

**Assume ideal behaviour unless stated otherwise.**

1. A sample consisting of 3.00 mol of diatomic perfect gas molecules at 200 K is compressed reversibly and adiabatically until its temperature reaches 250 K. Given that  $C_{V,m} = 27.5 \text{ J K}^{-1} \text{ mol}^{-1}$ , calculate  $q, w, \Delta U, \Delta H$  and  $\Delta S$ .
2. Calculate  $\Delta S$  (for the system) when the state of 3.00 mol of a perfect gas, for which  $C_{p,m} = 5/2 R$ , is changed from 25 °C and 1.00 atm to 125 °C and 5.00 atm. How do you rationalize the sign of  $\Delta S$ ?
3. Consider a system consisting of 2.0 mol  $\text{CO}_2(\text{g})$ , initially at 25 °C and 10 atm and confined to a cylinder of cross-section  $10.0 \text{ cm}^2$ . It is allowed to expand adiabatically against an external pressure of 1.0 atm until the piston has moved outwards through 20 cm. Assume that carbon dioxide may be considered a perfect gas with  $C_{V,m} = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$  and calculate  $q, w, \Delta U, \Delta T$  and  $\Delta S$ .
4. Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when a sample of nitrogen gas of mass 14 g at 298 K and 1.00 bar doubles its volume in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against  $p_{\text{ext}} = 0$ , and (c) an adiabatic reversible expansion.
5. The molar heat capacity,  $C_{p,m}$  (in  $\text{Joule K}^{-1} \text{ mol}^{-1}$ ) of chloroform ( $\text{CHCl}_3$ ) in the range 240 K to 330 K is given by  $C_{p,m} = 91.47 + 7.5 \times 10^{-2} T$  where  $T$  is the absolute temperature. In a particular experiment, 1.00 mol  $\text{CHCl}_3$  is heated from 273 K to 300 K. Calculate  $\Delta S$ .
6. 20 lit of nitrogen gas at 100 atm and 200 °C expands adiabatically against a constant external pressure of 1 atm until the equilibrium is attained. Calculate  $\Delta S$  for (a) the change and (b) if the process is carried out reversibly to the same final pressure. Given,  $C_{p,m} = 7 \text{ cal/mol/K}$ .
7. If  $\alpha$  (isobaric expansion coefficient) =  $1.82 \times 10^{-4} \text{ K}^{-1}$  and  $\kappa$  (isothermal compressibility) =  $3.87 \times 10^{-5} \text{ atm}^{-1}$  at 20 °C for mercury, then determine  $\left(\frac{\partial p}{\partial T}\right)_V$  for mercury.

8. The enthalpy of vaporization of ethanol is 43.5 kJ/mol at its normal boiling point of 352 K. Calculate (a) the entropy of vaporization of ethanol at this temperature and (b) the entropy change of its surroundings.
9. Calculate the difference in the molar entropy between liquid water and ice at  $-5^{\circ}\text{C}$  and 1 atm. The difference in the heat capacities on melting is 37.3 J/K. Calculate the change in entropy for the system, surrounding, and universe, and conclude if ice would melt spontaneously at  $-5^{\circ}\text{C}$  at 1 atm.