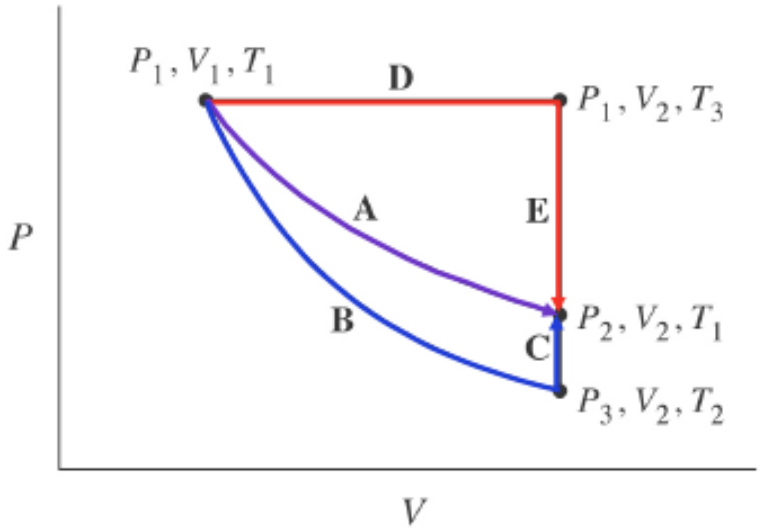
Lets solve some problems: Application of 1st Law

Q1. Calculate ΔU, W, q for three reversible paths

$$P_1, V_1, T_1 \quad \rightarrow \quad P_2, V_2, T_1$$



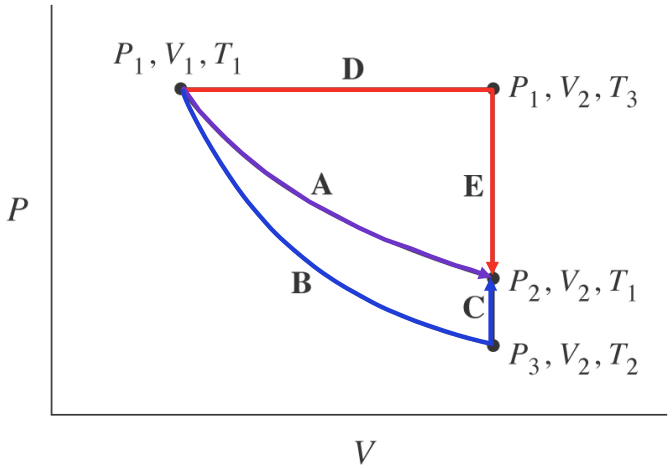
Path A: reversible isothermal expansion

Path B+C: reversible *adiabatic* expansion followed by heating at constant volume.

Path D+E: reversible constant-pressure expansion followed by cooling at constant volume.

All Reversible Roads Lead To...

$$P_1, V_1, T_1 \quad \rightarrow \quad P_2, V_2, T_1$$



ΔU must be the same for all paths, but q and w?

Path A: reversible isothermal expansion

Path B+C: reversible *adiabatic* expansion followed by heating at constant volume.

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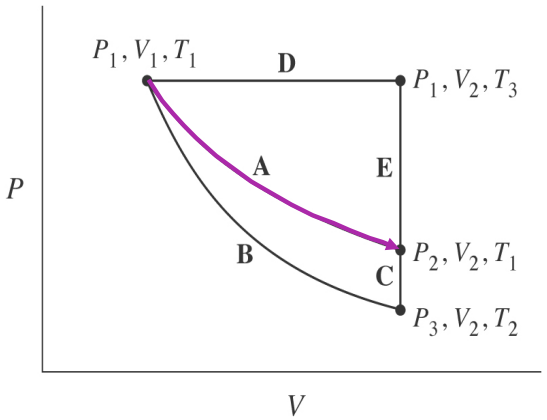
Path A



$$P_1, V_1, T_1 \quad \rightarrow \quad P_2, V_2, T_1$$

Reversible *isothermal* expansion

Since the energy of an ideal gas depends only on T

$$\Delta U_A = 0 \xrightarrow{\Delta U = q + w} -q_{\text{rev,A}} = w_{\text{rev,A}}$$

