Q1) A sample containing two moles of He gas behaves ideally. In state A, it is at (P_A, V_A, T_A). In the first step of a four step process, it expands isothermally and reversibly to state B, in which $V_B = 2\ V_A$. In the second step, it expands adiabatically and reversibly to state C, in which $T = T_C$. In the third step, it is compressed isothermally and reversibly to state D, in which $V_D = (1/2)\ V_C$. In the fourth and final step, the system returns adiabatically and reversibly to state A.

a) Determine the entropy change for the system for each of the four steps, expressed to three significant figures, in units of J/K. In the space below, provide a justification in words and/or with calculations, as appropriate, for each answer.

ANSWER:

Step 1: isothermal reversible expansion from V_A *to* $V_B = 2V_A$

$$\Delta S_1 = nR\ ln\frac{V_B}{V_A} = (2\ mol)(8.314\ J\ mol^{-1}\ K^{-1})ln\frac{2V_A}{V_A} = 11.5\ J\ K^{-1}$$

Step 2: adiabatic reversible expansion, $\therefore$ *Q=0 and* $\Delta S_2 = 0$

Step 3: isothermal reversible compression from V_C *to* $V_D = ½\ V_C$

$$\Delta S_3 = nR\ ln\frac{V_D}{V_C} = (2\ mol)(8.314\ J\ mol^{-1}\ K^{-1})ln\frac{V_D}{2V_D} = -11.5\ J\ K^{-1}$$

Step 4: adiabatic reversible compression, $\therefore$ *Q=0 and* $\Delta S_4 = 0$

ASIDE: For an isothermal reversible expansion or compression of an ideal gas, $\Delta U=0$,

$$\therefore Q_{rev} = -W_{rev} = \int_{V_{initial}}^{V_{final}} \frac{nRT}{V} dV = nRT\ ln\frac{V_{final}}{V_{initial}}$$

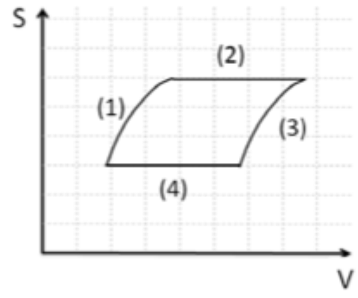
$$\therefore \Delta S = \frac{Q_{rev}}{T} = nR\ ln\frac{V_B}{V_A}$$

b) The sketches below are not to scale. Which of the shapes in sketches A through E best represents the cycle described in part a)? Note that the vertical axis is entropy, S, and the horizontal axis is volume, V. Each of the four steps is numbered in parentheses. No justification beyond what you presented in part a) is required.

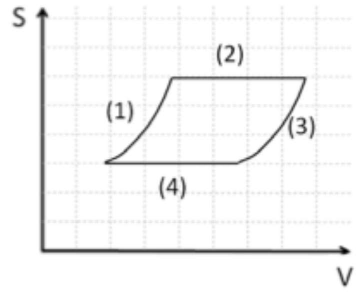
ANSWER: A

ASIDE: Steps 2 and 4 have $\Delta S=0$*, which is true for all five diagrams below. Steps 1 and 3 should have the shape of a logarithmic function (think of a plot of log x vs x ; log x increases more slowly than x).*

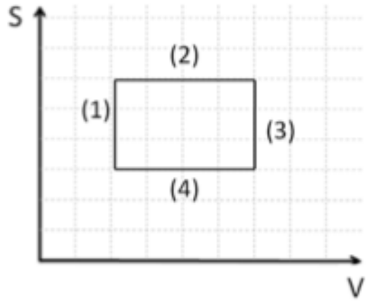
(A)



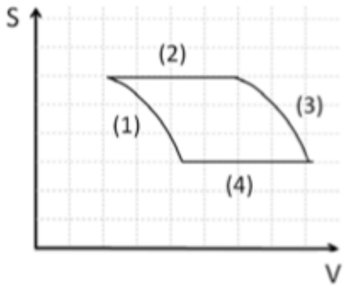
(B)



