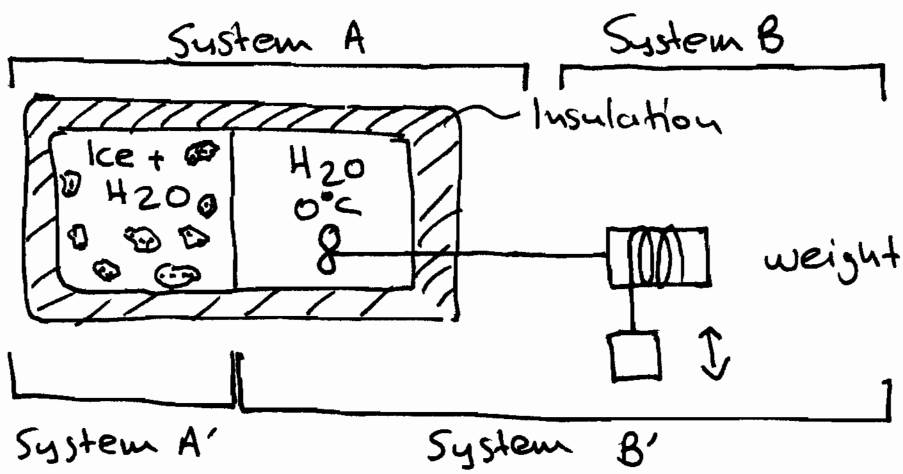
Adiabatic Work Interactions - CHAPTER 3

An interaction between two closed systems for which all events external to each of the two systems can be duplicated entirely by the rise and fall of equal weights in a gravitational field

Example :



Is this an adiabatic work interaction?

Between which systems? $A \Leftrightarrow B$ Yes ✓

$A' \Leftrightarrow B'$ No ✗

Definition of Energy - $\boxed{\text{POSTULATE III}}$

For any equilibrium states A and B of a closed system, there is at least one process that involves just adiabatic work interactions between the system and its environment and takes the system from state A→B or from B→A. The amount of work required (or produced) is determined uniquely by specifying states A and B

This allows us to define the energy difference $\underline{E}_A - E_B = -W_{A\to B}$

↑ negative!

From postulate I: for simple systems,

$$\underline{E} = \underline{u} = f\,(N+2 \text{ independent variables})$$

$\underline{E}$ ↓ for composite

$\underline{u}$ ↓ for simple

Definition of heat Q

For a non-adiabatic process:

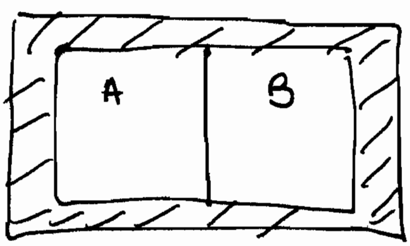
$$Q = \underline{E}_{final} - \underline{E}_{initial} - \mathcal{W} \quad (\text{"missing work"})$$

Old Sign convention from days of heat engines (~~not~~ used)

$\mathcal{W}$ is positive when performed by the system

Q is positive when "added" to the system

Now, we need to make a link between thermometric temperature and the direction of heat interactions - consider insulated composite system with an internal diathermal wall:



Any interaction between A and B must be a pure heat interaction

$$\left.\begin{array}{l} \Delta E_A = -\Delta E_B \\ \mathcal{W} = \phi \end{array}\right\} \Rightarrow Q_A = -Q_B$$

From experience, we know that heat interactions stop when the thermometric temperatures of A and B are the same ⟶ generalize as

$\boxed{\text{POSTULATE IV}}$

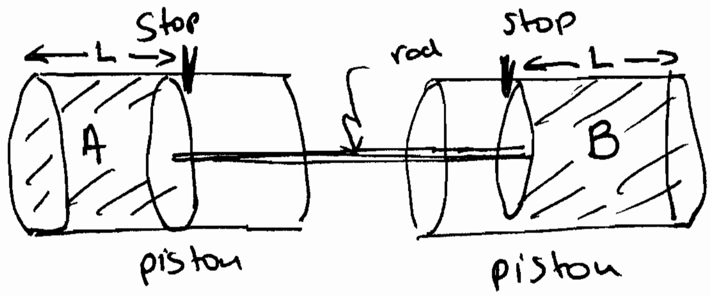
If the systems A–C and B–C have no heat interactions when connected by nonadiabatic walls, there will be no heat interaction if A and B are also connected

FIRST LAW, CLOSED SYSTEMS

$\Delta \underline{E} = Q + W$

$d\underline{E} = \delta Q + \delta W$; use δ to distinguish between state function $\underline{E}$ and non-state functions Q, W.

Examples 3.3 + 3.4



A: He 2 bar 300 K

B: He 1 bar 300 K

L = 10 cm

When stops are removed, pistons move – there is some friction, and the pistons eventually stop when the pressures are equal.

