2008 Fall Physical Chemistry Qualification Exam.

1. Show that the van der Waals equation leads to values of $Z < 1$ and $Z > 1$, and identify the conditions for which these values are obtained. (10%)
2. **(a)** A sample consisting of 1.00 mol Ar is expanded isothermally at 0°C from 22.4 dm^3 to 44.8 dm^3 (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q, w, ΔU, and ΔH. (12%)
3. (a) Express $(\partial C_V/\partial V)_T$ as a second derivative of U and find its relation to $(\partial U/\partial V)_T$. (b) From these relations show that $(\partial C_V/\partial V)_T = 0$ for a perfect gas. (8%)
4. Calculate ΔS (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{p,m} = {}^7/_2R$, is changed from 25°C and 1.50 atm to 135°C and 7.00 atm. How do you rationalize the sign of ΔS? (10%)
5. The fugacity coefficient of a certain gas at 200 K and 50 bar is 0.72. Calculate the difference of its molar Gibbs energy from that of a perfect gas in the same state. (10%)

Advanced Physical chemistry

6.The wavelength of the emission maximum from a small pinhole in an electrically heated container was determined at a series of temperatures, and the results are given below. Deduce a value for Plank's constant. Also explain why Plank's introduction of quantization accounted for the properties of black-body radiation?

θ/°C	1000	1500	2000	2500	3000	3500
λ_{max}/nm	2181	1600	1240	1035	878	763

10%

7.Proof that the transmission probability T for a particle with internal energy E tunneling through a barrier (length a with height V) is

$$T = \{1+\frac{(e^{ka} - e^{-ka})^2}{16r(1-r)}\}$$

Where r=E/V. Calculate the ratio of transmission between a deuteron and a tritium tunnel through a barrier of height 0.5eV and length 30pm when both their energy is 1.5eV.

15%

8.What is the degree of the degeneracy if three quantum numbers n1, n2, n3 of the possible stationary-state energies for a particle in a three-dimension box can have the values 1, 2 and 3? What are they?

10%

9.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.

15%