CHEMISTRY

Section I

Time— 30 minutes

NO CALCULATOR MAY BE USED WITH SECTION I.

Note: For all questions, assume that the temperature is 298 K, the pressure is 1.00 atmosphere, and solutions are aqueous unless otherwise specified.

Throughout the test the following symbols have the definitions specified unless otherwise noted.

T	= temperature	L, mL	= liter(s), milliliter(s)
P	= pressure	g	= gram(s)
V	= volume	nm	= nanometer(s)
S	= entropy	atm	= atmosphere(s)
H	= enthalpy	mm Hg	= millimeters of mercury
G	= Gibbs free energy	J, kJ	= joule(s), kilojoule(s)
R	= molar gas constant	V	= volt(s)
n	= number of moles	mol	= mole(s)
M	= molar		
m	= molal		

Part A

Directions: Each set of lettered choices below refers to the numbered statements immediately following it. Select the one that is best in each case and then place the letter of your choice in the corresponding box on the student answer sheet. A choice may be used once, more than once, or not at all in each set.

Questions 1-4 refer to the following chemical compounds.

(A) CH_4
(B) CCl_3F
(C) H_2S
(D) H_2O_2
(E) K_2CrO_4

1. Commonly used as a disinfectant for minor skin wounds
2. A refrigerant implicated in the thinning of the stratospheric ozone layer
3. A major component of the fuel known as natural gas
4. A yellow solid at room temperature and 1 atm

Questions 5-7 refer to the following molecules.

(A) CO
(B) CH_4
(C) HF
(D) PH_3
(E) F_2

5. Contains two π-bonds
6. Has the highest dipole moment
7. Has a molecular geometry that is trigonal pyramidal

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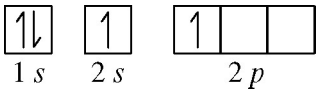
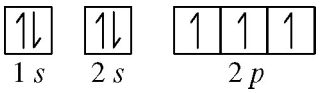
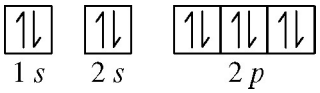
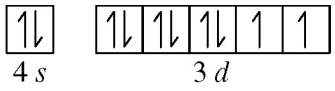
Questions 8-11 refer to neutral atoms for which the atomic orbitals are represented below

(A) 

(B) 

(C) 

(D) 

(E) [Ar] 

8. Is in an excited state

9. Has exactly five valence electrons

10. Has the highest first ionization energy

11. Forms an aqueous cation that is colored

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Questions 12-15 refer to the chemical reactions represented below.

(A) $HC_2H_3O_2(aq) + NH_3(aq) \rightarrow C_2H_3O_2^-(aq) + NH_4^+(aq)$

(B) $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

(C) $Zn(OH)_2(s) + 2\ OH^-(aq) \rightarrow [Zn(OH)_4]^{2-}(aq)$

(D) $2\ K(s) + Br_2(l) \rightarrow 2\ KBr(s)$

(E) $N_2O_4(g) \rightarrow 2\ NO_2(g)$

12. An oxidation-reduction reaction

13. A precipitation reaction

14. A reaction in which a coordination complex is formed

15. A Lewis acid-base reaction that is not a Brønsted-Lowry acid-base reaction

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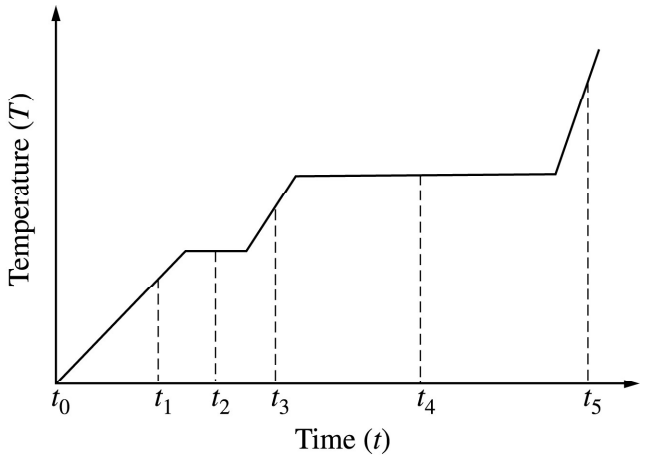
Questions 16-17 refer to various points in time during an experiment conducted at 1.0 atm. Heat is added at a constant rate to a sample of a pure substance that is solid at time t_0. The graph below shows the temperature of the sample as a function of time.



