1.(a) Show that for n moles of a perfect gas that change from V_1 at T_1 to a volume V_2 at T_2 ($S=f(T,V)$)

$$\frac{\Delta S}{n} = \int_{T_1}^{T_2} \frac{C_P}{T} dT - R\ln \frac{T_2}{T_1} + R\ln \frac{V_2}{V_1} \qquad (5\%)$$

(b) Derive an explicit equation for the reversible work of an isothermal expansion for the following case: dV is obtained from the equation of state, $PV=RT+BP+CP^2$ (5%)

2. As one mole $CO_2(g)$ at 27℃ expands, its Pressure falls from 3 bar to 1 bar. Calculate for this change values of ΔG and ΔA, if (a) CO_2 is assumed to be a perfect gas; and (b) CO_2 is a real gas obey the equation: $PV=RT+BP$ with $B=0.0428$ l mol^{-1}. (8%)

3. When N_2O_4 is allowed to dissociate to form NO_2 at 25℃ at a total pressure of 1 bar, it is 18.5% dissociated at equilibrium, and so K=0.141. (a) If N_2 is added to the system at constant volume, will the equilibrium shift? (b) If the system is allowed to expand as N_2 is added at a constant total pressure of 1 bar. What will be the equilibrium degree of dissociation when the N_2 partial pressure is 0.6 bar. (8%)

4. Benzene and toluene form very nearly ideal solutions. At 80℃ the vapor pressure of benzene and toluene are as follows: benzene, $P^{sat}=100.4$kPa; toluene, $P^{sat}=38.7$kPa. (a) For a solution containing 0.5 mole fraction of benzene and 0.5 mole fraction of toluene, what is the composition of the vapor and the total vapor pressure at 80℃? (b) What is the composition of the liquid phase in equilibrium at 80℃ with benzene-toluene vapor having 0.75 mole fraction benzene? (8%)

5. Write the Slater determinants of the ground states for a) He atom, b) H_2 molecule, c) Li atom (9%)

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6. $\phi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{\frac{3}{2}} \exp\left(-\frac{Z}{a_o} r\right)$ is the 1s orbital of H atom

a) Write the probability density $\rho_{1s}(r)$ and radial probability density $P_{1s}(r)$

b) Locate the distance r where $\rho_{1s}(r)$ and $P_{1s}(r)$ have the maximum values.

c) Write the LCAO-MO of H_2^+ using ϕ_{1s} AO. (16%)

7. Write the following potential functions

a) Morse potential, b) Harmonic oscillator potential, c) Coulomb potential in H atom, d) Lennard-Jones potential. (8%)

8. For the elementary reaction $A \rightleftharpoons 2C$, show that if a system in equilibrium is subjected to a small perturbation, then $[A]-[A]_{eq}$ is given by the equation following

$$\frac{d\{[A]-[A]_{eq}\}}{dt} = \frac{\{[A]-[A]_{eq}\}}{\tau}$$

if τ is defined as $\tau^{-1}=K_f+4K_b[C]_{eq}$ (10%)

9. A commonly-used rule of thumb is that rate constant will double for each 10℃ rise in temperature. Assuming it applies in the vicinity of room temperature, what does this rule suggest about typical activation energies? (7%)

10. Estimate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ at 600 K for the dimerization of butadiene

$2C_4H_6 \rightarrow C_8H_{12}$ (3-vinylcyclohexene)

From 440 to 660 K, the experimental rate constant is

$k = 9.2 \times 10^9 \exp(-99.12\ KJ/RT)\ cm^3\ mol^{-1} S^{-1}$ (8%)

11. The reaction A+B -> C takes place in two steps by the mechanism $2A \rightleftharpoons D$ followed by $B+D \xrightarrow{k_2} A+C$. The first step comes to a rapid equilibrium (Constant K_1). Derive an expression for the rate of formation of C in terms of K_1, k_2, [A], [B]. (8%)

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