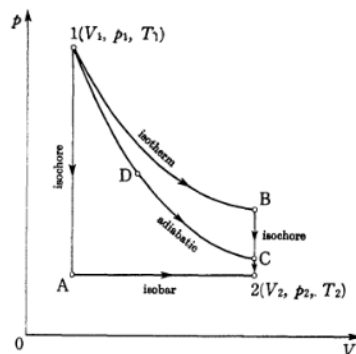


Statistical Thermodynamics (CHM422-2015)

Assignment 1

submission due on 23/01/2015 (by 5 p.m.). There is no mark for assignment.
However, it will help you to solve problems in quiz and exams.

1. An ideal gas is changed from an initial state (p_1, V_1, T_1) to a final state (p_2, V_2, T_2) by the following three quasi-static processes as seen in the figure: (i) 1A2, (ii) 1B2, and (iii) 1DC2. What is the increase in the internal energy for $1 \rightarrow 2$? Also obtain the work that must be done to the system and the heat that must be added in each process. Assume that the specific heat is constant.



2. Show that the relation $PV^\gamma = \text{const}$ (Poisson's equation) holds in a quasi-static adiabatic process of an ideal gas and derive the work W which the gas does to its surroundings in a quasi-static adiabatic process from (P_1, V_1, T_1) to (P_2, V_2, T_2) . Assume the specific heat to be constant.

3. Show that the following relation exists between the adiabatic compressibility κ_{ad} and isothermal compressibility κ_T , where,

$$\kappa_{ad} = (-1/v)(\partial v / \partial p)_{ad} \quad \text{and} \quad \kappa_T = (-1/v)(\partial v / \partial p)_T$$

4. It is found that a particular system obeys the relation, $U=PV$ and $P=BT^2$, where B is a constant. Find the fundamental equation of this system.

5. Find the three equations of state in the entropy representation for a system with the fundamental equation,

$$u = \left(\frac{v_0^{1/2}}{R^{3/2}} \right) \frac{s^{5/2}}{v^{1/2}}$$

6. Consider the following fundamental equation, $S = AU^N V^m N^r$, where A is a positive constant. Evaluate the permissible values of the three constants n , m , and r if the fundamental equation is to satisfy the thermodynamic postulates and if, in addition, we wish to have P increase with U/V , at constant N . [Zero of energy can be taken as the energy of the zero temperature state]

7. One mole of a monatomic ideal gas is contained in a cylinder of volume 10^{-3} m^3 at a temperature of 400 K. The gas is to be brought to a final state of volume $2 \times 10^{-3} \text{ m}^3$ and temperature 400 K. A thermal reservoir of temperature 300 K is available, as is a reversible work source. What is the maximum work that can be delivered 'to the reversible work source'?

8. The enthalpy of a particular system is $H=AS^2N^{-1} \ln(P/P_0)$, where A is a positive constant. Calculate the molar heat capacity at constant volume (c_v) as a function of T and P.

9. Show the following fundamental equation follows the conditions of postulate III and IV. R, v_0 , θ .

$$S = \left(\frac{R^2}{v_0\theta} \right)^{1/3} (NVU)^{1/3}$$

10. The following ten equations are purported to be fundamental equations of various thermodynamic systems. However, **five** are inconsistent with one or more of postulates II, III, and IV and consequently are not physically acceptable. Find those five equations that are not physically permissible and indicate the postulates violated by each. The quantities v_0 , θ , and R are positive constants, and in all cases in which fractional exponents appear only the real positive root is to be taken.

$$a) S = \left(\frac{R^2}{v_0\theta} \right)^{1/3} (NVU)^{1/3}$$

$$b) S = \left(\frac{R}{\theta^2} \right)^{1/3} \left(\frac{NU}{V} \right)^{2/3}$$

$$c) S = \left(\frac{R}{\theta} \right)^{1/2} \left(NU + \frac{R\theta V^2}{v_0^2} \right)^{1/2}$$

$$d) S = \left(\frac{R^2\theta}{v_0^3} \right) V^3/NU$$

$$e) S = \left(\frac{R^3}{v_0\theta^2} \right)^{1/5} [N^2VU^2]^{1/5}$$

$$f) S = NR \ln(UV/N^2R\theta v_0)$$

$$g) S = \left(\frac{R}{\theta} \right)^{1/2} [NU]^{1/2} \exp(-V^2/2N^2v_0^2)$$

$$h) S = \left(\frac{R}{\theta} \right)^{1/2} (NU)^{1/2} \exp\left(-\frac{UV}{NR\theta v_0}\right)$$

$$i) U = \left(\frac{v_0\theta}{R} \right) \frac{S^2}{V} \exp(S/NR)$$

$$j) U = \left(\frac{R\theta}{v_0} \right) NV \left(1 + \frac{S}{NR} \right) \exp(-S/NR)$$