2007 Fall Physical Chemistry Qualification Exam.

1. Calculate the force constants of the bonds of the following diatomic molecules with the data of the IR absorption (cm^{-1}) and arrange them in order of <u>increasing</u> stiffness. 10%

HCl	HBr	HI	CO	NO
2990	2650	2310	2170	1904

2. A second order reaction of the type A + B → P was carried out in a solution that was initially 0.075mol/L in A and 0.030mol/L in B. After 1.0 hour the concentration of A had fallen to 0.020 mol/L. (1) Obtain the rate law. (2) Calculate the rate constant. (3) What is the half-life time of the reactant? (4) What is the time constant τ? In addition, obtain the answers for A + 2B → P type reaction. 16%

3. Consider a H atom with the electron in the ***3p*** orbital. 24%
(m_e=9.10x10^{-31}kg, m_p=m_n=1.67x10^{-27}kg)
(1) Obtain the complete wave functions for all three orbital with the table.
(2) Evaluate the probability density of the electron for z-direction orbital at the (r, θ, ϕ)=(a_0, $\pi/2$, $\pi/2$)
(3) Locate the nodal surfaces in all three orbital.
(4) Calculate the average values of the kinetic and potential energies for this atom.

n	l	$R_{n,l}$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$
2	0	$\frac{1}{2(2)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\frac{1}{2}\rho)e^{-\rho/4}$
2	1	$\frac{1}{4(6)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}\rho e^{-\rho/4}$
3	0	$\frac{1}{9(3)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}(6-2\rho+\frac{1}{9}\rho^2)e^{-\rho/6}$
3	1	$\frac{1}{27(6)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}(4-\frac{1}{3}\rho)\rho e^{-\rho/6}$
3	2	$\frac{1}{81(30)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}\rho^2 e^{-\rho/6}$

l	m_l	Y_{l,m_l}
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\, e^{\pm i\phi}$
	±2	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$
	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta\, e^{\pm i\phi}$
	±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\, e^{\pm 3i\phi}$

4. The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression $C_p/(\mathrm{J\ K^{-1}}) = 20.17 + 0.03665(T/\mathrm{K})$. Calculate q, w, ΔU, and ΔH when the temperature is raised from 25°C to 300°C (a) at constant pressure, (b) at constant volume. 12%

5. One mole of supercooled water at -10 ℃ and 1 atmpressure turns into ice. Take the heat capacities ($C_{p,m}$) of water and ice to be constant at 75.3 and 37.7 J/K·mol, respectively, and the latent heat of fusion of ice as 6.02 kJ/mol. Calculate the entropy change in the system and in the surroundings.

10%

6. Use the Maxwell relations to express the derivatives $(\partial p/\partial S)_V$ in terms of the heat capacities, the expansion coefficient α, and the isothermal compressibility, κ_T.
$(\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p,\quad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T)$ 8%

7. A Carnot cycle uses 1.00 mol of a monatomic perfect gas as the working substance from an initial state of 10.0 atm and 600 K. It expands isothermally to a pressure of 1.00 atm (step 1), and then adiabatically to a temperature of 300 K (step 2). This expansion is followed by an isothermal compression (step 3), and then an adiabatic compression (step 4) back to the initial state. Determine the values of q, w, ΔU, ΔH, and ΔS for each stage of the cycle. Express your answer as a table of values. 20%