題號: 199

國立臺灣大學 106 學年度碩士班招生考試試題

科目:物理化學(B)

節次: 4

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注	贲	事	項	
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1. 請勿在答案本第一頁(制式表格)中作答。所有答案皆須寫在答案本第二頁之後。

2. Part I, Part II, Part III(亦即所有選擇題)必須依題號次序標示題號後作答,未標示題號或未依題序答題者,不予記

I. 單選題(每題 1.5 分)

No penalty will be applied for incorrect answers.

1. An endothermic reaction causes the surroundings to

(A) cool down.

(B) become acidic.

(C) release H₂O.

(D) become basic.

(E) evaporate.

warm up

2. Which of the following wave properties of light is mainly responsible for contact lenses being able to focus light?

(A) diffraction

(B) refraction (C) reflection

(D) deflection

dispersion (E)

(F) none of the above

3. The triple bond in acetylene (C₂H₂) consists of

(A) no σ bonds and three π bonds.

(B) one σ bond and two π bonds. (C) two σ bonds and one π bond.

(D) three σ bonds and no π bonds.

(E) two σ bonds and two π bonds. (F) none of the above.

4. The most likely reason that many spontaneous reactions have very slow reaction rates is that

(A) the activation energy of the reaction is large.

(B) ΔG° for the reaction is positive.

such reactions are endothermic. (C)

(D) such reactions are exothermic.

(E) K_p for the reaction is less than one.

(F) ΔS for the reaction is negative.

5. The orientation in space of an atomic orbital is associated with

(A) the principal quantum number (n).

the angular momentum quantum number (l). (B)

the magnetic quantum number (m_l) . (C)

(D) the spin quantum number (m_s) .

(E) both n and m_l .

both n and l(F)

6. Given $H_2(g) + (1/2)O_2(g) \rightarrow H_2O(l)$, $\Delta H^{\circ} = -285.6$ kJ/mol, determine the standard enthalpy change for the reaction $2H_2O(1) \rightarrow 2H_2(g) + O_2(g)$.

(A) $\Delta H^{\circ} = +142.8 \text{ kJ/mol}$

 Δ H° = -142.8 kJ/mol (B)

(C) $\Delta H^{\circ} = +571.2 \text{ kJ/mol}$

(D) $\Delta H^{\circ} = +285.6 \text{ kJ/mol}$

(E) $\Delta H^{\circ} = -285.6 \text{ kJ/mol}$

(F) $\Delta H^{\circ} = -571.2 \text{ kJ/mol}$

7. What is the overall order of the reaction with the rate constant of 2.37 L mol⁻¹s⁻¹.?

(A) zero

(B) first

(C) second

(D) third

(E) fourth

(F) none of the above

8. Based on the ionic product for water, K_w , for $H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$, the signs/values of ΔS° and ΔH° for the reaction at 25°C are predicted to be

