STATISTICAL MOLECULAR THERMODYNAMICS

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Video 5.5
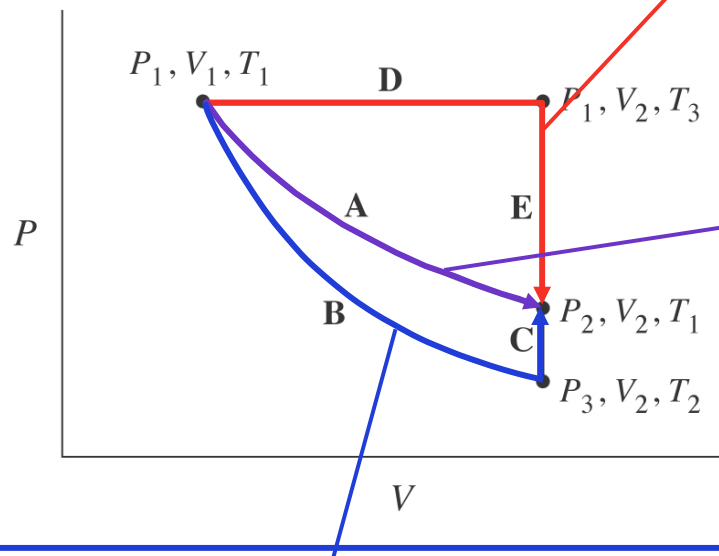
Adiabatic Processes

COMPARISON OF PATHS

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

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

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

$$q_{\text{rev},A} = RT_1 \ln \frac{V_2}{V_1}$$
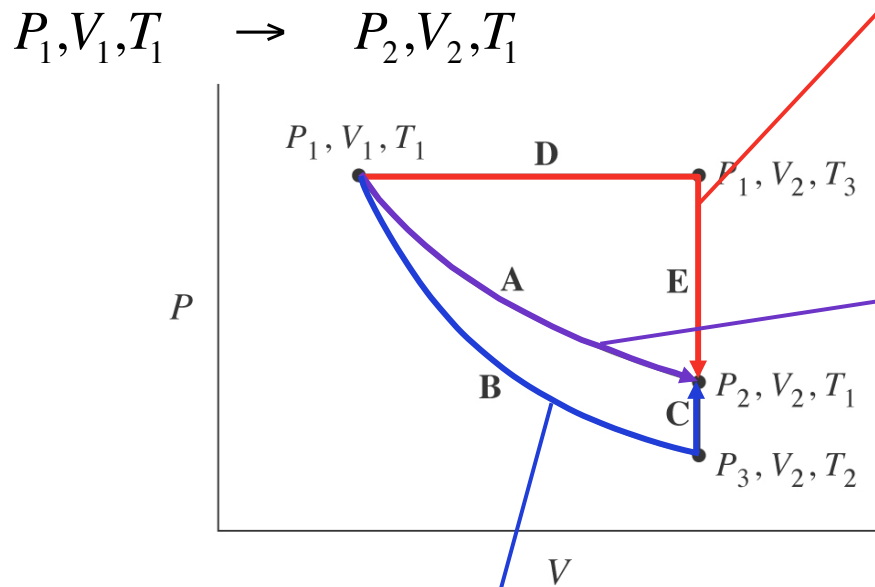
$$w_{\text{rev},B+C} = \int_{T_1}^{T_2} C_V(T)\,dT \qquad q_{\text{rev},B+C} = \int_{T_2}^{T_1} C_V(T)\,dT$$

$\Delta U = 0$ 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:

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

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

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

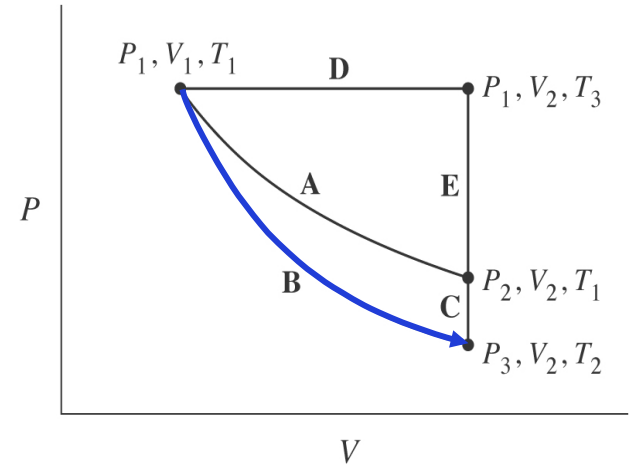$$q_{\text{rev},A} = 139 \text{ J}$$

$$\Delta U_A = 0$$

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

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,

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

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

$$\frac{3R}{2}\int_{T_1}^{T_2}\frac{dT}{T} = \frac{3R}{2}\ln\frac{T_2}{T_1} = -R\ln\frac{V_2}{V_1} \quad \longrightarrow \quad \left(\frac{T_2}{T_1}\right)^{3/2} = \frac{V_1}{V_2} \qquad \textit{The gas cools as it expands}$$

ADIABATIC VS ISOTHERMAL IDEAL GAS LAW

Boyle's law for an *isothermal process*:

$$P_1 V_1 = P_2 V_2$$

Cf. an adiabatic process (ideal monatomic gas):

$$\left(\frac{T_2}{T_1}\right)^{3/2} = \frac{V_1}{V_2} \xrightarrow{\;PV = nRT\;} \left(\frac{P_2 V_2}{P_1 V_1}\right)^{3/2} = \frac{V_1}{V_2}$$

$$P_1 V_1^{5/3} = P_2 V_2^{5/3}$$

less compression; with nowhere to dump heat, temperature rises