Physical constant: R=8.314 $JK^{-1}mol^{-1}$, amu=1.660×10^{-27} kg, $k_B=1.381\times10^{-23}$ J K^{-1}

Single Choice Questions: (2 points each)

1. Which operator below in atomic units will give the correct eigenvalue equation for Lithium?

   A. $\sum_{i=1}^{3}\left(-\frac{1}{2}\nabla_i^2-\frac{3}{r_i}+\sum_{j>i}^{3}\frac{1}{r_{ij}}\right)$; B. $\sum_{i=1}^{3}\left(-\frac{1}{2}\nabla_i^2-\frac{3}{r_i}+\sum_{j\neq i}^{3}\frac{1}{r_{ij}}\right)$

   C. $\sum_{i=1}^{3}\left(-\frac{1}{2}\nabla_i^2-\frac{3}{r_i}+\sum_{j=1}^{3}\frac{1}{r_{ij}}\right)$; D. $\sum_{i=1}^{3}\left(\frac{1}{2}\nabla_i^2-\frac{3}{r_i}-\sum_{j>i}^{3}\frac{1}{r_{ij}}\right)$

   E. $\sum_{i=1}^{3}\left(\frac{1}{2}\nabla_i^2-\frac{3}{r_i}-\sum_{j\neq i}^{3}\frac{1}{r_{ij}}\right)$; F. $\sum_{i=1}^{3}\left(\frac{1}{2}\nabla_i^2-\frac{3}{r_i}-\sum_{j=1}^{3}\frac{1}{r_{ij}}\right)$

2. Heisenberg's uncertainty principle states:

   A. $\Delta y\times\Delta p_y \leq h/2\pi$
   B. $\Delta x\times\Delta p_x \leq h/4\pi$
   C. $\Delta y\times\Delta p_y \geq h/4\pi$
   D. $\Delta x\times\Delta p_x \geq 2h/4\pi$
   E. $\Delta x\times\Delta p_x \geq h/2\pi$
   F. $\Delta x\times\Delta p_y \geq h/4\pi$

3. A particle in a one-dimensional box of length L can be excited from the ground state to the first excited state by light of frequency v. If the box length is doubled, the frequency needed to produce the transition is

   A. $2v$; B. $4v$; C. $v/4$; D. $v/2$; E. $6v$; F. $v/6$

4. A linear rigid rotor with a moment of inertia, I, has rotational energy of $6\hbar^2/(2I)$. How many rotational orientations relative to the z axis are allowed?

   A. 1; B. 2; C. 3; D. 4; E. 5; F. unlimited.

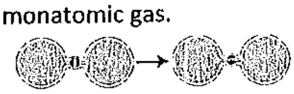
5. The force constant of $^{35}Cl^{35}Cl$ is 319 N m^{-1}. The fundamental vibrational frequency is

   A. 1.0 Hz; B. 1.5×10^{11} Hz; C. 1.9×10^{12} Hz; D. 1.7×10^{13} Hz; E. 1.0×10^{14} Hz

6. For an ideal gas at constant temperature, which of the following statements is true?

   A. The Gibbs energy increases when the pressure increases
   B. The Gibbs energy decreases when the pressure increases
   C. The Gibbs energy does not change when the pressure increases
   D. The Gibbs energy is independent to pressure.

7. Image you have two containers of equal volume separated by a valve. In each container there is one mole of the same ideal, monatomic gas.



   What is the change in entropy for this system if the valve is initially closed and you open it?

   A. $\Delta S_{close\to open}$ = -2R(ln2); B. $\Delta S_{close\to open}$ = -R(ln2); C. $\Delta S_{close\to open}$ = -2R; D. $\Delta S_{close\to open}$ = 0;
   E. $\Delta S_{close\to open}$ = 2R; F. $\Delta S_{close\to open}$ = R(ln2); G. $\Delta S_{close\to open}$ = 2R(ln2)

8. Below are the seven lowest orbitals for the neutral water molecule, arranged in the alphabetic order with decrease in energy. This is that A is the highest in energy and G is the lowest in energy. Select the one that would be the LUMO state for a water molecule.

A.

B.

C.

D.

E.

F.

G.


9. A reaction A → P shows complex behavior with the following elementary steps:

A+A→A*+A　k_2
A*+A→A+A　k_{-2}
A*→P　k_1

The rate of reaction is given by

$$-\frac{d[A]}{dt}=\frac{k_1k_2[A]^2}{k_1+k_{-2}[A]}$$

Which of the following statements are correct?

A. At atmospheric pressure the reaction is first order
B. At low pressure the reaction is second order
C. At atmospheric pressure the reaction is second order
D. At low pressure the reaction is first order

10. For the gas-phase bimolecular elementary reaction 2Cl· → Cl_2, which following rate equation shows the relationship between the rate of consumption of reactant and rate of reaction?