(A) $\Delta S^{\circ} = + \text{ and } \Delta H^{\circ} = +$

(B) $\Delta S^{\circ} = + \text{ and } \Delta H^{\circ} = 0$

(C) $\Delta S^{\circ} = + \text{ and } \Delta H^{\circ} = -$

(D) $\Delta S^{\circ} = - \text{ and } \Delta H^{\circ} = +$

(E) $\Delta S^{\circ} = 0$ and $\Delta H^{\circ} = +$

(F) $\Delta S^{\circ} = -$ and $\Delta H^{\circ} = -$

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	9. According to VSEPR theory, what molecular shape does a molecule with the general formula A (A) bent (B) tetrahedral (C) trigonal planar (D) trigonal pyramidal (E) T-shaped (F) see-saw	X₂E have'	?	
	10. Which of these species would you expect to have the lowest standard entropy (S°)? (A) H ₂ O(g) (B) C ₂ H ₄ (g) (C) NH ₃ (g) (D) CH ₄ (g) (E) HF(g) (F) C ₃ I	H ₈ (g)		
	11. A reaction has the following rate law: Rate = $k[A][B]^2$ In experiment X, the concentrations of B are both 0.10 mol L ⁻¹ ; in experiment Y, the concentrations are both 0.20 mol L ⁻¹ . If the temperate stays constant, the value of the ratio Rate(Y)/Rate(X) is? (A) 2.0 (B) 3.0 (C) 4.0 (D) 8.0 (E) 9.0 (F) none of the above	f A and ure		
	12. Evaporation of 1.00 g water at body temperature requires energy 2.40 kJ. Evaporating the persponding the causes a person to feel chilly after extensive exercise, because the body loses heat. A typical perspires 12 mL of water after 10. minutes of exercise. The amount of body heat (in kJ) this person to evaporate the perspiration after continuous exercise for an hour is (A) 28.8 (B) 574.3 (C) 1436.7 (D) 172.8 (E) 68.4 (F) none of the	person 1 loses		
	II. 單選題(每題 2.5 分) No penalty will be applied for incorrect answers.			
	13. A FM station broadcasts classical music at 97.7 MHz. The wavelength of these waves is (A) 1.82×10^{-2} m (B) 5.28×10^{2} m (C) 0.820 m (D) 3.07 m (E) 7.49×10^{3} m (F) none of the above	;	·	
	14. The ΔH° _f values (in kJ/mol) for O ₃ , NO ₂ , and NO are 142.2, 33.85, and 90.4, respectively. Ozd in the atmosphere can react with nitric oxide (NO) to produce nitrogen dioxide and oxygen gas. W 5.00 L of ozone reacts with 8.00 L of nitric oxide, both at 1.00 atm and 25°C, the enthalpy change of the reaction is	hen		
	(A) -198.8 (B) +198.8 (C) -1590 (D) -993.4 (E) -44.4 (F) -40.7			
	15. Ammonium cyanate (NH ₄ CNO) reacts to form urea (NH ₂ CONH ₂). The rate constant at 80°C i mol ⁻¹ s ⁻¹ . The rate law for this reaction is (A) Rate = 3.75 mol L ⁻¹ s ⁻¹ [NH ₄ CNO] (B) Rate = 3.75 mol L ⁻¹ s ⁻¹ [NH ₄ CNO] ² (C) Rate = 7.50 L mol ⁻¹ s ⁻¹ [NH ₂ CONH ₂] ⁻¹ (D) Rate = 7.50 L mol ⁻¹ s ⁻¹ [NH ₄ CNO] (E) Rate = 7.50 L mol ⁻¹ s ⁻¹ [NH ₄ CNO] ² (F) More information is needed to determine the			
	16. For the dimerization of formic acid in the gas phase, $2HCOOH(g) \rightarrow (HCOOH)_2(g)$, $\Delta G^\circ = -160.1$ kJ/mol and $\Delta H^\circ = -60.1$ kJ/mol at 25°C. The equilibrium constant of the reaction at 75 °C is (A) 0.120 (B) 1.20×10^{-4} (C) 5742 (D) 8.33 (E) 273 (F) 74		-	•
	17. According to the Rydberg equation (Rydberg constant: $1.096776 \times 10^7 \text{ m}^{-1}$), the longest wavelenm) in the series of H-atom lines with $n_1 = 3$ is (A) 1875 (B) 1342 (C) 3968 (D) 265 (E) 831 (F) none of the above			

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18. The S° values (in J/K·mol) for HgO, O₂, and Hg are 70.29, 205.0, and 76.02, respectively. Under standard state conditions, the temperature at which the reaction HgO(s) \rightarrow Hg(l) + $^{1}/_{2}$ O₂(g) (with Δ H° = 90.84 kJ/mol) becomes spontaneous is

(A) 432 K

(B) 528 K

(C) 607 K

(D) 683 K

(E) 762 K

(F) 840 K

19. An antibiotic breaks down in the body with a first order rate constant of 1.9×10^{-2} min⁻¹. How long (t, in min) will it take for the body concentration of the antibiotic to drop from 0.0200 nM to 0.0100 nM if its production/regeneration is not considered?

(A) t < 0.5

(B) 0.5 < t < 10

(C) 10 < t < 30

(D) 30 < t < 100

(E) 100 < t < 300

(F) t > 300

20. For $C_6H_{15}B(l)$ and $C_6H_{15}B(g)$, the ΔH°_f values (in kJ/mol, at 25°C) are -194.6 and -157.7, respectively, and the ΔG°_f values (in kJ/mol, at 25°C) are 9.4 and 16.1, respectively. The normal boiling point of triethylborane ($C_6H_{15}B$) is

(A) -38°C

(B) 38°C

(C) 92°C

(D) 108°C

(E) 216°C

(F) 348°C

III. 複選題(共 18 分)

Penalty of 50% credit to the correct answer will be applied for the incorrect answer. No penalty will be applied for failure to answer the question.

- 21. Which of the following describe(s) the first law of thermodynamics?
- (A) In an isolated system, entropy never decreases.
- (B) A temperature of absolute zero is unreachable.
- (C) Energy is being created as time passes.
- (D) Change in the internal energy of a system is given by the difference of the heat that flows across its boundaries and the work done on the system by the surroundings
- (E) If the surroundings do work on a system, the internal energy increases and the sign of q and w are positive
- (F) Energy is neither lost nor gained in any energy transformations

22. Which of the following statements about orbital hybridization is (are) correct?

(A) The C in CO_2 is sp hybridized.

