Qualifying Examine 2004 (Thermodynamics)

Part I. (50 %)

1. A non-ideal gas obeys the following equation of state

   $P\underline{V} = RT + APT - BP$

   where $\underline{V}$ is the molar volume and A, B are constants. Determine its critical point. (15%)

2. Methane reacts with water vapor at 25°C by the following reaction:

   $$CH_{4(g)} + H_2O_{(g)} \Leftrightarrow CO_{(g)} + 3H_{2(g)}$$

   Using the data of Table 1, (a) calculate the standard Gibbs free-energy change for this reaction, and (b) determine if this reaction will proceed forward (i.e., $CH_4 + H_2O \longrightarrow CO + 3\ H_2$) ? (15%)

   Table 1. Data at 298.15 K

	ΔH° (kcal/mol)	ΔS° (kcal/K mol)
$CH_{4\,(g)}$	-17.89	44.5
$CO_{(g)}$	-26.40	47.3
$H_{2\,(g)}$	0	31.2
$H_2O_{(g)}$	-57.80	45.1

3. Three processes are described below for a single phase fluid whose internal energy depends only on temperature. Use thermodynamics principles (first law and relationship of internal energy to temperature) to determine which process (or processes) is impossible and explain why.
   (a) A fluid contracts as it is pushed by a piston in an adiabatic process and its temperature remains constant.
   (b) A fluid contracts as it is pushed by a piston and cooled, and its temperature goes up. ("cooled" means heat transfer out)
   (c) A fluid expands pushing a piston as it is heated, and its temperature goes down.

   (20%)

Part II. (50 %)

1. In vapor-liquid equilibrium calculation, the fugacity of each species in vapor phase is usually calculated from an equation of state. For the fugacity in liquid phase, we may use either an equation of state or an activity coefficient model. Now we are trying to simulate two following processes with a commercially available simulation package.
   (a) Separate the mixtures of water + acetone with a distillation column at atmospheric pressure.
   (b) Recover DMF from wastewater with supercritical carbon dioxide at 313 K and 200 bar.
   Please select an appropriate method to calculate the fugacities in the vapor and the liquid phases, respectively, for each case and explain why. (15%)

2. List any possible types of intermolecular interactions that may involve in each following binary mixture:
   (a) tetrahydrofuran (THF) + toluene,
   (b) water + 1-propanol,
   (c) carbon dioxide + dimethyl ether. (15%)

3. Hydrogen fluoride in the gas phase forms trimer, $(HF)_3$, and tetramer, $(HF)_4$. The equilibrium constants (K_i) of the associations are given by

   $$K_3 = \exp [(6430/T) - 24.0]$$

   $$K_4 = \exp [(12300/T) - 45.0]$$

   where T in K. Describe the method to calculate the compressibility (Z) of the substance at 30 bar and 350 K by using Chemical Theory and assuming that the gas phase is ideal physically. (Note: List all the necessary equations, but you don't need to solve them) (20%)