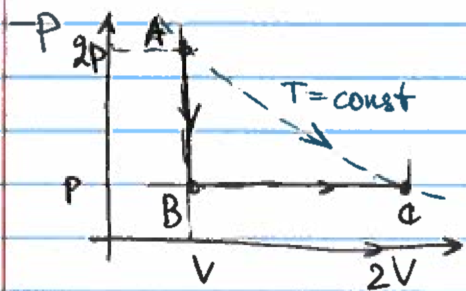
Entropy calculations



Problem from PollEv
What is the change of entropy along the path ABC?

Solution 1: Entropy is a state variable so $\Delta S_{ABC} = S_C - S_A$ independent of the path

One can get from A to C following an isothermal process $T_A = T_C = 2PV/nR$

Since there is no change of temperature

$$\Delta S_{AC} = \frac{Q_{AC}}{T_A} = \frac{W_{AC}}{T_A} = \frac{nRT_A \ln V_C/V_A}{T_A} = nR \ln \frac{V_C}{V_A} = nR \ln 2$$

Solution 2: Isochoric process $A \to B$ $\quad Q_{AB} = nC_V (T_B - T_A)$

Isobaric process $B \to C$ $\quad Q_{BC} = nC_P (T_C - T_B)$

Assuming ideal monoatomic gas $C_V = \frac{3}{2}R$, $C_P = \frac{5}{2}R$

$$T_B = PV/nR = T_A/2 \quad , \quad T_C = T_A$$

However! Since the temperature is changing as gas progresses $A \to B$ and $B \to C$, we must approach the enthropy calculations carefully

$$\Delta S_{A \to B} = \int_{T_A}^{T_B} \frac{dQ}{T} = \int_{T_A}^{T_B} \frac{nC_V\,dT}{T} = nC_V \ln \frac{T_B}{T_A} = -\frac{3}{2} nR \ln 2$$

$$\Delta S_{B \to C} = \int_{T_B}^{T_C} \frac{dQ}{T} = \int_{T_B}^{T_A} \frac{nC_P\,dT}{T} = nC_P \ln \frac{T_A}{T_B} = \frac{5}{2} nR \ln 2$$

Total change $\Delta S_{AC} = nR \ln 2$, as expected.

Entropy calculations for non-ideal gas

Problem: a sample of n moles of a monoatomic Van der Waals gas is expanded isothermically and reversibly at a constant temperature T from volume V to volume 3V. The Van der Waals equation of state for a gas is:

$$\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$$

where a and b are known constants.
Find the change in entropy ~~of~~ ΔS of the system

a. Isothermal reversible prosess: $\Delta S = \frac{Q}{T} = \frac{W}{T}$

($T = const \longrightarrow$ no change in internal energy)

$$W = \int_V^{3V} P\,dV = \int_V^{3V} \left[\frac{nRT}{(V-nb)} - a\left(\frac{n}{V}\right)^2\right] dV =$$

$$= \int_V^{3V} \frac{nRT}{V-nb}\,dV - \int_V^{3V} \frac{an^2\,dV}{V^2} = nRT \ln(V-nb)\Big|_V^{3V} +$$

$$+ \frac{an^2}{V}\Big|_V^{3V} = nRT \ln\left(\frac{3V-nb}{V-nb}\right) - \frac{2an^2}{3V}$$

$$\Delta S = \frac{W}{T} = nR \ln\left(\frac{3V-nb}{V-nb}\right) - \frac{2an^2}{3TV}$$