

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

- Initially 0.1 mol of methane is at 1 bar pressure and 80°C. 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.
  - What are the initial and final volumes of the gas?
  - What is the final temperature?
  - Calculate  $\Delta U$  and  $\Delta H$  for the process. (15%)
- Liquid water at 100 °C is in equilibrium with water vapor at 1 atm pressure. If the enthalpy change associated with vaporization of liquid water at 100 °C is 40.60 kJ/mol, what are  $\Delta G$  and  $\Delta S$ ?
  - Suppose that water at 100 °C is in contact with water vapor at 0.9 atm. Calculate  $\Delta G$  and  $\Delta S$  for the vaporization process. (16%)
- 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%)
- The half-life of thermal denaturation of hemoglobin, a first-order process, has been found to be 3460 s at 60 °C and 530 s at 65 °C. Calculate the enthalpy of activation and entropy of activation at 60 °C, assuming the Arrhenius equation to apply. (15%)
- 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
$$\begin{array}{ll} O_3 \rightarrow O_2 + O & k_a \\ O_2 + O \rightarrow O_3 & k_a' \\ O + O_3 \rightarrow 2O_2 & k_b \end{array}$$
- Find  $\langle r \rangle$  for the  $2P_z$  state of hydrogenlike atom. (12%)
- 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%)
- Determine the AO coefficients for the lowest energy Hückel  $\pi$  MO for butadiene. (12%)

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.

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

TABLE A.5 Integrals

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

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

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

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

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

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

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

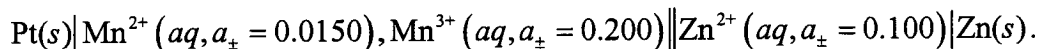
$$\int_0^{\infty} e^{-bx^2} \, dx = \frac{1}{2} \left(\frac{\pi}{b}\right)^{1/2}, \quad b > 0 \quad (\text{A.8})$$

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

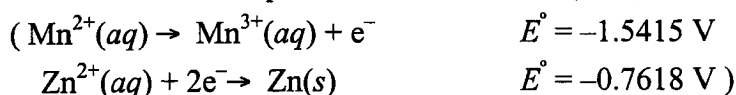
$$\int_0^{\infty} z^n e^{-az} \, dz = \frac{n!}{a^{n+1}} e^{-a} \left(1 + at + \frac{a^2 t^2}{2!} + \cdots + \frac{a^n t^n}{n!}\right), \quad n = 0, 1, 2, \dots, a > 0 \quad (\text{A.10})$$

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



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



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

$\text{Pt}(s) | \text{H}_2(g, f = 1 \text{ atm}) | \text{HCl}(aq, m = 0.100) | \text{AgCl}(s) | \text{Ag}(s)$  is described by the equation

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

temperature on the Celsius scale. Write the cell reaction and calculate  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  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  $\Delta H_{\text{vaporization}}$  and  $\Delta H_{\text{sublimation}}$ . (6%)

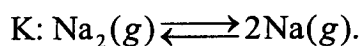
b) Calculate  $\Delta H_{\text{fusion}}$ . (4%)

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

4. Determine the bond length, force constant and internal energy of HCl ( $B = 10.59 \text{ cm}^{-1}$  – rotational constant, and  $\tilde{\nu} = 2886 \text{ cm}^{-1}$  – 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



For  $\text{Na}_2$ ,  $B = 0.155 \text{ cm}^{-1}$ ,  $\tilde{\nu} = 159 \text{ cm}^{-1}$ , the dissociation energy is  $70.4 \text{ kJ/mol}$ , and the ground-state electronic degeneracy for Na is 2. (15%)

7. Calculate the energy levels of the  $\pi$ -network in octatetraene,  $\text{C}_8\text{H}_{10}$ , 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  $A = -2.04$ ,  $B = -1176 \text{ K}$ , and  $C = 2.1 \times 10^7 \text{ K}^3$ . Calculate the standard reaction enthalpy and standard reaction entropy at 450 K. (12%)