



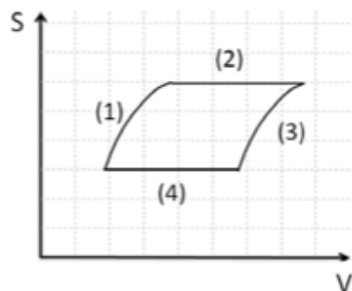
**Q1)** A sample containing two moles of He gas behaves ideally. In state A, it is at  $(P_A, V_A, T_A)$ . In the first step of a four step process, it expands isothermally and reversibly to state B, in which  $V_B = 2 V_A$ . In the second step, it expands adiabatically and reversibly to state C, in 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.

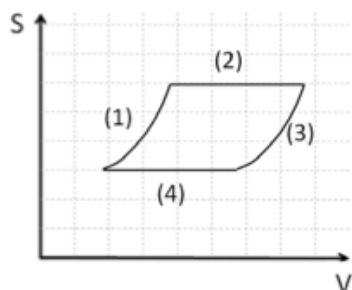
- b) The sketches below are not to scale. Which of the shapes in sketches A through E best represents the cycle described in part a)? Note that the vertical axis is entropy,  $S$ , and the horizontal axis is volume,  $V$ . Each of the four steps is numbered in parentheses. No justification beyond what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

ANSWER: \_\_\_\_\_

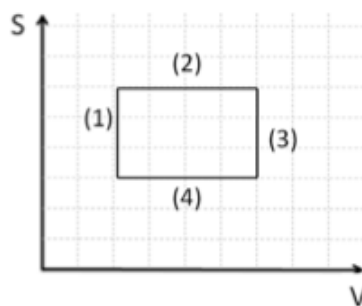
(A)



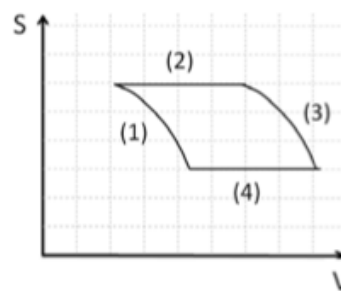
(B)



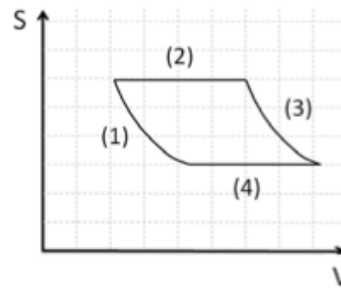
(C)



(D)



(E)



**Q2)** The four Maxwell relations are:

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

- 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:

$$dH = T dS + V dP$$

- b) Using the above information, show that:

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

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

Integrate the expression for  $dS$  from part b) to get one for  $\Delta S$  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.

**Q3)** For benzene in a container open to the atmosphere,  $T_m = 5.42\text{ }^\circ\text{C} = 278.5\text{ K}$   
and  $T_b = 87.1\text{ }^\circ\text{C} = 360.3\text{ K}$ .

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

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

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

a) Determine the enthalpy **and** entropy changes for melting of one mole of solid benzene to the liquid phase at  $-100\text{ }^\circ\text{C}$  in an open container.

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

**Q4)** Silver carbonate decomposes when heated:  $\text{Ag}_2\text{CO}_3(\text{s}) \rightleftharpoons \text{Ag}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$

At 400K, the equilibrium constant for this reaction is  $1.41 \times 10^{-2}$ .

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  $\Delta G_{\text{rx}} = \Delta G_{\text{rx}}^{\circ} + RT \ln Q$  to determine  $\Delta H_{\text{rx}}^{\circ}$  **and**  $\Delta S_{\text{rx}}^{\circ}$  for the decomposition, assuming both to be temperature-independent.