A. $-\frac{d[Cl\cdot]}{dt}=k[Cl\cdot]^2$; B. $-\frac{d[Cl\cdot]}{dt}=2\times k[Cl\cdot]^2$; C. $-2\frac{d[Cl\cdot]}{dt}=k[Cl\cdot]^2$;
D. $-2\frac{d[Cl\cdot]}{dt}=k[Cl\cdot]$

11. Which of the following is the half life of the reaction in the question 10?

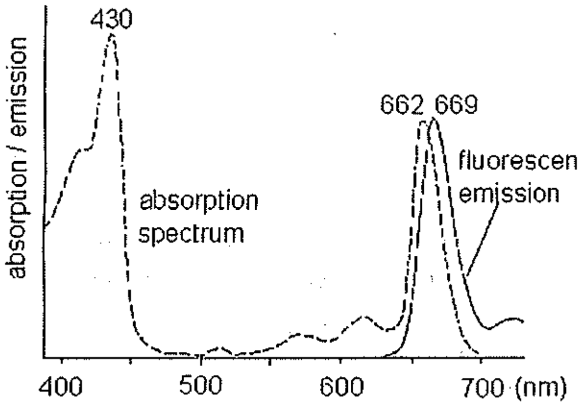
A. $t_{1/2}=\frac{\ln 2}{k}$; B. $t_{1/2}=\frac{1}{k[Cl\cdot]_0}$; C. $t_{1/2}=\frac{1}{2k[Cl\cdot]_0}$; D. $t_{1/2}=\frac{[Cl\cdot]_0}{2k}$

Text Questions

1. A molecule contains 4 atoms. As you heat its gas to very high temperature, you observe the heat capacity approaching an asymptotic value of 9.5R. Is the molecule linear or non-linear? Provide your reasoning. (6)

2. A reaction has an enthalpy change of +14 kJ mol^{-1} and an entropy change of +37 J K^{-1} mol^{-1}. At what temperature (℃) does this endothermic reaction become spontaneous? (6)

3. The absorption and fluorescence spectra of chlorophyll a (Chl a) in methanol are plotted below. The absorption spectrum has two major peaks at 430 nm and 662 nm. The fluorescence spectrum excited by 428 nm light has the peak at 669 nm.



(i) What is the color of the sample? (3)

(ii) What is the color of the fluorescence light? (3)

(iii) The fluorescence lifetime of Chl a in methanol was measured as 6 ns. Chl a molecules form aggregates in light harvesting complexes in plants, which absorb sunlight and transfer the energy efficiently to the photosynthetic reaction center. What do you expect the time scale of energy transfer of Chl a in light harvesting complexes to be? Will it be nanosecond, sub-nanosecond, or tens nanoseconds? Give the reasoning about your answer. (4)

4. The reaction of atomic chlorine with ozone is the first step in the catalytic decomposition of stratospheric ozone by Cl・:

   $Cl\cdot_{(g)} + O_{3(g)} \rightarrow ClO\cdot_{(g)} + O_{2(g)}$

   At 298 K the rate constant for this reaction is 6.7×10^{9} $M^{-1}s^{-1}$. Experimentally, the Arrhenius pre-exponential factor was determined to be 1.4×10^{10} $M^{-1}s^{-1}$. Using this information determine the activation energy for this reaction. (6)

分析化學部份（總分 50 分）　計算題會考慮計算過程來評分

1. Write each answer with the correct number of significance figure.
   (a) $0.0730 \div (2.3112 \times 10^{-4}) =$　(2 分)
   (b) $107.868 - (2.113\times10^{2}) + (5.623\times10^{3}) =$　(2 分)
   (c) $2.0164(\pm0.0008)+1.233(\pm0.002)+4.61(\pm0.01) =$　(3 分)

2. Using 1.0×10^{-6} M as the criterion for quantitative removal, determine whether it is feasible to use SO_4^{2-} to separate Ba^{2+} and Sr^{2+} in a solution that is initially 0.040 M in Sr^{2+} and 0.20 M in Ba^{2+}. $BaSO_4$, $K_{sp} = 1.1\times10^{-10}$; $SrSO_4$, $K_{sp} = 3.2\times10^{-7}$. (8 分)

3. Consider the diprotic acid H_2A with $K_1 = 1.00\times10^{-4}$ and $K_2 = 1.00\times10^{-8}$. Find the pH and concentration of H_2A, HA^-, and A^{2-} in 0.100 M H_2A. (8 分)

4. Balance the net ionic equations for the follow reactions. Supply H^+ and /or H_2O needed to obtain the balance.
   (a) $Fe^{3+} + Sn^{2+} \leftrightarrows Fe^{2+} + Sn^{4+}$ (1 分)
   (b) Write the Nernst equation of each half-reaction of 4(a). (2 分)
   (c) Calculate E° and numerical values of K_{eq} of 4(a). (6分)　$E^0_{Fe^{3+}/Fe^{2+}} = +0.771V$;　$E^0_{Sn^{4+}/Sn^{2+}} = +0.154V$

5. Consider the peaks for pentafluorbenzene and benzene from a gas chromatography separation, the open tubular column is 30 m in length and 0.530 mm in diameter, with a layer of stationary phase 3.0 μm on the inner wall. The elution time for unretained solute is 1.00 min and the retention times for pentafluorbenzene and benzene are 13.00 min and 13.30 min, respectively. Based on the chromatogram, the peak widths at half maximum are 0.121 min and 0.120 min, respectively for pentafluorbenzene and benzene.
   (a) Find the retention factors for both compounds. (2 分)
   (b) Find the selectivity and resolution of the separation. (4 分)
   (c) Find the average column efficiency. (2 分)
   (d) Find the plate height of the column. (2 分)

6. (a) Name three methods employed for background correction in AAS (atomic absorption spectrometry). (3 分)
   (b) Explain the term and describe the difference between limit of detection and limit of quantitation in AAS. (2 分)
   (c) How many types of emission would be observed by aspirating a brine solution in to an oxyhydrogen flame in AAS? Is it a spectral interference or chemical interference? (3 分)

Appendix:

For the reaction, $aA + ne^- \leftrightarrows bB$; The Nernst equation is:

$$E = E^o - \frac{RT}{nF}\ln\frac{A_B^b}{A_A^a}$$

F: 96490 C/mol;　R: 8.314 J/(mol.K); V.C/(mol.K)