Statistical Molecular Thermodynamics

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Video 5.5

Adiabatic Processes
**Comparison of Paths**

\[ w_{\text{rev},D+E} = -P_1(V_2 - V_1) \quad q_{\text{rev},D+E} = P_1(V_2 - V_1) \]

\[ P_1,V_1,T_1 \rightarrow P_2,V_2,T_1 \]

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

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

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

\[ \Delta U = 0 \text{ for all paths (state function), but } q_{\text{rev}} \text{ and } w_{\text{rev}} \text{ differ} \]
Quantitative Comparison of Paths

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

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

$w_{\text{rev,A}} = -139 \text{ J} \quad q_{\text{rev,A}} = 139 \text{ J} \quad \Delta U_A = 0$

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

\[
dw = dU = C_V(T)\,dT \quad \text{and} \quad dw = -P\,dV = -\frac{nRT\,dV}{V}
\]

Putting them together,

\[
C_V(T)\,dT = -\frac{nRT}{V}\,dV \quad \rightarrow \quad \int_{T_1}^{T_2} \frac{C_V(T)}{T}\,dT = -R \int_{V_1}^{V_2} \frac{dV}{V} = -R \ln \frac{V_2}{V_1}
\]

For a monatomic ideal gas, \( \overline{C}_v = \frac{3R}{2} \)

\[
\frac{3R}{2} \int_{T_1}^{T_2} \frac{dT}{T} = \frac{3R}{2} \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} \quad \rightarrow \quad \left( \frac{T_2}{T_1} \right)^{3/2} = \frac{V_1}{V_2}
\]

The gas cools as it expands.
Adiabatic vs Isothermal Ideal Gas Law

Boyle’s law for an *isothermal process*:

\[ PV_1 = PV_2 \]

Cf. an adiabatic process (ideal monatomic gas):

\[
\left( \frac{T_2}{T_1} \right)^{3/2} = \frac{V_1}{V_2} \quad \Rightarrow \quad \left( \frac{P_2 V_2}{P_1 V_1} \right)^{3/2} = \frac{V_1}{V_2}
\]

\[
PV_1^{5/3} = PV_2^{5/3}
\]

*less compression; with nowhere to dump heat, temperature rises*