(A) t_1
(B) t_2
(C) t_3
(D) t_4
(E) t_5

16. Time when the average distance between the particles is greatest

17. Time when the temperature of the substance is between its melting point and its boiling point

Part B

Directions: Each of the questions or incomplete statements below is followed by five suggested answers or completions. Select the one that is best in each case and place the letter of your choice in the corresponding box on the student answer sheet.

18. Which of the following is the correct name for the compound with formula Ca_3P_2 ?

(A) Tricalcium diphosphorus
(B) Calcium phosphite
(C) Calcium phosphate
(D) Calcium diphosphate
(E) Calcium phosphide

19. What mass of KBr (molar mass 119 g mol^{-1}) is required to make 250. mL of a 0.400 *M* KBr solution?

(A) 0.595 g
(B) 1.19 g
(C) 2.50 g
(D) 11.9 g
(E) 47.6 g

20. The value of the acid-dissociation constant, K_a, for a weak monoprotic acid HA is 2.5×10^{-6}. The pH of 0.40 *M* HA is closest to

(A) 2.0
(B) 3.0
(C) 4.0
(D) 6.0
(E) 8.0

21. Which of the systems in equilibrium represented below will exhibit a shift to the left (toward reactants) when the pressure on the system is increased by reducing the volume of the system? (Assume that temperature is constant.)

(A) $2\ Mg(s) + O_2(g) \rightleftarrows 2\ MgO(s)$
(B) $SF_4(g) + F_2(g) \rightleftarrows SF_6(g)$
(C) $H_2(g) + Br_2(g) \rightleftarrows 2\ HBr(g)$
(D) $N_2(g) + 3\ H_2(g) \rightleftarrows 2\ NH_3(g)$
(E) $SO_2Cl_2(g) \rightleftarrows SO_2(g) + Cl_2(g)$

22. The standard enthalpy of formation, ΔH_f°, of $HI(g)$ is +26 kJ mol^{-1}. Which of the following is the approximate mass of $HI(g)$ that must decompose into $H_2(g)$ and $I_2(s)$ to release 500. kJ of energy?

(A) 250 g
(B) 650 g
(C) 1,300 g
(D) 2,500 g
(E) 13,000 g

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$$CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2\ Cl^-(aq)$$

23. For the process of solid calcium chloride dissolving in water, represented above, the entropy change might be expected to be positive. However, ΔS for the process is actually negative. Which of the following best helps to account for the net loss of entropy?

(A) Cl^- ions are much larger in size than Ca^{2+} ions.
(B) The particles in solid calcium chloride are more ordered than are particles in amorphous solids.
(C) Water molecules in the hydration shells of Ca^{2+} and Cl^- ions are more ordered than they are in the pure water.
(D) The $Ca^{2+}(aq)$ and $Cl^-(aq)$ ions are more free to move around in solution than they are in $CaCl_2(s)$.
(E) In the solution, the average distance between $Ca^{2+}(aq)$ and $Cl^-(aq)$ is greater than the average distance between Ca^{2+} and Cl^- in $CaCl_2(s)$.

$$\ldots CH_3OCH_3(g) + \ldots O_2(g) \rightarrow \ldots CO_2(g) + \ldots H_2O(g)$$

24. When the equation above is balanced using the lowest whole-number coefficients, the coefficient for $O_2(g)$ is

(A) 6
(B) 4
(C) 3
(D) 2
(E) 1

25. For which of the following processes does entropy decrease ($\Delta S < 0$) ?

(A) $H_2O(s) \rightarrow H_2O(l)$
(B) $Br_2(l) \rightarrow Br_2(g)$
(C) Crystallization of $I_2(s)$ from an ethanol solution
(D) Thermal expansion of a balloon filled with $CO_2(g)$
(E) Mixing of equal volumes of $H_2O(l)$ and $CH_3OH(l)$

