

CHM225 Problem Set 3– October 20, 2008

1. A Carnot cycle consists of the following sequence of reversible isothermal and adiabatic state changes:

$$(T_1, V_1) \rightarrow (T_1, V_1') \rightarrow (T_2, V_2) \rightarrow (T_2, V_2') \rightarrow (T_1, V_1).$$

One mole of the working gas for the cycle satisfies the equation of state, $P(V - b) = RT$, where b is a constant. The heat capacity at constant volume for this gas is $C_V = 3R/2$.

- (i) For the state change $(T_1, V_1) \rightarrow (T_1, V_1')$ compute $\Delta U_{1 \rightarrow 1'}$, $q_{1 \rightarrow 1'}$ and $w_{1 \rightarrow 1'}$.
 - (ii) Compute ΔU , q and w for the entire cycle.
 - (iii) Compute the efficiency of the Carnot cycle engine and comment on your result.
2. A gas satisfies the equation of state $P(V - b) = RT$, where b is a constant. The heat capacity at constant volume for the gas is $C_V = 3R/2$. Consider a change of state,

$$(T_1, V_1) \rightarrow (T_2, V_2),$$

by two different paths (a) and (b). Path (a) is a reversible process and path (b) is a spontaneous (irreversible) process.

- (i) Suppose the entropy is regarded as a function of T and V , $S = S(T, V)$. Compute the entropy change between the two states for path (a), $\Delta S_{1 \rightarrow 2}^{(a)}$.
- (ii) Repeat the calculation for path (a) regarding the entropy as function of T and P , $S = S(T, P)$. Comment on your result.
- (iii) Compute the entropy change $\Delta S_{1 \rightarrow 2}^{(b)}$ when path (b) is taken.
- (iv) Consider the cyclic process,

$$(T_1, V_1) \xrightarrow{(a)} (T_2, V_2) \xrightarrow{(c)} (T_1, V_1),$$

involving the reversible path (a) and the spontaneous (irreversible) path (c). Compute the entropy change for the cycle.

3. Show that the condition for spontaneity for a system at fixed (T, P) is $\Delta G < 0$.
4. A nonideal Van der Waals gas undergoes a reversible isothermal expansion from V_1 to V_2 . Compute the entropy change and compare it with that for an ideal gas undergoing a reversible isothermal expansion between the same volumes.