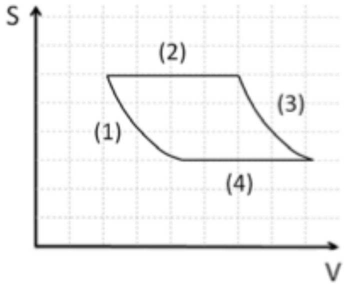
(C)



(D)



(E)



Q2) The four Maxwell relations are:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

a) Starting from the definition of enthalpy, derive the following general expression for a system at constant composition in which only expansion/compression work is performed: $dH = T\,dS + V\,dP$

ANSWER: $H \equiv U + PV \quad \rightarrow \quad dH = dU + PdV + VdP$

For a reversible process, this leads to $dH = dQ_{rev} - PdV + PdV + VdP$

$$= (T/T)\, dQ_{rev} + VdP$$

$$= TdS + VdP$$

Because this final equation involves only state functions, it will hold true regardless of whether the process was performed reversibly or not.

b) Using the above information, show that: $$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

ANSWER: Consider S(T,P)

$$\therefore dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = \left(\frac{T}{T}\right)\left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$= \left(\frac{1}{T}\right)\left(\frac{\partial Q_{rev}}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = \left(\frac{1}{T}\right)\left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$= \left(\frac{1}{T}\right) C_P\, dT + \left(\frac{\partial S}{\partial P}\right)_T dP = \left(\frac{C_P}{T}\right) dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

ASIDE: The final step above involved a Maxwell relation.

a) For a Clausius gas: $P(V - nb) = nRT$

Integrate the expression for dS from part b) to get one for ΔS for a closed system that consists of 1 mole of a Clausius gas that goes from an initial state at (P_1, V_1, T_1) to a final state at (P_2, V_2, T_2). Assume C_P for the gas to be independent of temperature.

ANSWER: *The equation of state can be rewritten as:*

$$V = \frac{nRT}{P} + nb \qquad and \quad \therefore \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

$$\therefore \Delta S = \int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} \frac{C_P}{T}\, dT - \int_{P_1}^{P_2} \frac{nR}{P}\, dP = C_P\, ln\frac{T_2}{T_1} - nR\, ln\frac{P_2}{P_1}$$

Q3) For benzene in a container open to the atmosphere, $T_m = 5.42\ ^{\circ}C = 278.5\ K$

and $T_b = 87.1\ ^{\circ}C = 360.3\ K$.

Also: $C_{p,\,m,\,solid} = 118.4\ J\ mol^{-1}\ K^{-1}$ (assume to be independent of T)

$C_{p,\,m,\,liquid} = 134.8\ J\ mol^{-1}\ K^{-1}$ (assume to be independent of T)

ΔH_{fusion} at $T_m = 9.90$ kJ/mol and $\Delta H_{vaporization}$ at $T_b = 30.77$ kJ/mol

a) Determine the enthalpy **and** entropy changes for melting of one mole of solid benzene to the liquid phase at -100 °C in an open container.

ANSWER: Set this up as a three step process that will take one mole of solid benzene to the liquid phase at -100 °C as follows:

Step 1: one mole of solid benzene is warmed reversibly from 173.2 K to T_m

$\Delta H_1 = n\, C_{p,\,m,\,solid}\ (T_m - 173.2\ K) = 12.47\ kJ$

$$\Delta S_1 = \int_{173.2K}^{T_m} \frac{nC_{P,m,solid}}{T}\, dT \ = (118.4\, J\, K^{-1}) \ln\left(\frac{278.5}{173.2}\right) = 56.24\, J\, K^{-1}$$

Step 2: one mole of solid benzene converted to liquid at T_m, therefore, reversibly

$\Delta H_2 = n\, \Delta H_{fusion} = 9.90$ kJ

$$\Delta S_2 = \frac{\Delta H_2}{T_m} = 35.55\, J\, K^{-1}$$

Step 3: one mole of liquid benzene is cooled reversibly from T_m to 173.2 K

$\Delta H_3 = n\, C_{p,\,m,\,liquid}\ (173.2\ K - T_m) = -14.19\ kJ$

$$\Delta S_3 = \int_{T_m}^{173.2K} \frac{nC_{P,m,liqud}}{T}\, dT \ = (134.8\, J\, K^{-1}) \ln\left(\frac{173.2}{278.5}\right) = -64.03\, J\, K^{-1}$$

$$\therefore\ Overall\colon\ \Delta H = \sum \Delta H_i = 8.18\ kJ \qquad and \qquad \Delta S = \sum \Delta S_i = 27.8\, JK^{-1}$$

b) Determine the enthalpy **and** entropy changes for the surroundings in the process described in part a).

