Statistical Molecular Thermodynamics

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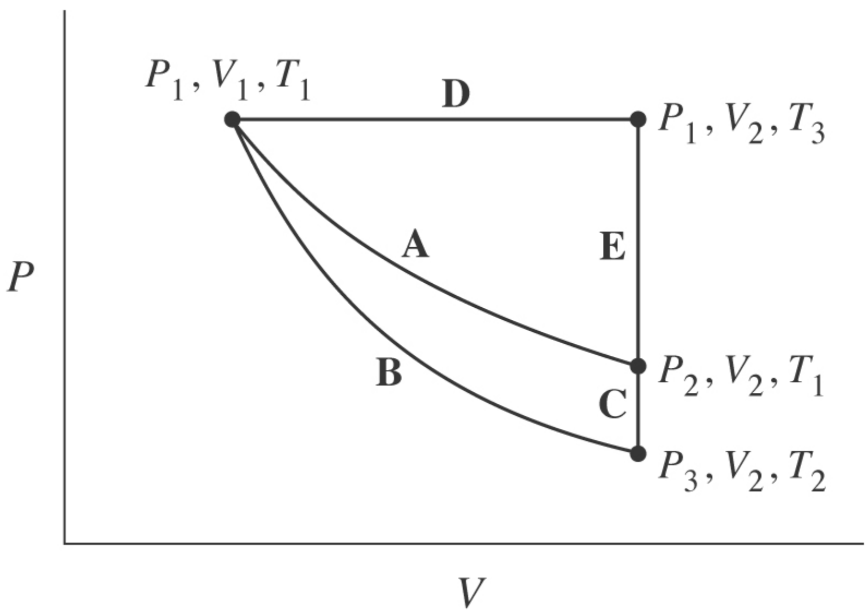
Video 6.2

Entropy as a State Function

Different Paths, Same Destination

$$\oint dS = \oint \frac{\delta q_{rev}}{T} = \Delta S = 0$$

Since entropy is a state function (like energy), the change in entropy for a cyclic process is 0 by definition. Let's revisit our old ideal gas roadmap…



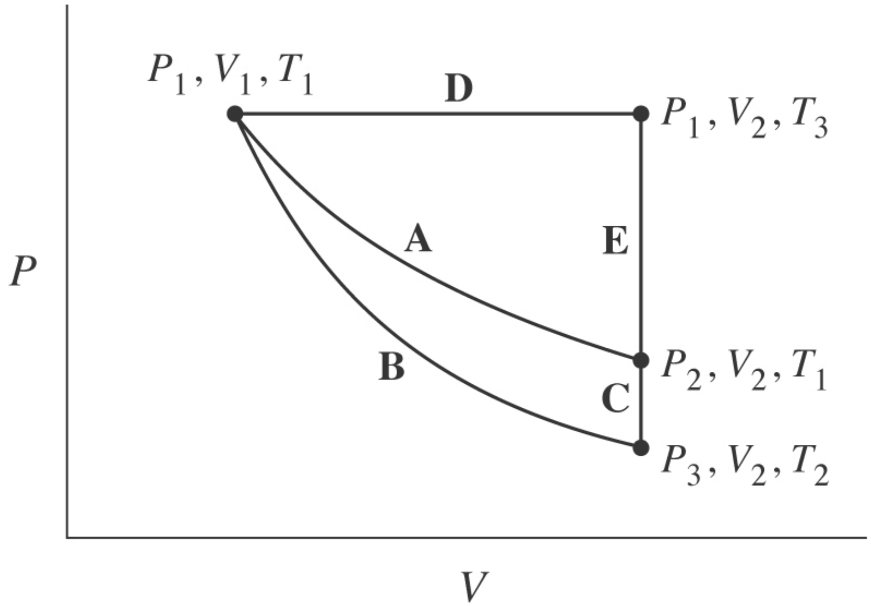
Path A vs. Path B + Path C:
Is the change in entropy the same for these two *different* paths? (It should be)

Recall:

$$\delta q_{rev,A} = -\delta w_{rev,A} = \frac{nRT_1}{V} dV$$

$$q_{rev,A} = nRT_1 \ln \frac{V_2}{V_1}$$

Comparison of Paths — Path A

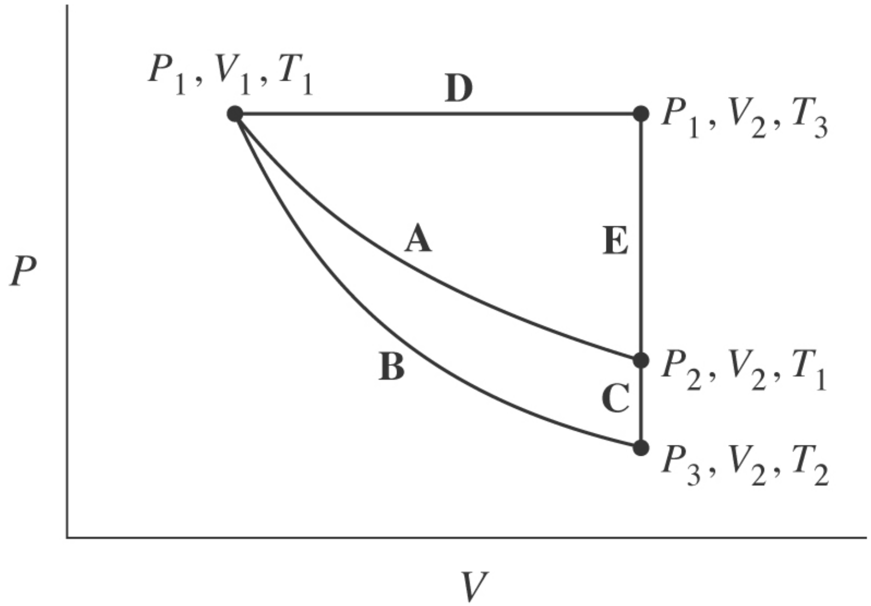


$$\delta q_{rev,A} = -\delta w_{rev,A} = \frac{nRT_1}{V} dV$$

$$\Delta S_A = \int_1^2 \frac{\delta q_{A,rev}}{T_1} = \int_{V_1}^{V_2} \frac{1}{T_1} \frac{nRT_1}{V} dV = nR \ln \frac{V_2}{V_1}$$

note that an increase in volume leads to an increase in entropy

Comparison of Paths — Paths B+C



$$\delta q_{rev,B} = 0$$

$$\Delta S_B = \int_1^2 \frac{\delta q_{B,rev}}{T_1} = 0$$

Recall (video 5.4):

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

$$\Delta S_C = \int_1^2 \frac{\delta q_{C,rev}}{T} = -\int_{T_1}^{T_2} \frac{C_V(T)}{T}\,dT = nR\ln\frac{V_2}{V_1} \quad ✓$$

proven for an ideal gas in Video 5.5

Entropy Change and Temperature

$$dS = \frac{\delta q_{rev}}{T}$$

Entropy is related to the disorder of a system. If you add energy as heat to a system, then its entropy increases because the thermal disorder increases.

Note that the same heat delivered at lower T contributes more to an entropy increase than heat delivered at a higher T.