Since the process is reversible,

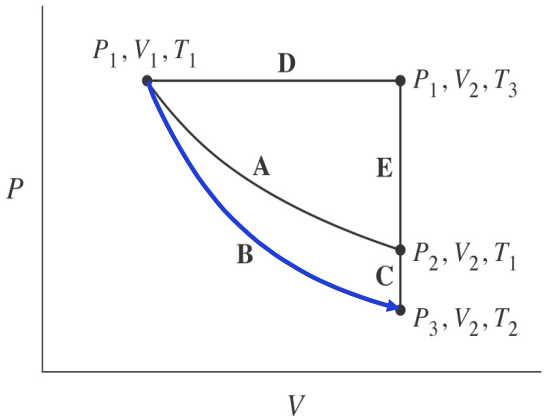
$$-\delta q_{\text{rev,A}} = \delta w_{\text{rev,A}} = -P_{\text{gas}} dV = -\frac{RT_1}{V} dV$$

And we have,

$$-q_{\text{rev,A}} = w_{\text{rev,A}} = -RT_1 \int_{V_1}^{V_2} \frac{dV}{V} = -RT_1 \ln \frac{V_2}{V_1}$$

Note that heat transfer in is required to maintain temperature

Path B



$$P_1, V_1, T_1 \longrightarrow P_3, V_2, T_2$$

Reversible *adiabatic* expansion

Adiabatic means *no energy is transferred as heat*, i.e., $q = 0$, and therefore $\Delta U = w$ and $dU = \delta w$

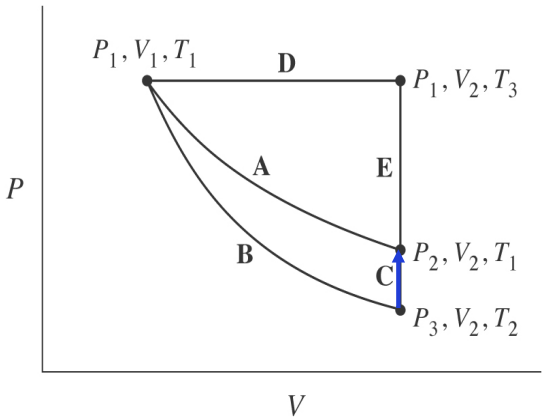
For an ideal gas, U depends only on T

$$C_V(T) = \left(\frac{\partial U}{\partial T}\right)_V \xrightarrow{\text{ideal gas}} C_V(T) = \frac{dU}{dT} \longrightarrow dU = C_V(T)dT$$

$$w_{\text{rev,B}} = \Delta U_{\text{B}} = \int_{T_1}^{T_2} dU = \int_{T_1}^{T_2} C_V(T)dT$$

(from T_1 to T_2)

Path C



$$P_3, V_2, T_2 \xrightarrow{\text{C}} P_2, V_2, T_1$$

Reversibly heat at constant volume

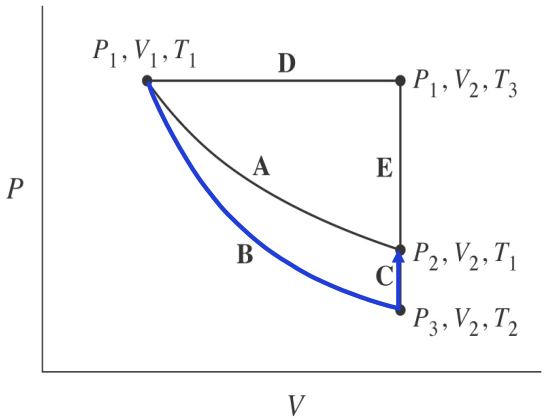
$\Delta V = 0$, so $w_{\text{rev,C}} = -PdV = 0$

That leaves only heat, i.e., $\Delta U_{\text{C}} = q_{\text{rev,C}} + w_{\text{rev,C}} = q_{\text{rev,C}} + 0$

$$q_{\text{rev,C}} = \Delta U_{\text{C}} = \int_{T_2}^{T_1} C_V(T)dT$$

(from T_2 to T_1)

Paths B + C



For the sum of B + C

$$q_{\text{rev,B+C}} = q_{\text{rev,B}} + q_{\text{rev,C}} = 0 + \int_{T_2}^{T_1} C_V(T)dT$$

