3.020 Lecture 3

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1 Processes in thermodynamics

- Thermodynamics doesn't describe real-world processes
- Concept of state functions – history-independent – allows us to do calculations and make predictions

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- Any process connecting A$\longrightarrow$B will give same result for $P_B, T_B, \ldots$ because they are state functions

  Conceptualized the simplest process to calculate

- Simplest processes to calculate are *reversible*

Reversible Processes =
- System & surroundings are in equilibrium at all times
- Violates our day-to-day notion of arrow of time
- In practice, would take forever

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2 Describing processes: Work, heat, adding/substracting stuff

VERBS

- Work = mechanical exchange of energy

$$W(\frac{kg \cdot m^2}{s^2}) \propto (\frac{kg \cdot m}{s^2}) \times (m) = \text{force} \times \text{distance}$$
$$\propto (\frac{kg}{m \cdot s^2}) \times (m^3) = \text{pressure} \times \text{volume}$$

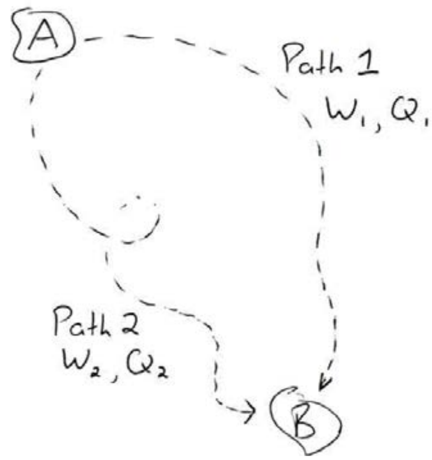
– Heat = process that exchanges energy without mechanical work or mass transfer

Q(J)

- Process variables are process-dependent
- Infinitesimal increments of process variables are denoted as "inexact differentials"

  e.g. δQ δW $\Rightarrow$ "δ" says "path-dependent"
- Infinitesimal increments of state variables are denoted as exact differentials

  e.g. dT, dV, dS, ...



Classifying processes

- Isothermal = fixed T
- Adiabatic = no heating across boundary
- Isobaric = fixed P
- Isochoric = fixed V

  (no work across boundary)

Classifying boundaries

- Insulating = no heat flow
- Diathermal = heat but no mass transfer
- Open/closed = mass transfer allowed/disallowed
- Rigid = fixed volume, immobile

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3 Heat Capacity:

$$C = \frac{\overbrace{\delta Q}^{\textbf{heat increment}}}{\underbrace{dT}_{\textbf{temp increment}}}$$

Q: How much heat energy is needed to go from $T_1 \longrightarrow T_2$?

C is path-dependent (δQ is a process/inexact differential), so it's useful to define particular cases.

$$C_v = \frac{\delta Q}{dR}_V \quad \text{– constant volume}$$
$$C_p = \frac{\delta Q}{dT}_p \quad \text{– constant pressure}$$

- C is an empirical observable, recorded in databases

  Q: What has large C ?

  Big pot of water / small pot of water
  Bread / cheese
  Al foil / potato

- C is tabulated as a specific, intensive quantity

  e.g. $J/(K \cdot g)$ or $J/(K \cdot mol)$

- C can be calculated for simple physical models

  e.g. Kinetic theory of ideal gas:

$$C_v = \frac{3}{2}R$$
$$C_p = C_v + R = \frac{5}{2}$$

	C $J/(g \cdot K)$
Water	4.18
Al	0.897
Potato	3.43
Cheese	3.15

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4 First law of thermodynamics

"The energy of the Universe is conserved"

Q: how is this useful ? A. Because it applies locally

- Energy of *system* + *surroundings* is constant
- Use boundary for bookkeeping, tracking exchanges

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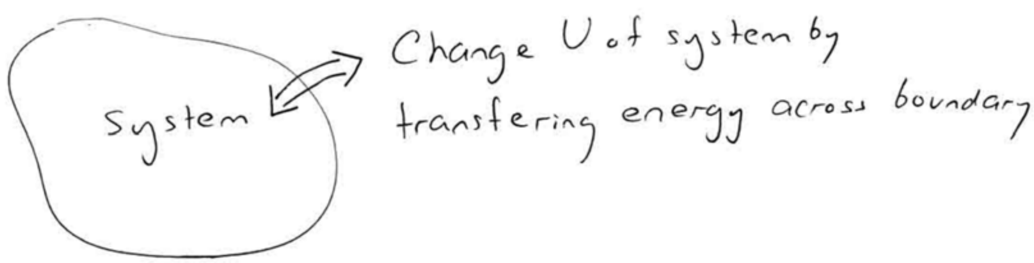
5 First law bookkeeping

- Types of energy: Kinetic, potential, internal(U) thermodynamics
- Relevant processes: Heat, Work, Mass transfer



$$dU = \delta Q + \delta W + \mu_i dN_i$$

- Heat δQ applied <u>to</u> system
- Work δW performed <u>on</u> system

– Energy μdN of mass added to system

$$N_i = \#\ \text{moles of component i}$$

$$\mu_i = \frac{\partial U}{\partial N_i}_{S,V,N_{j\neq i}} \quad \Leftarrow \quad \text{Chemical Potential of i}$$

$$\underbrace{\delta W}_{\text{process var.}} = - \overbrace{P}^{\text{integration constant}} \underbrace{dV}_{\text{state var.}}$$