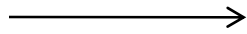
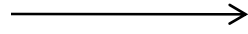


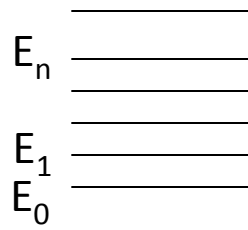
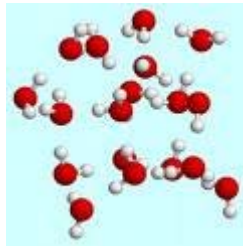
Quantum Mech.



Stat Mech



Thermodynamics



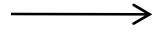
fluctuations



phase transitions dynamics



large #
of particles



statistical
(average) + fluctuations away from average.
properties

Concepts

Equilibrium states

characterized macroscopically by a small
of variables

e.g., $E, V, n_1, n_2, \dots, n_r$ ← moles of various species

Walls and constraints → Boundary Conditions

e.g., system enclosed by an **adiabatic** wall (which does not allow heat to enter or leave the system)

Quasistatic process : Consider a gas in a cylinder fitted with a moving piston. If the piston is pushed at a vanishingly slow rate i.e. infinitely slow the process is termed quasistatic

1st Law

- Internal energy, E , is extensive (additive)
- Internal Energy is conserved

$$dE = \underbrace{\delta Q}_{\substack{\text{heat} \\ \text{flow} \\ \text{into} \\ \text{system}}} + \underbrace{\delta W}_{\substack{\text{work} \\ \text{done} \\ \text{on} \\ \text{system}}}$$

e.g., $\delta W = -p_{\text{ext}}dV$

$\delta Q, \delta W$
inexact
differentials

E_1	E_2
-------	-------

$$E = E_1 + E_2$$

Exact differential

$$\int_a^b df = f(b) - f(a)$$

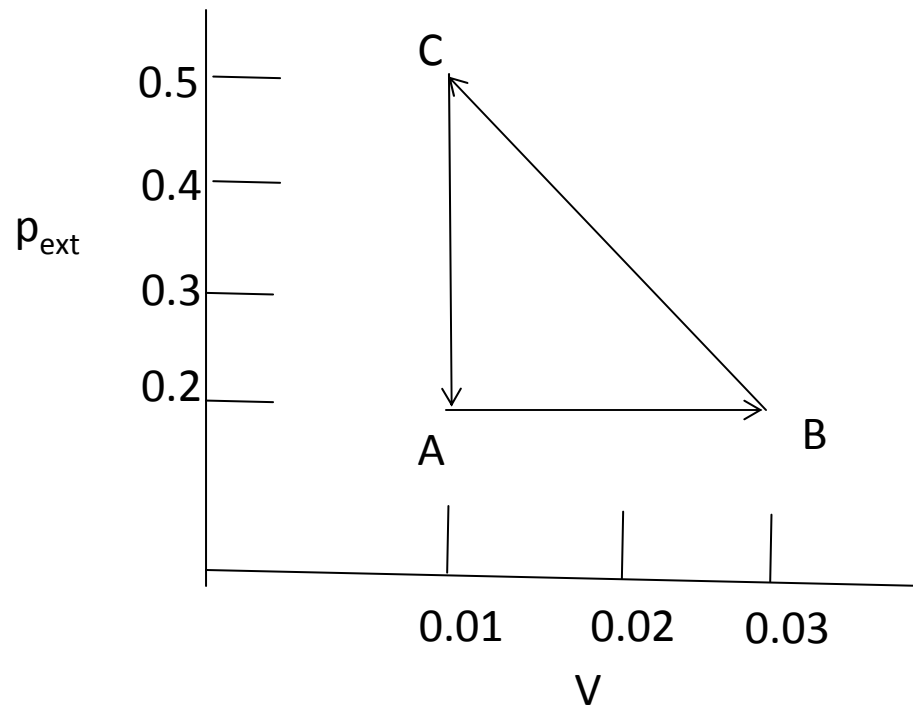
Inexact differential
:Integration depends on
path

