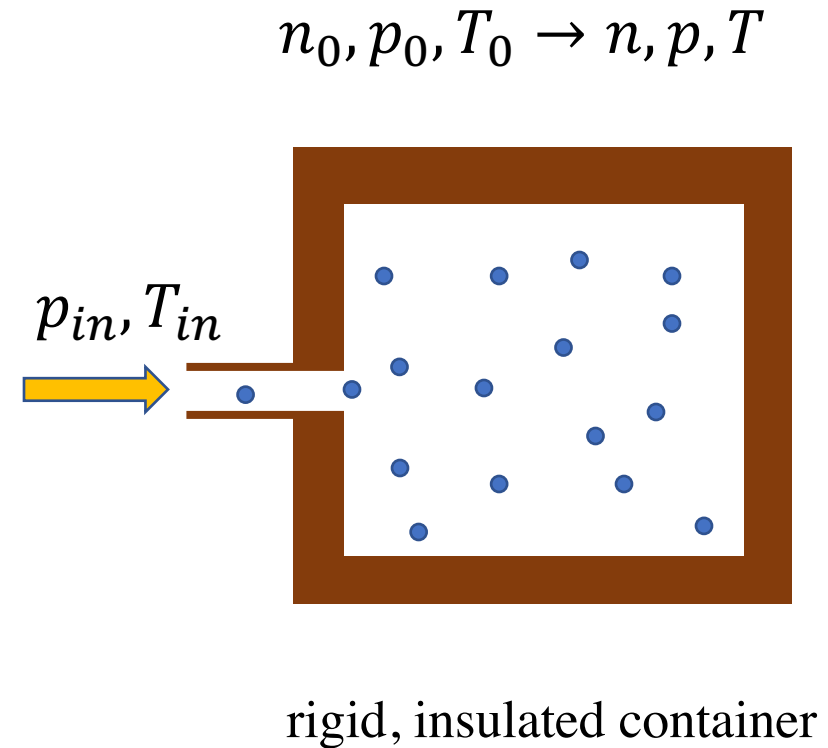$$nu(T) - n_0 u(T_0) = h_{in}(T_{in})n_{in}$$

For constant c_v

$$T = \frac{\gamma T_{in}}{1 + \frac{P_0}{P}\left(\frac{\gamma T_{in}}{T_0} - 1\right)}$$

Initially empty tank, P_0=0

$$T = \gamma T_{in}$$

tank hotter than incoming stream

$n_0, p_0, T_0 \rightarrow n, p, T$

p_{in}, T_{in}

rigid, insulated container

Examples

$$n_0, p_0, T_0 \rightarrow n, p, T$$

<u>Tank emptying</u>: Determine final temperature Outgoing stream has same property as gas in tank – changes with process. Use differential form
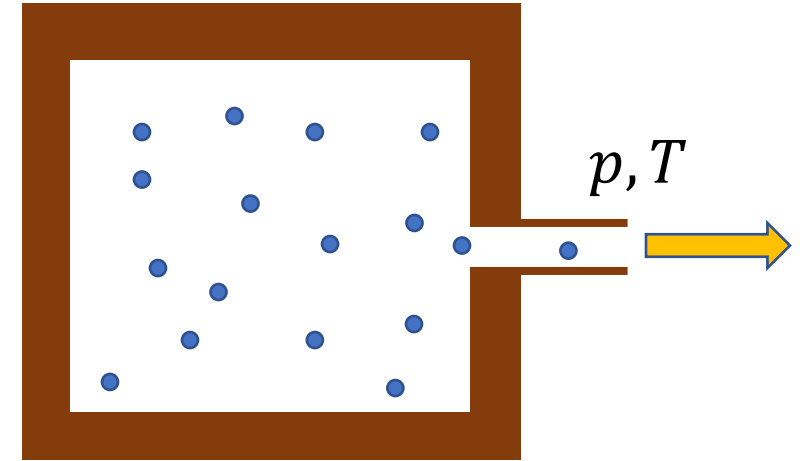
$$dU = -h_{out}\delta n$$

$$udn + ndu = hdn$$

p, T

$$T = T_0 \left(\frac{P}{P_0}\right)^{\frac{R}{c_V - R}}$$

Determine number of unknowns, use EOS and appropriate first law to solve

Questions to Think about

- What's the motivation for introducing enthalpy?

- Comparing a monatomic gas with a diatomic gas, which one has a higher heat capacity and why?

- Why introducing adiabatic steps in a Carnot cycle?

- Why the work terms during the adiabatic steps exactly cancel?