No credit will be honored for answers without explaination:

Gas constant R: 8.314 J/K/mol, Plank constant h: 6.6252×10^{-34} J sec, Boltzmann cosntant: k: 1.3807×10^{-23} J /K

I. (30%) Several equation of state have been devised to describ the temperature, pressure and volume relationships of real gases. One equation of state is the virial equation of state:

$$\frac{P\overline{V}}{RT} = 1 + \frac{B_2}{\overline{V}} + \frac{B_3}{\overline{V}^2} + \frac{B_4}{\overline{V}^3} + \frac{B_5}{\overline{V}^4} + \ldots$$

which is a power series of the independent variable 1/V. Where B is called the virial coefficents R is the gas constant, and V is the molar volume.

(1) Show that $\left(\frac{\partial \overline{U}}{\partial \overline{V}}\right)_{T,n} = \frac{RT^2}{V^2}\frac{dB_2}{dT}$ using the truncated virial equation. (5%)

(2) For argon gas at 298.15 K, B_2 is approximately -15.8 cm^3/mol, and the differntial $\frac{dB_2}{dT}$ equals 0.25 cm^3/mol/K. The molar constant-volume heat capacity of argon gas is nearly constant and equals to 3R/2. Please find ΔU, q and w for a reversible isothermal expansion of 1.0 mole of argon at 298.15 K from a volume of 2.0 L to a volumn of 20.0 L. (10%)

(3) Compare this results with ideal gas behavior. (For idea gas ΔU=0. Calculate only q,w) (5%)

(4) Joule expansion coefficient is defined as $\mu_{=} \lim_{\Delta V \to 0}\left(\frac{\Delta T}{\Delta V}\right) = \left(\frac{\partial T}{\partial V}\right)_{U,n}$. Please find the value of Joule coefficient for argon at 298.15 K with a molar volume of 20.0 L. (Hint: you can derive the answer from (1) and (2)). (10%)

II. (30%) The standard deviation of an arbitraty "observables" can be shown to be

$$\sigma_A = \sqrt{\left(\langle A^2\rangle - \langle A\rangle^2\right)}$$

For a particle in a one dimensional well of infinite depth with the langth a,

(1) Please write down the Hamiltonian, the potential, and the bondary conditions. (5%)

(2) The normalized particle-in-a-well wave function is $\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$, please determine the expectation value of the positon of the particle $\langle x\rangle$, the square of

the position $\langle x^2 \rangle$, and the standard deviation of the position σ_x for the n=1 state. (10%)

(3) Please determine the expectation values of the momentum of the particle $\langle p \rangle$, $\langle p^2 \rangle$, and σ_p for the n=1 state. (5%)

(4) If we use the symbol Δx and Δp_x for the uncertainties of the postion and its conjugate momentum, please show that in the present case with n=1, $\Delta x \Delta p = \sigma_x \sigma_p \geq \frac{h}{4\pi}$, where h is the Plank constant. This is the famous Heisenberg uncertainty principle. (5%)

(5) For a free particle, where the uncertainty in x is infinite, what would the difference between $\langle p \rangle^2$ and $\langle p^2 \rangle$ be according to the uncertainty principle?(5%)

III. (20%) Assume that the benzene anion $C_6H_6^-$ has its unpair electron delocalized equally among the six corners of the moelcule.

(1) The energy level difference between two proton nuclear spin states at magnetic field strength of 2.0 Tesla equals to 5.644×10^{-26} J. Please calculate the population ratio between the two nuclear spin states at room temperature using Boltzmann distribution. (3%)

(2) Please predict the ESR spectrum. Asuming the Hyperfine coupling constant being A. (8%)

(3) How will the ESR spectrum change in liquid helium temperture (4K) ? (6%)

(4) Please predict the corresponding room temperature carbon-13 NMR spectrum of the same J coupling. (3%)

IV. (20%) The following gas-phase reaction describes the partition of NO_x

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

(1) What two species are in the steady state?(3%)

(2) Please determine the rate law expressed in the above rate constants using the steady state approximation. (8%)

(3) What's the order of reaction? The rate constant at 337.6 K is equal to $5.12 \times 10^{-3}\ s^{-1}$. If the partial pressure of N_2O_5 is 0.5 atm at t=0, find the partial pressure of N_2O_5 at t=60 sec. in a constant volume. Asuming ideal gas and negligible reverse reaction. (6%)

(4) Determine the half life in seconds for this reaction. (3%)