He is an ideal gas – a substance for which:

$P\underline{V} = NRT$

u = function of T only

define $C_v = \left.\frac{\partial u}{\partial T}\right)_V$

What is the final temperature in the two compartments?

For Helium, C_V = constant, so that $u = u_0 + C_V T$

First-Law balance, total system A+B:

$\Delta \underline{E} = \cancel{Q} + \cancel{W} \Rightarrow \Delta \underline{U}_A + \Delta \underline{U}_B = 0 \Rightarrow$

$\phantom{\Delta \underline{E} =} \emptyset \quad \emptyset$

$\Delta \underline{U}_A = -\Delta \underline{U}_B$ (1)

$\left.\begin{aligned} \Delta \underline{U}_A &= N_A \cdot \Delta u_A = N_A \cdot C_V \cdot (T_{A,f} - T_{A,i}) \\ \Delta \underline{U}_B &= N_B \cdot \Delta u_B = N_B \cdot C_V \cdot (T_{B,f} - T_{B,i}) \end{aligned}\right\} \overset{(1)}{\Longrightarrow}$

$$\Rightarrow \quad N_A \cdot \cancel{c_v} \cdot (T_{A,f} - T_{A,i}) = -N_B \cancel{c_v} (T_{B,f} - T_{B,i}) \quad (2)$$

From Equation-of-State: $N_A = \dfrac{P_{A,i} \underline{V}_{A,i}}{R T_{A,i}}$ (3)

$$N_B = \frac{P_{B,i} \cdot \underline{V}_{B,i}}{R T_{B,i}} \quad (4)$$

(a) Rod connecting pistons is metallic (diathermal)

$$T_{A,f} = T_{B,f} = T_f \overset{(2)}{\Longrightarrow} T_f = \frac{N_A T_{A,i} + N_B T_{B,i}}{N_A + N_B} \quad (5)$$

with $T_{A,i} = T_{B,i} = T_i \overset{(5)}{\Longrightarrow} T_f = T_i$

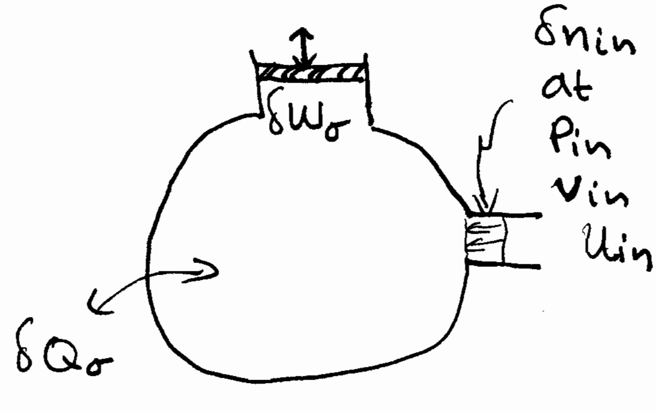
(b) Rod connecting pistons is insulating

→ problem cannot be solved without further assumptions on the path: how is friction distributed between A and B?

Two limiting cases: no friction in A → $T_{A,f} = 267\,K$, $T_{B,f} = 366\,K$
(see book) no friction in B → $T_{A,f} = 270\,K$, $T_{B,f} = 360\,K$

First Law, Open Systems

For open systems, we can redefine the boundaries so as to use the relationships of closed systems: Consider open system over a short period of time:



System σ that includes entering mass at pressure P_{in}, with sp. volume V_{in} and energy U_{in} is closed!

$$d\underline{E}_\sigma = \delta Q_\sigma + \delta W_\sigma + \underbrace{P_{in} \cdot V_{in} \cdot \delta n_{in}}_{} \quad ①$$

work performed on system by environment, to "push" δn_{in} moles into system against pressure P_{in}

Original (open) system: is initially missing δn_{in} $\quad d\underline{E} = d\underline{E}_\sigma + \delta n_{in} U_{in}$ ②

① + ② $\Rightarrow$ $\quad d\underline{E} = \delta Q_\sigma + \delta W_\sigma + (U_{in} + P_{in} V_{in})\,\delta n_{in}$ ③

Define enthalpy $H = U + PV$ (for simple systems only!)

③ $\Rightarrow$ $d\underline{E} = \delta Q_\sigma + \delta W_\sigma + H_{in}\,\delta n_{in}$

If system is simple, $\underline{E} \to \underline{U}$, generalize to multiple entering / leaving streams:

$$\boxed{d\underline{U} = \delta Q_\sigma + \delta W_\sigma + \sum_{in} H_{in}\,\delta n_{in} - \sum_{out} H_{out}\,\delta n_{out}}$$

First Law, Open Systems, differential form

or – to take into account kinetic + potential energy, composite systems

$$d\underline{E} = \delta Q_\sigma + \delta W_\sigma + \sum_{in} \left[H_{in} + g z_{in} + \frac{v_{in}^2}{2} \right] \delta n_{in} - \sum_{out} \left(\quad \right] \delta n_{out}$$