PHYSICAL CHEMISTRY I Final Exam (June 18th. Spring 2009)

1. (20 pt) Two finite solid bodies of constant total heat capacity per body with C_1 and C_2 are used as heat sources to drive heat engine. Their initial temperatures are T_1 and T_2 respectively.

(a) What is the final temperature of the two bodies when the two bodies are allowed to exchange the heat without any work being extracted?

(b) Show that entropy associated with the process in (a) is always greater than zero.

(c) Now, you want to extract the work out of the above mentioned thermal transfer process. Find the final temperature of the two bodies that you can extract maximum work from the system.

(d) What is the maximum work that you can extract from (b)?

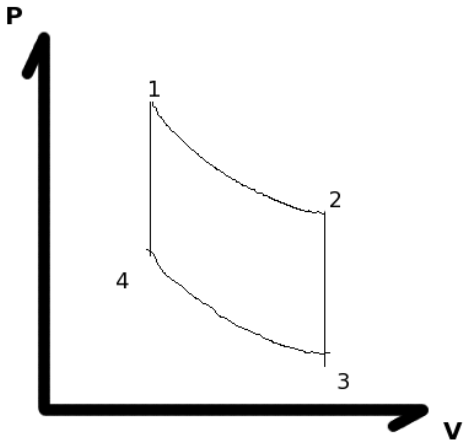
2. (20 pt) Consider a heat engine of an ideal gas. The engine is operated along the path consisting of two reversible adiabatic ($1 \rightarrow 2$, $3 \rightarrow 4$) and reversible isochoric processes ($2 \rightarrow 3$, $4 \rightarrow 1$) as in the figure.

(a) Express the ratio of temperatures (T_1/T_2) using V_1 and V_2.

(b) What is the input heat of this engine, Q_{in} ?

(c) Show that $\Delta S = 0$ by directly integrating $\oint \frac{\delta Q}{T}$ along the processes.

(c) What is the thermodynamic efficiency of this engine? $(\eta \equiv -W/Q_{in})$



3. (20 pt) (a) Using the temperature dependence of Gibbs free energy at constant pressure, derive the van't Hoff equation, i.e., the temperature dependence of an equilibrium constant $K_{eq}(T)$.

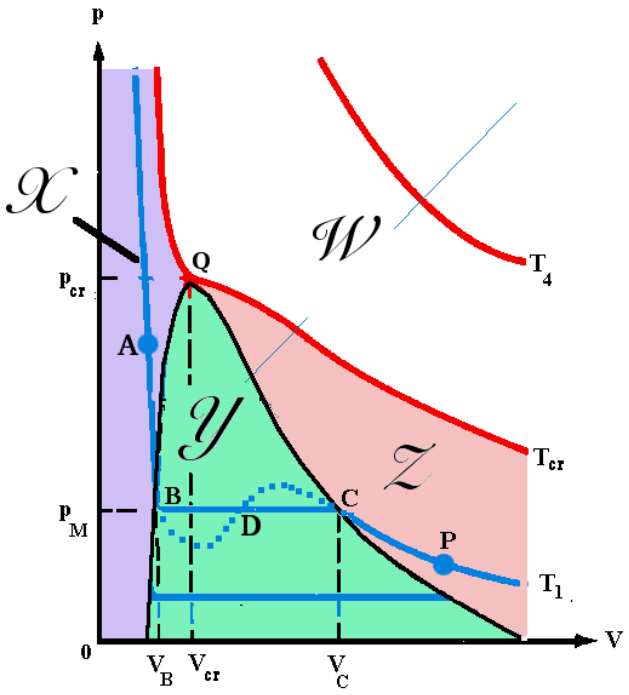
$$\left(\frac{\partial \log K_{eq}(T)}{\partial(1/T)}\right)_P = -\Delta H^o/R \tag{1}$$

(b) Use the above van't Hoff equation and calculate the solubility of AgCl at 40^oC. Thermody-

namic data for the formation enthalpy and Gibbs free energy at the standard condition (25^oC, 1 atm) are given in the table below.

	$\Delta H_f^o(kJ/mol)$	$\Delta G_f^o(kJ/mol)$
AgCl(s)	-127.068	-109.789
Ag^+(aq)	105.579	77.107
Cl^-(aq)	-167.159	-131.228

4. (40pt) The Van der Waals equation of state for one mole of gas reads $\left(P + \frac{a}{V^2}\right)(V - b) = RT$.



(a) Identify phase (e.g. liquid, gas, solid, or mixture of .... etc.) of van der Waals fluid at $\mathcal{X}$, $\mathcal{Y}$, $\mathcal{Z}$, and $\mathcal{W}$.

(b) Sketch a corresponding phase diagram in (p,T) space (pressure as a vertical axis and temperature as a horizontal axis) and indicate the point A, B, D, C, P, and Q on the diagram.

(c) Evaluate the dimensionless ratio $\frac{PV}{RT}$ at the critical point, i.e., Q.

(d) What does the Gibbs free energy profile look like with volume as an order parameter at points A, B, D, C, P and Q?

(e) What is the mole fraction of liquid at point D? Express your answer using V_B, V_C and V_D.

(f) Sketch the isothermal compressibility (κ_T) with increasing volume along the T_1 isotherm.

(g) The dotted line along the T_1 isotherm is unphysical and must be modified to the line of constant pressure p_M that connects the points B and C. The area under the modified isotherm should be equal to the original van der Waals isotherm. Explain the idea behind this new construction.