

## Physical Chemistry

## Constants

$h=6.626 \times 10^{-34} \text{ J s}$

$\hbar=1.055 \times 10^{-34} \text{ J s}$

$k=1.381 \times 10^{-23} \text{ J K}^{-1}$

$c=2.998 \times 10^8 \text{ m s}^{-1}$

$N_A=6.002 \times 10^{23} \text{ mol}^{-1}$

$\text{amu}=1.661 \times 10^{-27} \text{ kg}$

$R=8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$e=1.602 \times 10^{-19} \text{ C}$

1. A molecule absorbs a photon with a wavelength of 300.0 nm. Determine the energy separation of the two molecular electronic levels corresponding to this absorption. Approximate your answer to two decimal places in joules. (5)

Ans: \_\_\_\_\_

2. The eigenvalues of the rotational Hamiltonian of a rigid linear molecule are given

$$\text{as } E_J = \frac{\hbar^2}{2I} J(J+1), \quad J = 0, 1, 2, \dots,$$

where  $I$  is the moment of inertia,  $J$  is the rotational quantum number.

- (a) Calculate the energy of  $J=2$  state for  $^{14}\text{N}^{16}\text{O}$ . The atomic mass of  $^{14}\text{N}$  is 14.003 amu, the atomic mass of  $^{16}\text{O}$  is 15.995 amu, and the equilibrium bond length is 115 pm. Round your answer to two decimal places in joules. (5)

Ans: \_\_\_\_\_

- (b) What is the ratio of probability of  $^{14}\text{N}^{16}\text{O}$  in  $J=3$  vs.  $J=2$  states at 300 K? (5)

Ans:  $\frac{P(J=3)}{P(J=2)} =$  \_\_\_\_\_

3. The CO triple bond with the bond dissociation energy of 1072 kJ/mol represents the strongest chemical bond known. The center of the IR absorption band of CO appears at  $2143 \text{ cm}^{-1}$ . What is the approximate electronic potential well depth  $D_e$  of CO? Write your answer in the unit of kJ/mol. (5)

Ans: \_\_\_\_\_

4. Calculate the work done when one mole of an ideal gas is compressed reversibly from 1.00 bar to 2.718 bar at a constant temperature of 300 K. (5)

Ans: \_\_\_\_\_

5. (a) Which one is the mean speed of  $O_2$  molecule? (5)  
(i)  $(3RT/M)^{1/2}$  (ii)  $(8RT/\pi M)^{1/2}$  (iii)  $(2RT/M)^{1/2}$  (iv)  $(16RT/M)^{1/2}$  (v)  $(8RT/\mu)^{1/2}$   
(T: temperature, M: molar mass,  $\mu$ : reduced mass)

Ans: \_\_\_\_\_

- (b) Calculate the mean speed of  $O_2$  at 300 K. (5)

Ans: \_\_\_\_\_

6. The bottom-up synthesis of nanoparticles by reducing chemical precursors appears as an entropy reducing process for the system. For instance, a gold nanoparticle with a diameter of 20 nm contains millions of gold atoms reduced from  $Au^{3+}$  cations (*i.e.*  $n Au^{3+} \rightarrow Au_n$ ,  $n \sim$  millions). Why can the synthetic process occur spontaneously? (5)

Ans: \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

7. (a) What is the root mean square distance of a particle diffusing in two dimensions during time interval  $t$ ? (5)  
(i)  $(2Dt)^{1/2}$  (ii)  $(4Dt)^{1/2}$  (iii)  $(6Dt)^{1/2}$  (iv)  $(3Dt)^{1/2}$  (v)  $(5Dt)^{1/2}$

Ans: \_\_\_\_\_

- (b) The diffusion constant  $D$  of a protein in membrane is  $10^{-10} \text{ cm}^2/\text{s}$ . How long does it take in average for the protein to diffuse through a laser focal spot of  $1 \mu\text{m}$  in diameter? (5)

Ans: \_\_\_\_\_

## 分析化學的部份

- (10 分) Define and differentiate the following terms:
  - Accuracy and Precision,
  - Spectral interference and Chemical interference,
  - Limiting current and Residual current,
  - Hydrodynamic injection and Electrokinetic injection.
  - Alkaline error and Acid error in pH measurement.
  - Standard electrode potential and Formal potential
  - Concentration polarization and Kinetic polarization,
  - Fluorometers and Spectrofluorometers.
  - Detection limit and Characteristic concentration in AAS.
  - Isocratic elution and Gradient elution.
- (6 分) A Standard Reference Material is certified to contain 0.188 % of S in coal. Your analysis gives value of 0.131, 0.128, 0.165, 0.172, 0.201, and 0.119 %. The standard deviation of six measurements is 0.0318 %. (a) Calculate the 95% confidence intervals of your analysis. (b) Do your results different from the expected results?
- (10 分) A weak acid, HA, has  $K_a = 2.50 \times 10^{-5}$ . (a) Calculate the pH value of 1.00 M HA solution. (b) Determine the mass of NaOH that must be added to 1.00 L of 1.00 M HA solution to change the solution's pH value to 4.00. (Assume that the added NaOH (40.00 g/mol) does not change the volume of the solution.)
- (10 分) In a reversed-phase HPLC separation of compound 1 and 2, the retention times of 1 and 2 are 41 min and 43 min, respectively, and the dead time of the column used is 1 min with 20% (by volume) acetonitrile and 80 % water as the mobile phase. (a) Calculate the retention factors of both compounds and separation factor between two compounds. (b) Estimate the new eluent composition to reduce the retention factor of compound 1 to 5.
- (6 分) A 10.0-ppm solution of lead gives an atomic absorption signal of 40% absorption. What is the atomic absorption sensitivity (亦即 at 1% absorption)?
- (8 分) (a) Identify the anode and cathode for the follow electrochemical cell and write the oxidation and reduction occur at each electrode;  $\text{Pt} | \text{FeCl}_2 (0.010 \text{ M}), \text{FeCl}_3 (0.040 \text{ M}) || \text{AgNO}_3 (0.10 \text{ M}) | \text{Ag}$   
(b) Calculate the potential for this electrochemical cell using  $E^\circ (\text{Ag}^+/\text{Ag}) = +0.7996$ ;  $E^\circ (\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.771$ .

## Appendix

Table 1 Values of t for the 95% Confidence Interval

Degree of freedom	t
1	12.7
2	4.30
3	3.18
4	2.78
5	2.57
6	2.45
7	2.36
8	2.31
9	2.26
10	2.23
$\infty$	1.96

$\text{Log } 2 = 0.301, \text{Log } 3 = 0.477, \text{Log } 5 = 0.699, \text{Log } 0.6 = -0.222, \text{Log } 0.99 = -0.00435, \text{Log } 0.125 = -0.903, \text{Log } 10^a = a$

## Solvent Polarity Index:

water=10.2, dimethylsulfoxide=7.2, acetonitrile=5.8, methanol=5.1, dioxane=4.8, ethyl acetate=4.4, tetrahydrofuran=4.0, methylene chloride=3.1, n-hexane=0.01