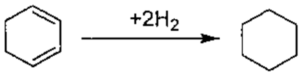
Part I　Physical Chemistry: 2 points each, 50 points

1. Estimate the enthalpy of hydrogenation of cyclohexadiene:



Given the following average bond enthalpies:
D(C-H) = 416 KJ/mol, D(C-C) = 346 KJ/mol, D(C=C) = 609 KJ/mol,
D(H-H) = 436 KJ/mol.

(A) 3594 KJ/mol (B) 2496 KJ/mol (C) 3408 KJ/mol (D) 2016 KJ/mol

2. For a spontaneous reaction, which of the following statements is correct: (A) The entropy change of the system must be > 0, (B) The entropy change of the surrounding must be > 0, (C) The total entropy change must be < 0, (D) the entropy change in the isolated system must be > 0, (E) the change of the system free energy must be > 0.

3. For N_2 at 25℃ and 1 atmosphere. (the collision cross-section = $0.43 nm^2$)
(A) The mean speed is 530.2 m/s (B) the mean free path is 6.7 x 10^{-5} m (C) the collision frequency is 7.3 x 10^{28} $m^{-3}s^{-1}$ (D) the mean speed is 682.5 m/s.

4. For the mixing of ideal gas at fixed T and P, which of the following are correct?
(a) $\Delta G_{mix}=0$ (b) $\Delta H_{mix}=0$ (c) $\Delta S_{mix}=0$ (d) $\Delta U_{mix}=0$ (e) $\Delta V_{mix}=0$
(f) $\Delta A_{mix}=0$
(A) (a) (d) (e) (B) (b) (d) (e) (C) (b) c) (e) (D) (a) (c) (d) (E) (b) (d) (f)

5. At 0 K, the CO_2 molecule only has two orientations. The entropy of 1 mole CO_2 is then calculated to be
(A) 2.98 JK^{-1}, (B) 5.76 JK^{-1}, (C) 3.65 JK^{-1}, (D) 6.67 JK^{-1}, (E) 12.4 JK^{-1}.

6. Analysis of the Joule-Thomson experiment is central to the technological problems associated with the liquefaction of gases. The Joule-Thomson coefficient μ is defined as $\mu = \left(\frac{\partial T}{\partial p}\right)_H$. A measurement shows that μ of an unknown substance > 0. Which the following statement is true?
(A) The substance is cooled under expansion at constant enthalpy
(B) The substance is heated under expansion at constant enthalpy
(C) The substance is heated at first and than cooled down under expansion at constant enthalpy
(D) The substance is cooled at first and than heated under expansion at constant enthalpy

7. Which one of the following gas is most corresponding to the property of the ideal gas (A) H_2 (B) He (C) Ne (D) Ar

8. When an ideal monatomic gas at 1 bar and 250K is allowed to expand adiabatically against a constant pressure of 0.4 bar until it reaches equilibrium, the final temperature is 200K. What is the entropy change $\Delta\overline{S}$ for this process? Given : $\overline{C_V} = \frac{3}{2}R$ and therefore $\overline{C_P} = \frac{5}{2}R$. (A) 7.62 (B) 2.98(C) 4.64 (D) 12.26 $JK^{-1}mol^{-1}$

見背面

9. Which of the following is the correct Maxwell relation?
(A) $(\partial T/\partial V)_S = -(\partial P/\partial S)_V$ (B) $(\partial S/\partial P)_T = -(\partial V/\partial S)_P$ (C) $(\partial S/\partial V)_T = -(\partial P/\partial V)_T$
(D) $-(\partial S/\partial T)_P = -(\partial V/\partial T)_P$

10. Which of the following condition will not increase the collision frequency of particles in the system?
(A) increase the pressure of the system
(B) increase the temperature of the system
(C) decrease the volume of the system
(D) increase the mean-free-path of the particle

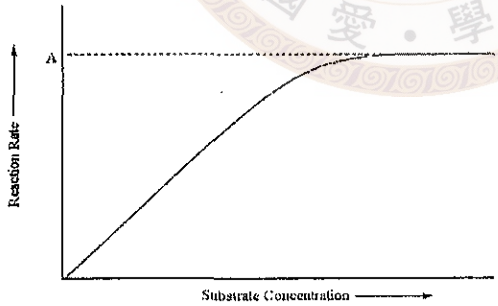
11. Assume a non-reversible reaction

$$A+B \rightarrow C \rightarrow D$$

where A and B are reactants, C is intermediate and D is product. What is steady state approximation?
(A) $\frac{d[A]}{dt} = 0$ (B) $\frac{d[A]}{dt} = -\frac{d[D]}{dt}$ (C) $\frac{d[C]}{dt} = 0$ (D) $\frac{d[D]}{dt} = 0$