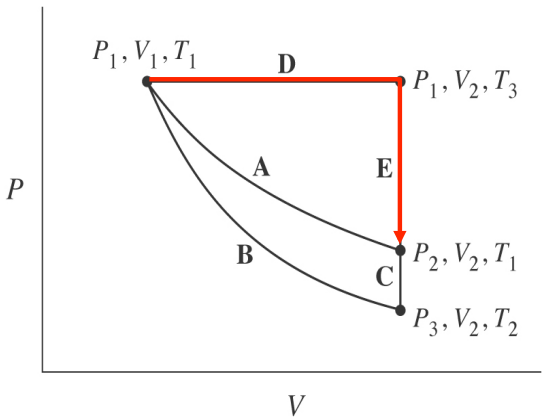
$$w_{\text{rev,B+C}} = w_{\text{rev,B}} + w_{\text{rev,C}} = \int_{T_1}^{T_2} C_V(T)dT + 0$$

For the energy,

$$\Delta U_{\text{B+C}} = \Delta U_{\text{B}} + \Delta U_{\text{C}} = \int_{T_1}^{T_2} C_V(T)dT + \int_{T_2}^{T_1} C_V(T)dT = 0$$

ΔU=0, the same as for path A (as must be true for a state function), but $w_{\text{rev,A}} \neq w_{\text{rev,B+C}}$, $q_{\text{rev,A}} \neq q_{\text{rev,B+C}}$

Paths D + E



For the sum of D + E

$$w_{\text{rev,D+E}} = w_{\text{rev,D}} + w_{\text{rev,E}} = -P_1\left(V_2 - V_1\right) + 0$$

$$\Delta U_{\text{D+E}} = \int_{T_1}^{T_3} C_V(T)dT + \int_{T_3}^{T_1} C_V(T)dT = 0$$

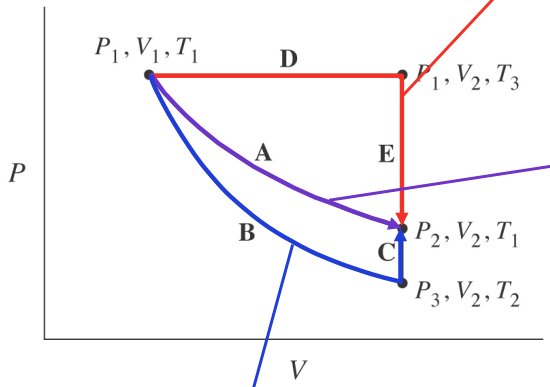
Another illustration that it's usually easiest to get q by difference from more easily computed ΔU and w

So, $q_{\text{rev,D+E}} = P_1\left(V_2 - V_1\right)$

Comparison of Paths

$$w_{\text{rev},D+\text{E}} = -P_1(V_2 - V_1) \qquad q_{\text{rev,D+E}} = P_1(V_2 - V_1)$$

$$P_1, V_1, T_1 \quad \rightarrow \quad P_2, V_2, T_1$$



$$w_{\text{rev,A}} = -RT_1 \ln \frac{V_2}{V_1}$$

$$q_{\text{rev,A}} = RT_1 \ln \frac{V_2}{V_1}$$

$$w_{\text{rev,B+C}} = \int_{T_1}^{T_2} C_V(T)dT \qquad q_{\text{rev,B+C}} = \int_{T_2}^{T_1} C_V(T)dT$$

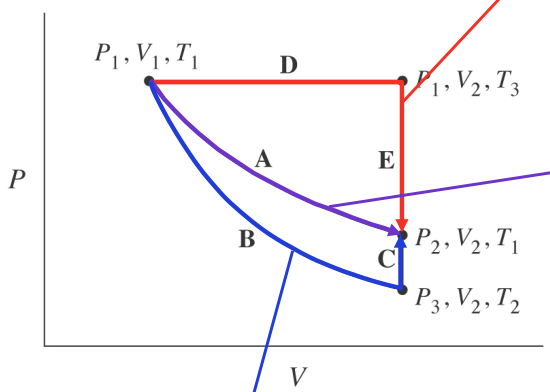
$\Delta U = 0$ for all paths (*state function*), but q_{rev} and w_{rev} differ