(B) The Si in SiH₄ is sp^3 hybridized.

(C) The B in BF₃ is sp^2 hybridized.

(D) The O in H_2O is sp^2 hybridized.

(E) The Be in BeCl₂ is sp^2 hybridized.

(F) The N in NH₃ is sp^2 hybridized.

23. Which of the following processes is (are) accompanied by an increase in entropy?

(A) $H_2O_2(l) \rightarrow H_2O(l) + \frac{1}{2}O_2(g)$

(B) $H_2O(l) \rightarrow H_2O(s)$

(C) $Br_2(1) \rightarrow Br_2(g)$

(D) $2SO_2(g) + O_2(g) \rightarrow SO_3(g)$

(E) $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

(F) $C_2H_6(g) + {}^{7}/_2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

24. Which of the following statements about the theory of molecular orbitals (MOs) is (are) correct?

- (A) A MO describes a region of space around two or more atoms inside which electrons may be found.
- (B) In a stable molecule having an even number of electrons, all electrons must be paired.

(C) A species with a bond order of zero will not be stable.

(D) Combination of two 2s orbitals may result in either σ or π MOs.

(E) A bonding MO has lower energy than the two atomic orbitals from which the bonding MO is formed.

(F) Combination of two atomic orbitals produces two bonding and two antibonding MOs.

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IV. 申述/計算/實驗題.

25.(19%) (a) "Because of the possible metal allergy, amalgam is considered an obsolete material. It contains mercury, silver, tin, copper and zinc. Crowns can contain gold, silver, palladium, copper, chromium, indium, gallium, iridium, nickel and more. Implants are often made of titanium, aluminium and vanadium. Zirconia tooth replacement is a solution to avoid metal allergy. Some common dental impression materials like polyether and silicones do not contain metals"

The paragraph above is rephrased from statements in web pages discussing common sources of metals encountered in dentistry and surgery that may cause allergy to some patients. Identify words in the paragraph that describe or hint chemical elements by simply writing down the chemical symbols of the elements in the order of appearance in the paragraph. Notice that (1) a word may hint more than one element and (2) some symbols may appear several times in your answer.

(b) (i) Write down the integrated rate laws for first-order and second-order reactions. (ii) Make graphical representations (with proper labels) of the two rate laws and indicate in your graphs how their rate constants may be determined.

(c) Commercially pure titanium is one of the most common implant biomaterials. The kinetics of titanium oxidation and desorption for the reaction products have been investigated by growing pure titanium on a substrate like tungsten. Suggest experiments that may be conducted and plots be made to derive the activation energy for the desorption of titanium oxide from the substrate.

26.(4%) Describe (a) the kinetic theory of heat and (b) thermodynamic explanations of heat.

27.(6%) (a) Draw the molecular orbital (MO) diagram for the nitrosonium ion, NO⁺. (b) Predict the magnetism of NO⁺ molecules. (c) Arrange the following molecules in order of increasing bond order: NO⁺, NO⁻, O₂⁻, NO, C₂²⁻, N₂²⁻

28.(15%) Carbonated calcium-deficient hydroxylapatite is the main mineral of which dental enamel and dentin are composed. The amorphous phase in hydroxyapatite coatings mostly consists of a dehydroxylated calcium phosphate. When the amorphous phase is heated, crystallization occurs over a range of temperatures and is dependent on the hydroxyl content of the amorphous phase and the partial water-vapor pressure. Crystallization of hydroxyl-rich areas produces hydroxyapatite, followed by diffusion of hydroxyl ions, thus increasing the amount of crystalline phase. The activation energies of crystallization to hydroxyapatite, diffusion of hydroxyl ions, and crystallization to oxyapatite are 274, 230, and 440 kJ/mol, respectively. (a) Among the three processes (crystallization to hydroxyapatite, diffusion of hydroxyl ions, and crystallization to oxyapatite), which will occur first in practice when an amorphous phase of dehydroxylated calcium phosphate is heated? Explain. (b) Assume that for crystallization to take place, a critical chemical bond in the species involved in the rate-determining step for crystallization has to be broken and the bond strength of the critical chemical bond is equivalent to the activation energy of crystallization. Calculate the longest wavelength of light that can cause this bond to be broken for each of the two crystallization processes (i.e., crystallizations to hydroxyapatite and oxyapatite, respectively). (c) Under the assumption stated in (b), will exposure of the amorphous phase to visible light during heating promote the crystallizations of (i) hydroxyapatite and (ii) oxyapatite? Explain. (d) Suggest and discuss two factors (other than exposure of light) that may promote the kinetics of the crystallization.

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