1. Two mole of argon gas at 300 K is reversibly and isothermally compressed from a volume of 25.0 L to a volume of 10.0 L. Assume the temperature of the surrounding remains essentially constant at 300K. Calculate the q, w, ΔU, ΔH, ΔG, ΔS, $\Delta S_{surrounding}$, and ΔS_{total}. (20%)

2. (a) The $^2S_{1/2} \rightarrow {}^2P_{3/2}$ transition in sodium has a wavelength of 589.0 nm. Calculate the ratio of the number of atoms in these two states at 300K and 3500K. (10%) (b) Two close prominent lines are found in the yellow region of sodium spectrum at 589.0 nm and 589.6 nm, respectively. What is the spin-orbital coupling constant (in terms of cm-1) in the fine structure? (10%)

3. The rigid rotor model can be improved by recognizing that in a realistic anharmonic potential. Therefore, the rotational constant depends on n, and it can be shown that $B_n = B - (n+1/2)\,\alpha$, where B is the rigid rotor value. The constant α can be obtained from experimental spectra. For $^1H^{35}Cl$, $B = 10.593$ cm^{-1} and $\alpha = 0.226$ cm^{-1}. Calculate the bond length of HBr in the ground state and estimate the percentage change in bond length for n =3 (20%).

4. For a particle in a two-dimensional box, the total energy

eigenfunctions are $\psi_{n_x n_y}(x,y) = N \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b}$. (a) Obtain an expression for $E_{n_x n_y}$ in terms of n_x, n_y, a, and b by substituting this wavefunction into the Schrödinger equation (10%). (b) Estimate the degeneracy for the first two excited energy level if $a = 2b$. (10%)

5. (a) Work out the irreducible representations of the translation, rotational, and vibration modes in NH_3 where the reducible representation of all four atoms is found to be with characters 12, 0, 2 (in the orders of operations in the character table) (15%). (b) How many IR and Raman active vibrations would you find in NH_3? (5%).

C_{3v} ($3m$)	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, 2xy)(xz, yz)$