1. (10pts) Answer the following questions.

(a) (5pts) Calculate the mass of water vapour present in a house of volume 1000 m^3 that contains air at 22°C on a day when the relative humidity is 48 percent indoors. (Saturated water vapour pressure in the house is 19.827 Torr at 22°C)

(c) (5pts) Compression factor (Z), virial equation of state, and van der Waals equation can be used for the explanation of a real gas state. Briefly explain these and also describe the conditions that a real gas approaches a perfect gas behavior in each case.

2. (20pts) Answer the following questions.

(a) (2pts) Explain the first law of thermodynamics.

(b) (3pts) Show that enthalpy (H) can be represented by a heat transfer at constant pressure.

(c) (5pts) Prove that $C_p - C_V = nR$ for a perfect gas, where C_V and C_p are heat capacities at constant volume and constant pressure, respectively.

(d) (10pts) Derive the following relation for a perfect gas performing a reversible adiabatic expansion from a volume V_i at a pressure p_i to V_f at p_f,

$$p_f V_f^{\gamma} = p_i V_i^{\gamma}, \quad \gamma = C_{p,m}/C_{V,m}$$

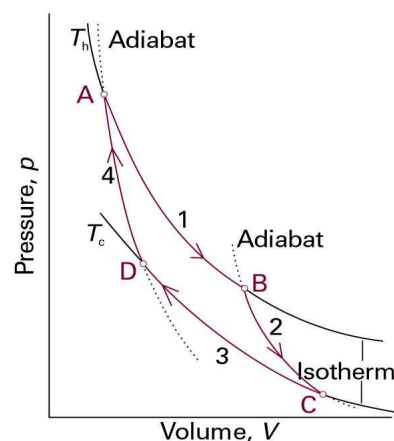Where, $C_{p,m}$ and $C_{v,m}$ are molar heat capacities at constant volume and constant pressure, respectively.

Fig. 3.6 The basic structure of a Carnot cycle. In Step 1, there is isothermal reversible expansion at the temperature T_h. Step 2 is a reversible adiabatic expansion in which the temperature falls from T_h to T_c. In Step 3 there is an isothermal reversible compression at T_c, and that isothermal step is followed by an adiabatic reversible compression, which restores the system to its initial state.

3. (15pts) Answer the following questions.

(a) (3pts) Explain the second law of thermodynamics in terms of the entropy S.

(b) (2pts) What is the thermodynamic definition of the entropy S?

(c) (10pts) Prove that the entropy is a state function by showing that the total change in entropy around one Carnot cycle, consisting of four reversible stages (Fig. 3.6), is zero.

4. (15pts) A sample consisting of 1 mol of perfect gas atoms (for which $C_{V,m} = {}^3/_2R$) is taken through the cycle shown in Fig. 2.34.

(a) (3pts) Determine the temperature at the points 1, 2, and 3.

(b) (7pts) Calculate heat q, work w, internal energy change ΔU, and enthalpy change ΔH for each step and for the overall cycle. If a numerical answer cannot be obtained from the information given, then write in $+$, $-$, 0, or ? as appropriate.
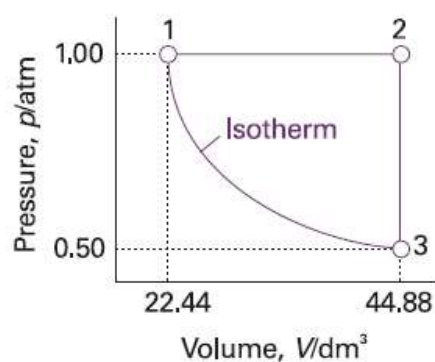

Fig. 2.34

(c) (5pts) A sample of oxygen of mass 96 g at 25.0°C is allowed to expand reversibly and adiabatically from 5.00 dm^3 to 10.00 dm^3. What is the work done by the gas?

5. (10pts) Answer the following questions.

(a) (5pts) Show that the criterion for a spontaneous change is given by Clausius inequality, $dS - dq/T \geq 0$.

(b) (5pts) Show that the Clausius inequality becomes $dA_{T,V} \leq 0$ and $dG_{T,p} \leq 0$ for Helmholtz energy A and Gibbs energy G, respectively.

6. (10pts) Answer the following questions.

(a) (5pts) Consider a system consisting of 3.0 mol $CO_2(g)$, initially at 35°C and 9.0 atm and confined to a cylinder of cross-section 100.0 cm^2. The sample is allowed to expand adiabatically against an external pressure of 2.5 atm until the piston has moved outwards through 25 cm. Assume that carbon dioxide may be considered a perfect gas with $C_{V,m} = 28.8$ J K^{-1} mol^{-1}, and calculate the entropy change, ΔS.

(b) (5pts) Suppose that 2.5 mol Ar(g) occupies 72 dm^3 at 298 K and expands to 100 dm^3. Calculate the Gibbs energy change, ΔG for the process.

7. (20pts) Answer the following questions.

(a) (8pts) Derive the fundamental equation of $dU = TdS - pdV$ for a reversible change in a closed system. Also, derive the fundamental equations for Enthalpy H, Helmholtz energy A and Gibbs energy G.

(b) (2pts) Derive the following relations:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$

(c) (6pts) Schematically draw the variations of the Gibbs energy G with temperature T at constant pressure for the gaseous, liquid, and solid phases of a material, respectively. Explain the reason briefly. Also plot G versus pressure p at constant T when T is below the meting point of the material, and briefly explain the reason.

(d) (4pts) Show that the Gibbs energy varies with pressure, $G(p_f) = G(p_i) + V_m\Delta p$ for a condensed phase, and $G(p_f) = G(p_i) + nRT\ln(p_f/p_i)$ for a perfect gas. Where p_i and p_f are initial and final pressure, V_m is the molar volume, and $\Delta p = p_f - p_i$.