12. The mechanism for a reaction is: $A + B \xrightarrow{k} P$, with $k = 10^5\ M^{-1}s^{-1}$ at 27 ℃. How long will it take to form 0.2 mM of P from 1 mM of A and 1 mM of B at 27 ℃?
(A) 1.25×10^{-6} s (B) 2.5×10^{-8} s (C) 2.5×10^{-6} s (D) 7.9×10^{-5} s.

13. In consecutive first-order reactions with $k_1 = 0.25\ s^{-1}$ and $k_2 = 0.15\ s^{-1}$ at what time will the intermediate reach its maximum concentration and what percent of the total material will be present as the intermediate at that time?
(A) 5.11 sec; 0.466 (B) 7.39 sec; 0.783 (C) 2.46 sec; 0.233 (D) 6.21 sec; 0.594.



14. Consider the plot shown above of reaction rate versus substrate concentration for an enzyme. *What is the name of the point labeled A?*
(A) Point A is the optimal rate of the reaction.
(B) Point A is the maximal rate of the reaction.
(C) Point A is the rate constant for the reaction.
(D) Point A is the maximum concentration of the substrate.
(E) Point A is the minimum concentration of enzyme for the reaction.

15. Consider the plot shown above of reaction rate versus substrate concentration for an enzyme. Why does the curve become flat with large substrate concentrations?
(A) Large substrate concentrations saturate all of the active sites on the enzyme molecules.
(B) Large amounts of substrate change the acidity of the reaction medium thus slowing the activity of the enzyme.
(C) Large substrate concentrations reduce the number of enzyme-substrate (ES) complexes being formed.
(D) LeChatlier's Principle doesn't apply to enzyme kinetics.
(E) Addition of large amounts of substrate change the effective temperature and thus the rate of the reaction changes.

接次頁

16. A population of $1.06\text{x}10^{21}$ particles has two energy states available to it with $\Delta\varepsilon$ = $4.14\text{x}10^{-21}$ J. Calculate the population of each energy level at 300K.
(A) $N_1=2.85\times10^{20}$; $N_2=7.749\times10^{20}$ (B) $N_1=3.88\times10^{20}$; $N_2=6.332\times10^{20}$ (C) $N_1=1.22\times10^{20}$; $N_2=8.84\times10^{20}$ (D) $N_1=3.85\times10^{20}$; $N_2=6.749\times10^{20}$

17. 12. A wave function is expressed as $\Psi=\frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}(27-18\sigma+2\sigma^2)e^{-\sigma/3}$,

specify the corresponding orbital?
(A) 1s (B) 2s (C) $2p_z$ (D) $2p_x$ (E) $3d_z2$ (F) 3s

18. The first bands in P and R branches of the v=0→1 vibration band in HBr are 2540 and 2573 cm^{-1}, respectively. (where v is the vibrational quantum number).Calculate the bond length of HBr.
(A) 158.64pm (B) 143.79pm (C) 169.77pm (D) 186.62pm

19. Assume the vibrational energy with anharmonicity is
$E_v/hc=(v+1/2)w_e-(v+1/2)2w_ex_e$; derive the formula for the maximum quantum number.
(A) $(w_e/2w_ex_e)-1/2$ (B) $2w_ex_e$ (C) $2w_ex_e-1/2$ (D) $(w_e/2w_ex_e)-1$

20. Find out which rotational quantum state J to have a maximum population at 500K for a diatomic molecule HCl with rotational constant equal to 10cm^{-1}
(A) J=1 (B) J=4 (C) J=7 (D) J=10 (E) J = 12

21. The quantum yield of a radiation-induced process is the number of times that a defined event (usually a chemical reaction step) occurs per photon absorbed by the system. Thus, the quantum yield is a measure of the efficiency with which absorbed light produces some effect. Now, there is a phosphorescence emitting dye in dichloromethane solution. The quantum yield of this compound after degassing process is 0.52 and the observed lifetime is 2.27 *us*. According to the information above, the accurate radiative rate of this compound is

(A) 2.29×10^{-5} (B) 4.37×10^{-6} (C) 2.29×10^{5} (D) 4.37×10^{5} (E) $5.29\times10^{5}\ \text{s}^{-1}$

