Qualify Exam-Physical Chemistry (2006-12-28)

1. Initially 0.1 mol of methane is at 1 bar pressure and 80℃. The gas behaves ideally and the value of C_p/C_v is 1.31. The gas is allowed to expand reversibly and adiabatically to a pressure of 0.1 bar.
   (a). What are the initial and final volumes of the gas?
   (b). What is the final temperature?
   (c). Calculate ΔU and ΔH for the process. (15%)
2. (a). Liquid water at 100 ℃ is in equilibrium with water vapor at 1 atm pressure. If the enthalpy change associated with vaporization of liquid water at 100 ℃ is 40.60 kJ/mol, what are ΔG and ΔS?
   (b). Suppose that water at 100 ℃ is in contact with water vapor at 0.9 atm. Calculate ΔG and ΔS for the vaporization process. (16%)
3. Prove the following relation: $\left(\frac{\partial H}{\partial V}\right)_T = -V^2\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial(T/V)}{\partial V}\right)_P$ (10%)
4. The half-life of thermal denaturation of hemoglobin, a first-order process, has been found to be 3460 s at 60 ℃ and 530 s at 65 ℃. Calculate the enthalpy of activation and entropy of activation at 60 ℃, assuming the Arrhenius equation to apply. (15%)
5. Derive the rate law for the decomposition of ozone in the reaction: (10%)
   $2\ O_3(g) \rightarrow 3\ O_2(g)$ on the basis of the (incomplete) mechanism

$$O_3 \rightarrow O_2 + O \qquad k_a$$
$$O_2 + O \rightarrow O_3 \qquad k_a'$$
$$O + O_3 \rightarrow 2O_2 \qquad k_b$$

6. Find < r > for the $2P_z$ state of hydrogenlike atom. (12%)
7. Using the trial function $\psi = x(a-x)$ to estimate the energy of a particle in a box, in which the boundaries of the box are 0 and a. (10%)
8. Determine the AO coefficients for the lowest energy Hückel π MO for butadiene. (12%)

TABLE [illegible]

The complete hydrogenlike atomic wave functions for $n = 1,\ 2,$ and 3. The quantity Z is the atomic number of the nucleus, and $\sigma = Zr/a_0$, where a_0 is the Bohr radius.

$n = 1,$	$l = 0,$	$m = 0$	$\psi_{100} = \dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
$n = 2,$	$l = 0,$	$m = 0$	$\psi_{200} = \dfrac{1}{\sqrt{32\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} (2 - \sigma)e^{-\sigma/2}$
	$l = 1,$	$m = 0$	$\psi_{210} = \dfrac{1}{\sqrt{32\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\cos\theta$
	$l = 1,$	$m = \pm 1$	$\psi_{21\pm 1} = \dfrac{1}{\sqrt{64\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\sin\theta e^{\pm i\phi}$
$n = 3,$	$l = 0,$	$m = 0$	$\psi_{300} = \dfrac{1}{81\sqrt{3\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} (27 - 18\sigma + 2\sigma^2)e^{-\sigma/3}$
	$l = 1,$	$m = 0$	$\psi_{310} = \dfrac{1}{81}\left(\dfrac{2}{\pi}\right)^{1/2}\left(\dfrac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2)e^{-\sigma/3}\cos\theta$
	$l = 1,$	$m = \pm 1$	$\psi_{31\pm 1} = \dfrac{1}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2)e^{-\sigma/3}\sin\theta e^{\pm i\phi}$
	$l = 2,$	$m = 0$	$\psi_{320} = \dfrac{1}{81\sqrt{6\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}(3\cos^2\theta - 1)$
	$l = 2,$	$m = \pm 1$	$\psi_{32\pm 1} = \dfrac{1}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin\theta\cos\theta e^{\pm i\phi}$
	$l = 2,$	$m = \pm 2$	$\psi_{32\pm 2} = \dfrac{1}{162\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin^2\theta e^{\pm 2i\phi}$

