1. Based on the definition, Helmholtz free energy, $F = U - TS$.

a) Please prove $dF = -SdT - pdV$ **(5%)**

b) Please prove $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$ **(5%)** **[注意：直接用 Maxwell relation 不給分]**

c) Apply b) relationship to prove $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$ **(5%)**

d) Apply c) relationship to prove that for van der Waal gas, $(p + \frac{n^2 a}{V^2})(V - nb) = nRT$, the heat capacity at constant volume, Cv, is independent of V (volume) **(10%)**

2. Give three examples showing "colligative properties" and provide short explanation **(3%×3)**

3. The equilibrium constant for the reaction $A + B \rightleftharpoons 2C$ is reported as 4.0 x 10^4. What would equilibrium constant be for the reactions written as

a) $2C \rightleftharpoons A + B$ **(3%)**　b) $2A + 2B \rightleftharpoons 4C$ **(3%)**　c) $\frac{1}{2}A + \frac{1}{2}B \rightleftharpoons C$ **(3%)**

What is the value of the equilibrium constant of a reaction for which $\Delta G_r = 0$? **(3%)**

4. Calculate a) the molar Gibbs energy of mixing **(5%)** and b) the molar entropy of mixing **(5%)** when N_2 and O_2 are mixed to form air at 25 °C. The mole fractions of N_2 and O_2 are 0.78 and 0.22, respectively.

5. For a ligand, L, and a receptor, R, to form a complex [L-R], give $\Delta H = -8.8$ kJ mol^{-1} and $\Delta S = 121$ J $K^{-1}mol^{-1}$ at 0 °C. Calculate the dissociation constant, K_D. **(10%)**

6. The Clausius-Clapeyron equation for the vapor pressure is known as $dlnp = \frac{\Delta H_{vap}}{RT^2} dT$. The vapor pressure of mercury at 20 °C is 160 mPa. What is its vapor pressure at 40 °C given that its enthalpy of vaporization is 59.30 kJ mol^{-1}? **(10%)**

7. Please draw phase diagrams to illustrate:

a) solution has only LCST **(3%)**　b) solution has only UCST **(3%)**

c) solution has both LCST and UCST (UCST is higher than LCST) **(4%)**

d) solution has both LCST and UCST (UCST is lower than LCST) **(4%)**

8. From the point of view of thermodynamics ($\Delta G, \Delta H, \Delta S$), a) explain the differences of mixing of small molecules compared to mixing of polymer solutions. **(5%)** b) Why the solubility of polymer decreases when the molecular weight of the polymer increases? **(5%)**

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