

- 1). In spherical coordinates the quantum mechanical operator for the z component of angular momentum is

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

Show that $\Phi_m = A \exp(im\phi)$ is an eigenfunction of \hat{L}_z with eigenvalue of $m\hbar$ but that $\sin m\phi$ and $\cos m\phi$ are not eigenfunctions. Further, show that the linear combination $\Phi'_m = \cos m\phi + i \sin m\phi$ is an eigenfunction of \hat{L}_z (14%)

- 2) The percentage transmittance of an aqueous solution of disodium fumarate at 250 nm and 25°C is 19.2% for a $5 \times 10^{-4} \text{ mol L}^{-1}$ solution in a 1-cm cell. Calculate the absorbance A and the molar absorption coefficient ϵ . What will be the percentage transmittance of a $1.75 \times 10^{-5} \text{ mol L}^{-1}$ solution in a 10-cm cell? (14%)

- 3). The hydrolysis of adenosine triphosphate ATP to adenosine diphosphate ADP and inorganic phosphate at pH 8 and 25°C.



has a standard enthalpy change of -13 kJ mol^{-1} . The standard enthalpy changes of acid dissociation of HATP^{-3} , HADP^{-2} , and $\text{H}_2\text{PO}_4^{-1}$ are -8 , 0 , and $+8 \text{ kJ mol}^{-1}$, respectively. Calculate the standard enthalpy change for the reaction. (12%)

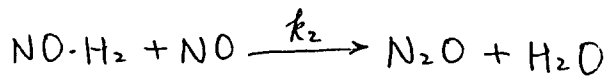
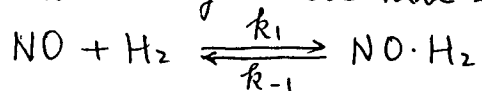
- 4) (a) Is the Joule-Thomson experiment reversible? Explain briefly.

(b). Is the entropy of the gas constant in the Joule-Thomson experiment? If not, express $(\partial S / \partial p)_H$ in term of any or all of the variables P, V, T, C_p , and C_v . (14%)

- 5). One mole of supercooled water at -10°C and 1 atm pressure turns into ice. Calculate the entropy change in the system and in the surroundings and the net entropy change. Take the heat capacities of water and ice to be constant at 75.3 and $37.7 \text{ JK}^{-1} \text{ mol}^{-1}$, respectively, and the heat of fusion of ice as 6.02 kJ mol^{-1} . (17%)

- b) Outline the kinetics of branching chain reactions, illustrating your answer with reference to the reactions between hydrogen and oxygen. (16%)

7) Derive the steady-state rate equation for the mechanism:



Show under what condition this reduces to the form of $\frac{d(\text{N}_2\text{O})}{dt} = kK(\text{NO})^2(\text{H}_2)$.

(13%)