TABLE A.5 Integrals

$$\int x \sin bx\, dx = \frac{1}{b^2}\sin bx - \frac{x}{b}\cos bx \quad \text{(A.1)}$$

$$\int \sin^2 bx\, dx = \frac{x}{2} - \frac{1}{4b}\sin(2bx) \quad \text{(A.2)}$$

$$\int x\sin^2 bx\, dx = \frac{x^2}{4} - \frac{x}{4b}\sin(2bx) - \frac{1}{8b^2}\cos(2bx) \quad \text{(A.3)}$$

$$\int x^2\sin^2 bx\, dx = \frac{x^3}{6} - \left(\frac{x^2}{4b} - \frac{1}{8b^3}\right)\sin(2bx) - \frac{x}{4b^2}\cos(2bx) \quad \text{(A.4)}$$

$$\int x e^{bx}\, dx = \frac{e^{bx}}{b^2}(bx - 1) \quad \text{(A.5)}$$

$$\int x^2 e^{bx}\, dx = e^{bx}\left(\frac{x^2}{b} - \frac{2x}{b^2} + \frac{2}{b^3}\right) \quad \text{(A.6)}$$

$$\int_0^\infty x^n e^{-qx}\, dx = \frac{n!}{q^{n+1}}, \qquad n > -1, q > 0 \quad \text{(A.7)}$$

$$\int_0^\infty e^{-bx^2}\, dx = \frac{1}{2}\left(\frac{\pi}{b}\right)^{1/2}, \qquad b > 0 \quad \text{(A.8)}$$

$$\int_0^\infty x^{2n} e^{-bx^2}\, dx = \frac{1\cdot 3\cdots(2n-1)}{2^{n+1}}\left(\frac{\pi}{b^{2n+1}}\right)^{1/2}, \qquad b > 0, n = 1, 2, 3, \ldots \quad \text{(A.9)}$$

$$\int_t^\infty z^n e^{-az}\, dz = \frac{n!}{a^{n+1}} e^{-at}\left(1 + at + \frac{a^2t^2}{2!} + \cdots + \frac{a^nt^n}{n!}\right), \qquad n = 0, 1, 2\ldots, a > 0 \quad \text{(A.10)}$$

Qualify Exam-Physical Chemistry (2007-5-29)

1. Determine the half-cell reactions and the overall cell reaction, calculate the **cell potential**, and determine the **equilibrium constant** at 298.15 K for the cell

$Pt(s)|Mn^{2+}(aq, a_\pm = 0.0150), Mn^{3+}(aq, a_\pm = 0.200)||Zn^{2+}(aq, a_\pm = 0.100)|Zn(s)$.

Is the cell reaction spontaneous as written? (12%)

($Mn^{2+}(aq) \rightarrow Mn^{3+}(aq) + e^-$ $\quad E^\circ = -1.5415$ V

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $\quad E^\circ = -0.7618$ V)

2. Between 0° and 90°C, the potential of the cell

$Pt(s)|H_2(g, f = 1\ \text{atm})|HCl(aq, m = 0.100)|AgCl(s)|Ag(s)$ is described by the

equation

$E(V) = 0.35510 - 0.3422 \times 10^{-4} t - 3.2347 \times 10^{-6} t^2 + 6.314 \times 10^{-9} t^3$ where t is the

temperature on the Celsius scale. Write the cell reaction and calculate ΔG, ΔH, and ΔS for the cell reaction at 50°C. (12%)

3. Carbon tetrachloride melts at 250 K. The vapor pressure of the liquid is 10,539 Pa at 290 K and 74,518 Pa at 340 K. The vapor pressure of the solid is 270 Pa at 232 K and 1092 Pa at 250 K.

a) Calculate $\Delta H_{vaporization}$ and $\Delta H_{sublimation}$. (6%)

b) Calculate ΔH_{fusion}. (4%)

c) Calculate the normal boiling point and $\Delta S_{vaporization}$ at the boiling point. (4%)

4. Determine the bond length, force constant and internal energy of HCl ($B = 10.59$ cm^{-1} – rotational constant, and $\tilde{\nu} = 2886$ cm^{-1} – vibration frequency of HCl) under standard thermodynamic conditions. (15%)

5. Derive the selection rule for IR using the approximation of harmonic oscillator. (10%)

6. Determine the equilibrium constant for the dissociation of sodium at 298

K: $Na_2(g) \rightleftharpoons 2Na(g)$.

For Na_2, $B = 0.155\ \text{cm}^{-1}$, $\tilde{\nu} = 159\ \text{cm}^{-1}$, the dissociation energy is 70.4 kJ/mol, and the ground-state electronic degeneracy for Na is 2. (15%)

7. Calculate the energy levels of the π-network in octatetraene, C_8H_{10}, using the particle in the box model. To calculate the box length, assume that the molecule is linear and use the values 135 and 154 pm for C=C and C–C bonds. What is the wavelength of light required to induce a transition from the ground state to the first excited state? (10%)

8. The equilibrium constant of a reaction is found to fit the expression $\ln K = A + B/T + C/T^3$ between 400 K and 500 K with $A = -2.04$, $B = -1176$ K, and $C = 2.1 \times 10^7\ \text{K}^3$. Calculate the standard reaction enthalpy and standard reaction entropy at 450 K. (12%)