$$\int_a^b \delta g \neq g(b) - g(a)$$

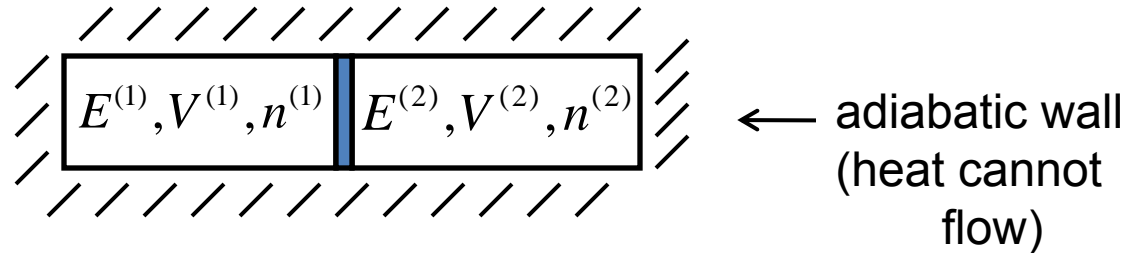
Sample Problem

Gaseous system for which the energy is $E=2.5PV+\text{constant}$

Consider the following process. The system is taken through the cycle A to B, B to C and C to A. Find the work done and heat change for each of the 3 processes



Changes of state



How does the system evolve if we

- move piston
- put hole in piston
- remove adiabatic wall

Need **2nd law** of thermodynamics

There exists an extensive state function S , i.e., $S(E, X)$ where E, X are extensive, E being the internal energy.

- monotonically increases with E
- if B is adiabatically accessible from $A \Rightarrow S_B \geq S_A$
for reversible adiabatic process $\Delta S_{ad} = 0$

$$\boxed{(\Delta S)_{ad} \geq 0}$$

$$\Delta S_{ad} = 0, \text{ reversible process}$$

$$\Delta S_{ad} > 0, \text{ irreversible process}$$

$$dS = \left(\frac{\partial S}{\partial E} \right)_X dE + \left(\frac{\partial S}{\partial X} \right)_E dX$$

for rev. process

$$dE = (dQ)_{rev} + f \cdot dX \quad (f \text{ is prop. of system})$$

$$dS = \left(\frac{\partial S}{\partial E} \right)_X (dQ)_{rev} + \left[\left(\frac{\partial S}{\partial X} \right)_E + \left(\frac{\partial S}{\partial E} \right)_X f \right] \cdot dX$$

if ad. and rev.

$$dQ = 0, \quad dS = 0$$

$$\left(\frac{\partial S}{\partial X} \right)_E = - \left(\frac{\partial S}{\partial E} \right)_X f$$

$$\left(\frac{\partial S}{\partial E} \right)_X > 0 \Rightarrow \left(\frac{\partial E}{\partial S} \right)_X \geq 0$$

Remember, S is a monotonically increasing function of E

e.g., $p_{ext} = p_{system}$

$f \cdot dX$ is the work done. If the number of particles remains the same $f \cdot dx = -pdV$. The work (called chemical work in this case) associated with a change in the number of particles is $\mu \cdot dN$ where μ is the chemical potential.

Since all variables are functions of state, this must hold for non-adiabatic case as well

$$T = \left(\frac{\partial E}{\partial S} \right)_X \geq 0, \quad T \text{ intensive}$$

$$\left(\frac{\partial S}{\partial X} \right)_E = -\frac{f}{T}$$

$$dS = \left(\frac{\partial S}{\partial E} \right)_X dE + \left(\frac{\partial S}{\partial X} \right)_E dX$$

$$dS = \frac{1}{T} dE - \frac{f}{T} dX$$

$$dE = TdS + f \cdot dX \Rightarrow E = E(S, X) \quad \text{for equilibrium states}$$