22. During the electronic transition, vertical transition is explained by
(A) Pauli exclusion principle
(B) Franck-Condon principle
(C) Hund's rule
(D) Heisenberg uncertainty principle
(E) Intersystem crossing
(F) Internal conversion

For 23. and 24.A system of N non-interacting distinguishable magnetic particles each with a magnetic moment μ and in a magnetic field, B . There are only two possible energy states E = 0 or $2\mu B$. Answer the following questions:

23. What is the number of microstates $\Omega(n)$? n is the number of particles in the upper.

(A) $\dfrac{N!}{(N+n)!n!}$ (B) $N!$ (C) $\dfrac{N!}{(N-n)!n!}$ (D) $\dfrac{N!}{(N+n)!(N-n)!}$

24. Knowing that entropy, $S(n) = k \ln \Omega(n)$ and Stirling formula, $\ln n! \approx n \ln n - n$, find the value of n for which S(n) is a maximum.

(A) N (B) N/2 (C) $\sqrt{N}$ (D) $\sqrt[3]{N}$

25. What is the probability of finding a particle in a one-dimensional box in energy level n = 3 between x=L/4 and x=L/2? (L is the length of the box)

(A) 12.5% (B) 25% (C) 33% (D) 37.5% (E) 50% (F) none of above

接次頁

Part II. Analytical Chemistry 50%

1. For a saturated solution of CaF_2 buffered at pH 3.0, answer the following questions. ($K_{sp} = 3.2 \times 10^{-11}$ for CaF_2; $K_a = 6.8 \times 10^{-4}$ for HF) 10%
   (a) Write the pertinent equilibrium constant expressions for the solution.
   (b) Write the mass balance equation.
   (c) Find the solubility of CaF_2 in the solution.

2. Answer the following questions. 10%
   (a) Find the pH of a 1:1 mixture of 0.010 M NaOH and 0.010 M fumaric acid (a dibasic acid with $K_1 = 1.0 \times 10^{-3}$ and $K_2 = 3.3 \times 10^{-5}$).
   (b) Find the pCa for a 0.010 M Ca-EDTA ($K_f = 4.6 \times 10^{10}$) solution buffered at pH 9.0 ($\alpha_Y = 4.0 \times 10^{-2}$).
   (c) Find the potential of the cell: SCE | solution X | Pt. Solution X contains 0.025 M Ce^{4+} and 0.010 M Sn^{2+} in 1.0 F HCl. The formal potentials for SCE, Ce^{4+}/Ce^{3+}, and Sn^{4+}/Sn^{2+} are 0.24, 1.47, and 0.14 V, respectively.

3. The retention times for solvent, solute A and solute B passing through a 25.0-cm column are 4.0, 10.0, and 12.0 min, respectively. If $w_{1/2} = 0.20$ and 0.22 min for peaks A and B, respectively, answer the following questions. 12%
   (a) Calculate the capacity factor (k′) for peak A.
   (b) What fraction of time is solute A spent in the stationary phase of the column?
   (c) Find the partition coefficient K for solute A if $V_{stationary} = 0.10\ V_{mobile}$.
   (d) Find the resolution between peaks A and B.
   (e) Calculate the number of theoretical plates of peak A.
   (f) Calculate the plate height of peak A.

4. An aqueous solution was made by dissolving (0.160 ± 0.001) g of compound X in water in a (50.0 ± 0.2) mL volumetric flask. A (1.00 ± 0.02) mL was withdrawn, placed in a (25.0 ± 0.1) mL volumetric flask, and diluted with water to the mark. The absorbance of this solution at 340 nm in a (0.50 ± 0.01) cm cuvet was (0.48 ± 0.01). The molar absorptivity of X at 340 nm is $\varepsilon_{340} = (2.40 \pm 0.02) \times 10^3\ M^{-1}\cdot cm^{-1}$. 8%
   (a) Find the molecular weight of compound X (include the uncertainty).
   (b) Find the percentage of light passing through the solution in the cuvet (include the uncertainty in the answer).

5. Answer the following questions. 10%
   (a) Describe how to use t-test to decide whether two results differ at 95% confidence level? The means of two results are $\bar{x}_1$ and $\bar{x}_2$; the number of measurements are n_1 and n_2 and the standard deviation (s) is the same for both results.
   (b) Describe how to use the method of standard addition graphically to determine the analyte in a sample.
   (c) Describe the principle of separating neutral molecules with micellar electrokinetic capillary electrophoresis.

試題隨卷繳回