Quantitative Comparison of Paths

For example if $P_1 = 4.0$ bar, $V_1 = 0.5$ dm^3, $P_2 = 2.0$ bar, $V_2 = 1.0$ dm^3, and we have 0.1 moles of ideal monatomic gas:

$$w_{\text{rev},D+\text{E}} = -200 \text{ J} \quad q_{\text{rev,D+E}} = 200 \text{ J} \quad \Delta U_{D+E} = 0$$

$$P_1, V_1, T_1 \rightarrow P_2, V_2, T_1$$



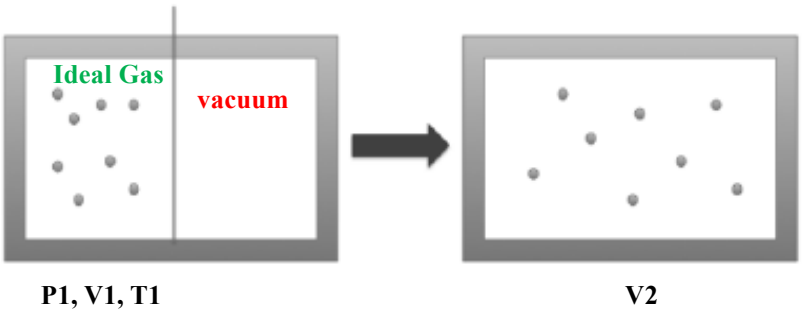
$$w_{\text{rev,A}} = -139 \text{ J}$$

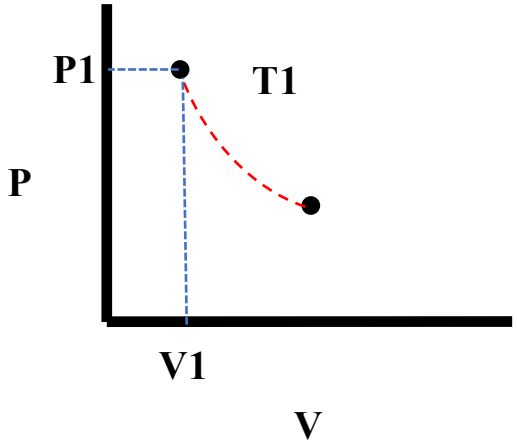
$$q_{\text{rev,A}} = 139 \text{ J}$$

$$\Delta U_A = 0$$

$$w_{\text{rev,B+C}} = -111 \text{ J} \quad q_{\text{rev,B+C}} = 111 \text{ J} \quad \Delta U_{B+C} = 0$$

Q1. When an ideal gas is expanded in vacuum (free expansion) what happen to ΔU, W, q, final temperature ?

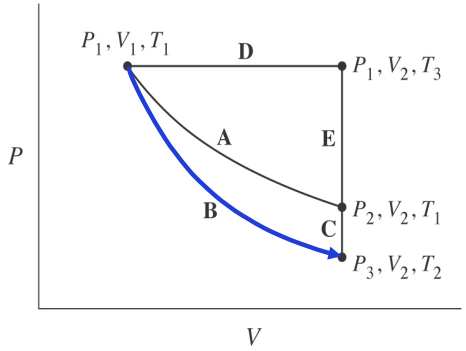




Adiabatic Expansion Cools a Gas

Adiabatic, so $q = 0$ and $dU = \delta w = dw$

(note that if either $\delta q = 0$ or $\delta w = 0$ then the remaining differential becomes exact)



For an ideal gas reversible expansion:

$$dw = dU = C_V(T)dT \quad \text{and} \quad dw = -PdV = -\frac{nRTdV}{V}$$

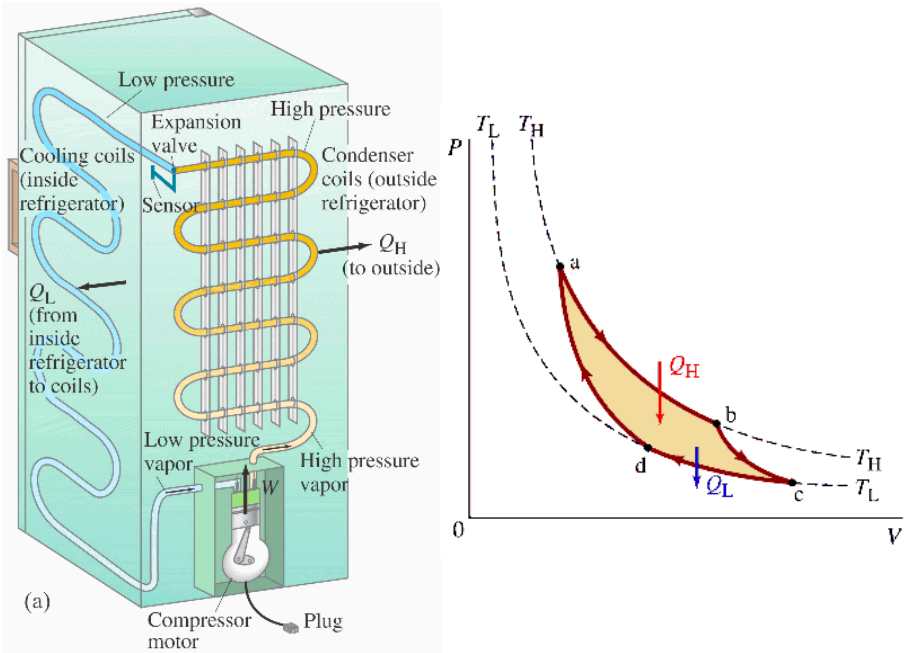
Putting them together,

$$C_V(T)dT = -\frac{nRT}{V}dV \longrightarrow \int_{T_1}^{T_2} \frac{\overline{C}_V(T)}{T}dT = -R\int_{V_1}^{V_2} \frac{dV}{V} = -R\ln\frac{V_2}{V_1}$$

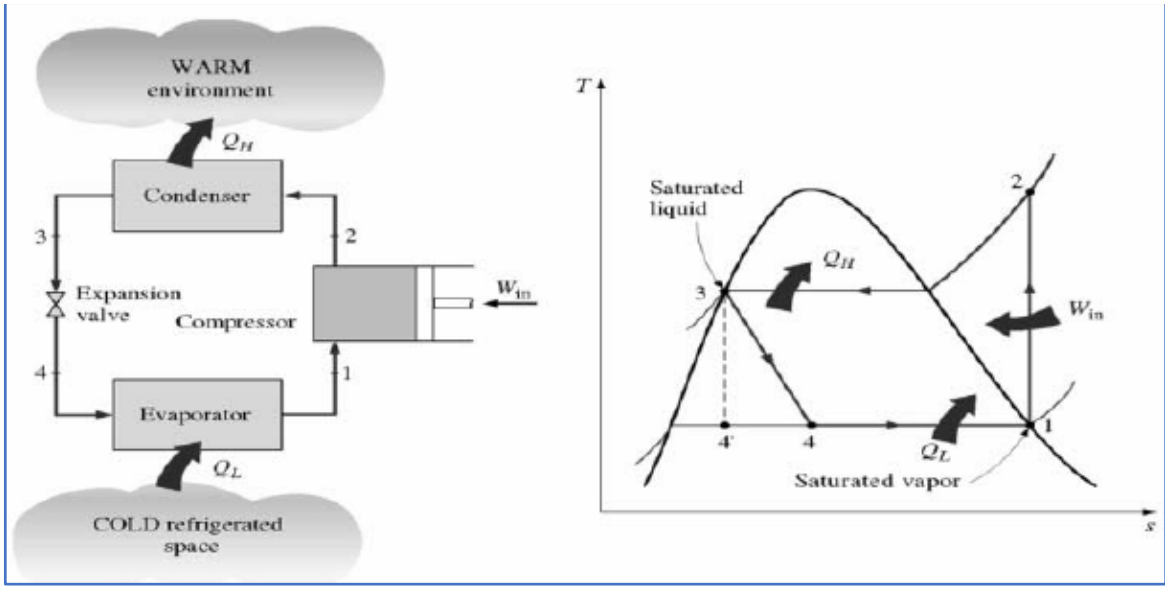
For a monatomic ideal gas, $\overline{C}_V = \frac{3R}{2}$

$$\frac{3R}{2}\int_{T_1}^{T_2} \frac{dT}{T} = \frac{3R}{2}\ln\frac{T_2}{T_1} = -R\ln\frac{V_2}{V_1} \longrightarrow \left(\frac{T_2}{T_1}\right)^{3/2} = \frac{V_1}{V_2}$$

The gas cools as it expands



https://www4.uwsp.edu/physastr/kmenning/Phys203/Lect42.html



https://www.researchgate.net/publication/257688202_Exergy_Analysis_of_Vapour_Compression_Refrigeration_System/figures?lo=1

Next: Application of calorimetry (heat measurement) in biology

- Batch Calorimetry
- Scanning calorimetry
- Differential scanning calorimetry
- Isothermal calorimetry