

PHYSICAL CHEMISTRY (for pre-med students) Mid-term exam (Fall 2008)

1. (a) Consider that an entropy S is as function of temperature T and volume V , i.e., $S = S(T, V)$. Derive the following relation. (10 pt)

$$c_p - c_v = \left[\left(\frac{\partial E}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p \quad (1)$$

(b) Change of internal energy as function of T and V is given by

$$dE = \left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV. \quad (2)$$

Meanwhile the change of internal energy as function of entropy S and volume V is given by

$$dE = TdS - pdV. \quad (3)$$

Using Eqs.(2),(3) and the property that entropy (S) is a state function (i.e., dS is an exact differential), derive the following identity. (10 pt)

$$\pi_T \equiv \left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p \quad (4)$$

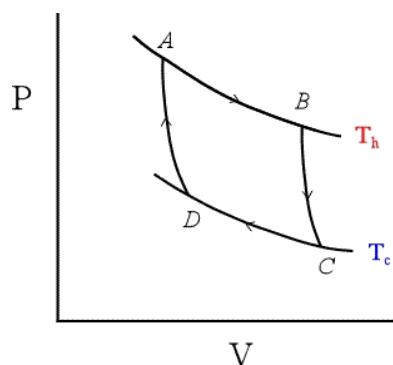
(c) Evaluate $c_p - c_v$ both for ideal gas and for van der Waals gases (5 pt).

2. N -moles of a monoatomic gas are to be employed in a Carnot cycle that undergoes isothermal expansion (A→B), adiabatic expansion (B→C), isothermal compression (C→D), and adiabatic compression (D→A). The ideal gas is initially in contact with a hot reservoir of temperature T_h , and in the first stage of the cycle it is expanded from volume V_A to volume V_B . The process follows quasi-statically along the arrow in the $p - V$ cycle.

(a) Calculate the work and heat transfers in each of the four steps of the cycle in terms of T_h , T_c , V_A , V_B and N . (10 pt)

(b) Redraw this process in $p - V$ plane onto $T - S$ plane. (5 pt)

(c) Compute the thermodynamic efficiency of the Carnot cycle using the results from (a). (5 pt)



3. Consider two boxes of gases that are thermally isolated from the world and, initially, from each other as well. Let the heat capacity of each gas be C_1 and C_2 . Box 1 starts with temperature $T_{i,1}$, whereas box 2 starts with $T_{i,2}$. (The subscript “ i ” means “initial,” and “ f ” will mean “final.”) Assume that both gases are ideal so that the internal energy is given by $E_i(T) = C_i T$. Note that the boxes are neither permeable nor deformable.

Now we put the boxes into thermal contact with each other but still isolated from the rest of the world. We know they’ll eventually come to the same temperature when the system reaches equilibrium.

(a) What is this final temperature? (5 pt)

(b) What is the change of entropy for entire system (ΔS_{tot}) and for each box ($\Delta S_1, \Delta S_2$)?

If $T_{i,1} < T_{i,2}$ then what is the sign of ΔS_1 and ΔS_2 ? (10 pt)

(c) Show that $\Delta S_{tot} \geq 0$ is always satisfied. (10 pt)

(d) Under a special circumstance, ΔS_{tot} will be zero: When? Why? (5 pt)

(e) Briefly discuss about the second law of thermodynamics using the above results. (5 pt)

4. (a) The mixing process of two ideal gases, n_A mol of A and n_B mol of B , that are initially in two separate flasks at the same temperature T and p is an irreversible and spontaneous process. Hence, we expect that there is a free energy change associated with this process. What is the change of Gibbs free energy (ΔG_{mix}) and change of entropy (ΔS_{mix}) after the gases in two flasks are mixed? Express your answer using n_A, n_B, R (gas constant) and T . (10 pt)

(b) The mixing entropy (ΔS_{mix}) in (a) can alternatively be obtained by using the Boltzmann’s definition of entropy $S = k_B \log \Omega$ where Ω is the number of configurations. By employing the Stirling approximation (when $N \rightarrow \infty$)

$$\log N! \approx N \log N - N \tag{5}$$

obtain the same answer you get in (a). (10 pt)