

CYL100 Physical Chemistry Homework 3

Handed out: Feb. 19, 2014

Due: Feb. 25, 2014

You will find any data that is not provided on the back pages of Atkins'. Consider the system to be an ideal gas, if it is not mentioned but required.

1. At high densities the molecules themselves make up an appreciable fraction of the available volume, and an equation of state of 1 mol of gas can be written in the form $P(V - b) = RT$, where 'b' is a constant which is related to the size of the molecules. (i) Calculate the work done when 1 mole of this nonideal gas at 298 K is compressed reversibly and isothermally from 22.4 L to 0.224 L if 'b' is 0.04L. (ii) What is the work done if the gas behaves ideally in (i) and explain why the answers differ in (i) and (ii).
2. Verify that the enthalpy of a perfect gas is independent of its pressure while it is dependent upon pressure for a van der Waals gas. [Use the approximate form of van der Waals equation $PV = nRT + nPb - (a/RT)$]
3. An important application of adiabatic cooling/heating is in atmospheric physics. Pressure varies with altitude as $dP/dh = -g\rho$, where ρ is the density. Calculate the change in temperature at the top of a mountain 2 km above the valley floor assuming the process is adiabatic and air behaves ideally.
4. The velocity of sound in a fluid is given as $c = 1/\sqrt{\rho\kappa_S}$, where κ_S , the adiabatic compressibility is given as $-1/V \left(\frac{\partial V}{\partial p} \right)_S$. What is the velocity of sound in an ideal gas?
5. Which of these cyclic integrals must vanish for a closed system with P-V work only? (a) $\oint PdV$; (b) $\oint (PdV + VdP)$; (c) $\oint VdV$; (d) $\oint HdT$; (e) $\oint dq_{rev}$; (f) $\oint dw_{rev}/P$.
6. One mol of hydrogen occupies a volume of 0.1 m³ at 300K and one mol of argon also occupies the same volume but at 400K. While isolated from their surroundings, each undergoes a free expansion, the hydrogen to 5 times and argon 8 times its initial volume. The two masses are then placed in contact with each other and reach thermal equilibrium. What is the total change in entropy? ($C_v^{H_2} = 10$ kJ/K/kg, $C_v^{Ar} = 0.31$ kJ/K/kg)
7. The molar heat capacity of oxygen at constant pressure for temperatures in the range 300 to 400 K and for low or moderate pressures can be approximated as $C_p(\text{J mol}^{-1} \text{K}^{-1}) = 25.73 + 0.013 T$. (a) Calculate q , w , ΔU , ΔH when 2 mol of O₂ is reversibly heated from 27 to 127 °C with P held fixed at 1 atm. (b) Repeat the calculation if the same change is effected at constant V .
8. By a thermodynamic analysis show that the following familiar processes are spontaneous: (a) A book is pushed off a table and falls to the floor. (b) One mole of an ideal gas in a vessel that is connected to another identical evacuated vessel through a valve. The valve is opened and the gas occupies both vessels. (c) Melting of ice when brought in contact with an object at a temperature above 0 °C.

9. 100 g of ice at 0 °C is dropped into an insulated beaker containing 150 g of water at 100 °C. Calculate ΔS for this process.
10. Calculate the maximum work and the maximum non-expansion work that can be obtained from the freezing of supercooled water at -5 °C and 1.0 atm. The densities of water and ice are 0.999 and 0.917 g cm⁻³, respectively at -5 °C.
11. Derive the relations: (i) $C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$; (ii) $C_p - C_v = \frac{\alpha^2 TV}{\beta}$; (iii) $\mu_{JT} = -(V/C_p)(\beta C_v \mu_J - \beta P + 1)$ (iv) $\left(\frac{\partial H}{\partial V}\right)_S = \gamma/\beta$ (v) $\left(\frac{\partial V}{\partial T}\right)_P = \frac{C_v \beta}{T \alpha}$.
12. At what pressure can graphite be converted to diamond. Use the data given below.

| | $\Delta H_0^{298} \text{ kJ mol}^{-1}$ | $S_0^{298} \text{ J K}^{-1} \text{ mol}^{-1}$ | $\rho_{298} \text{ g cm}^{-3}$ |
|----------|--|---|--------------------------------|
| graphite | 0 | 5.69 | 2.22 |
| diamond | 1.9 | 2.44 | 3.51 |