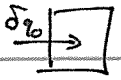
4 different processes can change an ideal gas
We will assume each one is performed reversibly.)

1) Constant Volume (isochoric)

initial state P_1, V_0, T_1 $\xrightarrow[\text{heat}]{\text{add}}$ δq_0 with V_0 fixed



Work can't be done because the volume is fixed.

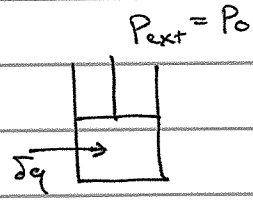
$\delta w = 0 \longleftarrow dV = 0$

$$\therefore \quad dU = \delta q = C_v (T_2 - T_1) = \frac{C_v}{Nk} V_0 (P_2 - P_1)$$

So if we are given N, P_1, V_0, T_1 and δq, we can compute: $\delta w, P_2, T_2, \Delta U$, and $\Delta S = C_v \ln\left(\frac{T_2}{T_1}\right)$

2) Constant pressure (isobaric)

initial state P_0, V_1, T_1 $\longrightarrow$ add heat δq with a constant external pressure



Now work can be done:

$$\delta w = -\int_{V_1}^{V_2} P_0 \, dV = -P_0 (V_2 - V_1) \qquad \text{Eq.(1)}$$

↑ assumes a quasistatic process such that

$$P_{int} = \frac{NkT}{V} = P_0$$

$$\Delta U = C_V (T_2 - T_1) = \frac{C_V P_0}{Nk} (V_2 - V_1) \qquad \text{Eq. (2)}$$

$$\delta q = \Delta U - \delta w = \left(\frac{C_V}{Nk} + 1\right) P_0 (V_2 - V_1) \qquad \text{Eq. (3)}$$

So if we are given P_0, V_1, C_V, N, and δq Eq. (3) above gives us V_2, Eq. (1) gives us δw Eq. (2) gives us T_2 and ΔU, and finally

$$\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right)$$

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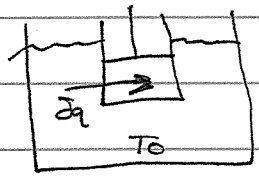
3) Constant temperature (isothermal)

initial state P_1, V_1, T_0 → add heat δq with a constant temperature



quasistatic implies: $P_{ext} = P_{int} = \frac{NkT_0}{V}$

$$\delta w = -\int_{V_1}^{V_2} P_{ext}\, dV = -\int_{V_1}^{V_2} P_{int}\, dV$$

$$= -\int_{V_1}^{V_2} \frac{NkT_0}{V}\, dV = -NkT_0 \ln\left(\frac{V_2}{V_1}\right) \qquad \text{ideal gas law}$$

$$= -NkT_0 \ln\left(\frac{P_1}{P_2}\right)$$

$\Delta U = C_V \Delta T = 0$ for isothermal changes

$$\therefore \delta q = -\delta w = NkT_0 \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = \frac{\delta q}{T_0} = N k \ln\left(\frac{V_2}{V_1}\right)$$

Once again we can calculate $P_2, V_2, \Delta U, \delta w$ and ΔS from the initial state N, P, T_0, V_1 and δq

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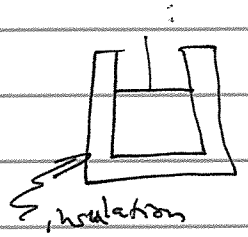
4) Adiabatic processes — No heat is transferred

initial state P_1, V_1, T_1 $\xrightarrow{\delta q = 0}$ final state P_2, V_2, T_2



We are allowed to reversibly change one variable $P, V,$ or T

$$dU = C_v dT = \cancel{\quad\quad} - P dV$$

because $\delta q = 0$ this must be work

For an ideal gas:

$$C_v dT = \frac{-N k_B T}{V} dV$$

$$\int_{T_1}^{T_2} C_v dT = \int_{V_1}^{V_2} -\frac{NkT}{V} dV$$

or move the T before integ

$$\int_{T_1}^{T_2} \frac{C_v}{T} dT = \int_{V_1}^{V_2} -\frac{Nk}{V} dV$$

$$C_v \ln\frac{T_2}{T_1} = -Nk \ln\left(\frac{V_2}{V_1}\right)$$

or:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{Nk/C_v}$$

T & V changes are related to each other in an adiabatic expansion

$\Delta S = 0$ because $\delta q_{rev} = 0$

Pathways are <u>combinations</u> of these processes

The four processes we have analyzed are <u>limited</u> because fixing one variable does not allow us to reach an arbitrary final state ($P_2 V_2 T_2$) from an arbitrary initial state ($P_1 V_1 T_1$)

We can <u>combine</u> 2 or more processes to form a pathway:

for example:

$$P_1 V_1 T_1 \xrightarrow{\text{isobaric}} P_1 V_2 T_x \xrightarrow{\text{isochoric}} P_2 V_2 T_2$$

<u>or</u>

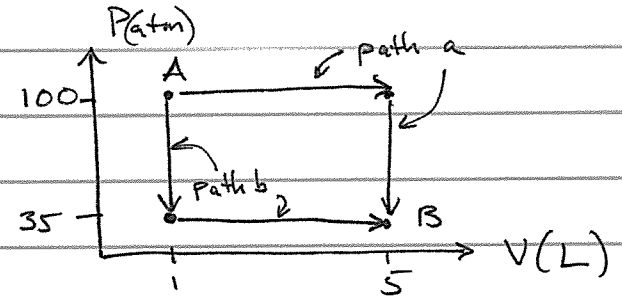
$$P_1 V_1 T_1 \xrightarrow{\text{isochoric}} P_2 V_1 T_y \xrightarrow{\text{isobaric}} P_2 V_2 T_2$$

These are 2 unique pathways that connect

$P_1 V_1 T_1 \longleftrightarrow P_2 V_2 T_2$

The values of <u>state functions</u> ΔU, ΔS will be identical for both paths, but δq & δw will be different.

Example:



1 mol of ideal gas

State A: $P_1 = 100$ atm $V_1 = 1$ L

State B: $P_2 = 35$ atm $V_2 = 5$ L

Path (a) isobaric → isochoric

$$\delta w_a = -P_1(V_2 - V_1) + 0 = -100(5-1) = -400 \text{ L·atm}$$

path (b) isochoric → isobaric

$$\delta w_b = 0 - P_2(V_2 - V_1) = -(35)(5-1) = -140 \text{ L·atm}$$

Work depended on the path

State A: $T_1 = \frac{P_1 V_1}{R} \cong 1200\,K$

State B: $T_2 = \frac{P_2 V_2}{R} \cong 2100\,K$

$$\therefore \quad \Delta U = C_V(T_2 - T_1) = \frac{3}{2}R(T_2 - T_1) = \frac{3}{2}R(2100 - 1200)$$

$$= 111 \text{ L·atm}$$

This is the energy change regardless of path

$$\Delta U = \delta q + \delta w \quad \leftarrow \text{1st Law of thermodynamics}$$

Lets check this by computing δq directly:

$$\delta q = C_V(T_2 - T_x) + P_1(V_2 - V_1) \leftarrow \text{isobaric}$$
$$+ C_V(T_x - T_1) \leftarrow \text{isochoric}$$

$$\delta q = C_V(T_2 - T_1 + P_1(V_2 - V_1)$$

$$\delta q + \delta w = C_V (T_2 - T_1) + P_1(V_2 - V_1) - P_1(V_2 - V_1)$$

$$= C_V (T_2 - T_1) \quad = \Delta U \quad \text{as expected}$$

Next time: Thermodynamic cycles