ANSWER: At constant pressure, $Q_P = \Delta H$. As $Q_{system} = -Q_{surroundings}$ and as we can assume the surroundings accepts or gives up heat reversibly:

$$\therefore\ Overall\colon\ \Delta H_{surr} = -8.18\ kJ \qquad and \qquad \Delta S_{surr} = \frac{\Delta H_{surr}}{T_{surr}} = \frac{-8.18\ kJ}{173.2\ K} = -47.2\, JK^{-1}$$

ASIDE:

$\Delta S_{total} = \Delta S_{surr} + \Delta S_{sys} = -19.4\, JK^{-1}$ *so this would NOT be a spontaneous process.*

Q4) Silver carbonate decomposes when heated: $Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$

At 400K, the equilibrium constant for this reaction is 1.41×10^{-2}.
At 500K, the equilibrium constant for this reaction is 1.48.

Use the above information, plus the definition of Gibbs free energy, plus the reaction equilibrium result that at a specified temperature and pressure $\Delta G_{rx} = \Delta G^{o}_{rx} + RT \ln Q$ to determine ΔH^{o}_{rx} **and** ΔS^{o}_{rx} for the decomposition, assuming both to be temperature-independent.

ANSWER: *At equilibrium:* $\Delta G_{rx} = \Delta G^{o}_{rx} + RT \ln Q = 0 = \Delta G^{o}_{rx} + RT \ln K$

$\therefore \Delta G^{o}_{rx} = -RT \ln K$

Also, $G \equiv H - TS \rightarrow \Delta G = \Delta H - T\Delta S$ *at a specified T.*

As a special case: $\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$

Combining equations gives:

$$\ln K = \left(\frac{-\Delta H^{o}_{rx}}{R}\right)\left(\frac{1}{T}\right) + \frac{\Delta S^{o}_{rx}}{R}$$

Now insert the two pairs of values you have for K and T to get two equations having the two unknowns: ΔH^{o}_{rx} ***and*** ΔS^{o}_{rx}*. Solve using standard algebraic methods.*

Or*: Think like a physical chemist and note that the above equation looks like* $y = mx + b$

$$\therefore \textit{slope of a plot of } \ln K \textit{ vs.} \left(\frac{1}{T}\right) = \left(\frac{-\Delta H^{o}_{rx}}{R}\right)$$

$$\left(\frac{-\Delta H^{o}_{rx}}{R}\right) = \frac{\ln K_2 - \ln K_1}{\left(1/T_2\right) - \left(1/T_1\right)} = \frac{\ln\left(\frac{1.48}{1.41 \times 10^{-2}}\right)}{\left(1/500\right) - \left(1/400\right)} = -9307\ K$$

$$\therefore \Delta H^{o}_{rx} = 9307R = 77.4\ kJ\ mol^{-1}$$

Now use this with either of the given K and T pairs to solve for ΔS^{o}_{rx} :

$$\ln(1.48) = \left(\frac{-9307}{500}\right) + \frac{\Delta S^{o}_{rx}}{8.314\ J\ mol^{-1}K^{-1}} \qquad \therefore \Delta S^{o}_{rx} = 158\ J\ mol^{-1}K^{-1}$$

$$\ln(0.0141) = \left(\frac{-9307}{400}\right) + \frac{\Delta S^{o}_{rx}}{8.314\ J\ mol^{-1}K^{-1}} \qquad \therefore \Delta S^{o}_{rx} = 158\ J\ mol^{-1}K^{-1}$$