

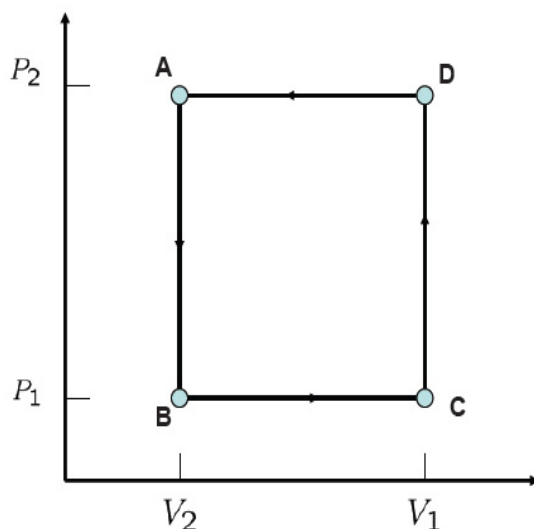
CHM225 Problem Set #1– September 10, 2008

1. A gas undergoes a reversible isothermal compression from a state 1 = (T_1, V_1) to a state 2 = (T_2, V_2) . The equation of state of the gas is

$$\frac{PV^2}{(V + c)} = RT,$$

where c is a constant.

- (i) Compute the work along this path from state 1 to state 2 .
 - (ii) Compute ΔU and q for this path from state 1 to state 2 .
 - (iii) Suppose the compression is carried out irreversibly at the external pressure P_2 corresponding to that of state 2 . What is work and how does it compare with that obtained in (i)?
 - (iv) Suppose the gas is ideal. What is the work for the isothermal compression taking the system from state 1 to state 2 and how does it compare to that obtained in (i)?
2. Suppose a system can exist in states $A = (P_2, V_2)$, $B = (P_1, V_2)$, $C = (P_1, V_1)$ and $D = (P_2, V_1)$. Consider the cyclic path $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$ shown in the figure.



- (i) Compute the work in each step of the cycle.
- (ii) For the entire cycle, compute the change in the internal energy, ΔU_{cycle} , the heat, q_{cycle} , and the work, w_{cycle} .
- (iii) Suppose the cycle is traversed in the reverse direction, $A \rightarrow D \rightarrow C \rightarrow B \rightarrow A$? Compute the work in each step of the reversed cycle as well as ΔU_{cycle} , the heat, q_{cycle} , and the work, w_{cycle} .

3. One mole of CO_2 at 100°C and 80 atm is compressed isothermally and reversibly to 100 atm . The pressure is then reduced to 80 atm by cooling reversibly at constant volume. Finally, the system returns to original state by warming reversibly at constant pressure. Assuming that CO_2 obeys the Van der Waals equation of state with constants $a = 3.592\text{ l}^2\text{atm/mol}^2$ and $b = 0.04265\text{ l/mol}$, calculate q and w for each step and for the cycle.

You can assume $C_V = \frac{3}{2}R$. To find C_P use the relation

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_P.$$

The partial derivatives on the right hand side must be calculated. To find $\left(\frac{\partial U}{\partial V} \right)_T$ use the relation

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P.$$

You will have to use the Van der Waals equation to obtain unknown quantities that specify the different states. For example, the gas is initially at $(T_1 = 100\text{ C}, P_1 = 80\text{ atm})$. Use the Van der Waals equation to find V_1 . This involves solving a cubic equation.

4. One mole of an ideal monatomic gas undergoes the following processes: 1. a reversible adiabatic expansion from (P_1, V_1, T_1) to (P_2, V_2, T_2) . 2. Return to the initial state by a reversible straight line path where $P = cV + b$, where the constants b and c can be determined from the initial and final points of the path. Calculate ΔU , q and w for each step and for the cycle if $P_1 = 2\text{ atm}$, $T_1 = 0^\circ\text{C}$ and $V_2 = 2V_1$.
5. A gas has internal energy $U = \frac{5}{2}PV + c$, where c is a constant. Consider three states of the system where $A = (P_A, V_A)$, state B has the same pressure as state A and state C has the same volume as state A . The gas undergoes a reversible, cyclic process $A \rightarrow B \rightarrow C \rightarrow A$. The process $A \rightarrow B$ occurs at constant pressure P_A . The process $B \rightarrow C$ occurs along a path where the pressure varies linearly with volume. The process $C \rightarrow A$ occurs at constant volume.
- Calculate q and w for each of the three steps in the cycle.
 - Calculate q and w for a reversible process from A to B along a parabolic path where $P = P_A + c_2[V^2 - V(V_A + V_B) + V_A V_B]$ and c_2 is a constant.
 - Find the forms of the curves $P = P(V)$ in the PV -plane along which $dq = 0$.