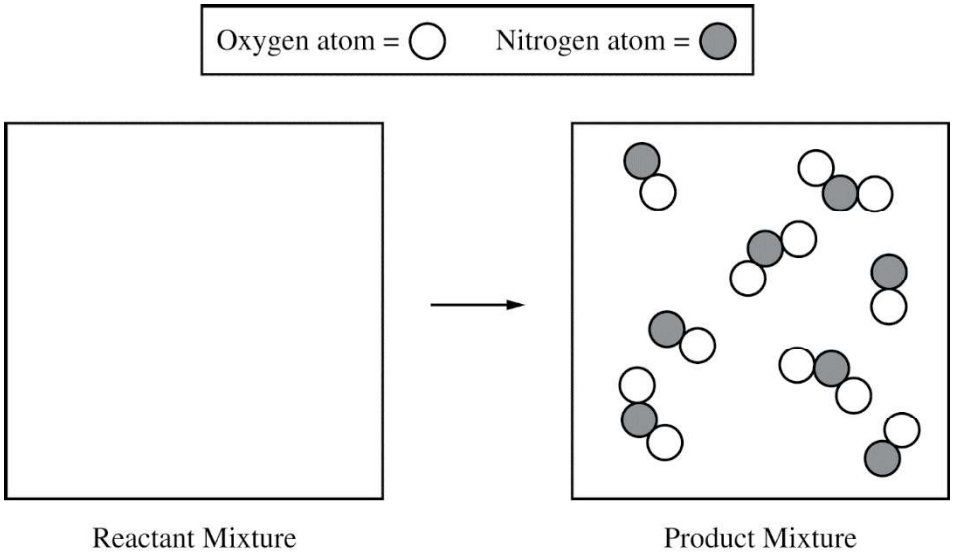
THE END

No.	Correct Answer
1	D
2	B
3	A
4	E
5	A
6	C
7	D
8	B
9	C
10	A
11	E
12	D
13	B
14	C
15	C
16	E
17	C
18	E
19	D
20	B
21	E
22	D
23	C
24	C
25	C

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

2. A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of $NO(g)$ and $NO_2(g)$, which the student produces by using the reaction represented above.

   (a) The particle-level representation of the equimolar mixture of $NO(g)$ and $NO_2(g)$ in the flask at the completion of the reaction between $NO(g)$ and $O_2(g)$ is shown below in the box on the right. In the box below on the left, draw the particle-level representation of the reactant mixture of $NO(g)$ and $O_2(g)$ that would yield the product mixture shown in the box on the right. In your drawing, represent oxygen atoms and nitrogen atoms as indicated below.



The student reads in a reference text that $NO(g)$ and $NO_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.

$$NO(g) + NO_2(g) \rightleftarrows N_2O_3(g)$$

ΔH°_{298}	ΔS°_{298}	ΔG°_{298}
$-40.4\ kJ/mol_{rxn}$	$-138.5\ J/(K \cdot mol_{rxn})$	$0.87\ kJ/mol_{rxn}$

   (b) The student begins with an equimolar mixture of $NO(g)$ and $NO_2(g)$ in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.

      (i) Calculate the value of the equilibrium constant, K, for the reaction at 298 K.

      (ii) If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{N_2O_3}$ at equilibrium be equal to 1.0 atm? Justify your answer.

   (c) The student hypothesizes that increasing the temperature will increase the amount of $N_2O_3(g)$ in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

$N_2O_3(g)$ reacts with water to form nitrous acid, $HNO_2(aq)$, a compound involved in the production of acid rain. The reaction is represented below.

$$N_2O_3(g) + H_2O(l) \rightarrow 2\ HNO_2(aq)$$

(d) The skeletal structure of the HNO_2 molecule is shown in the box below.

(i) Complete the Lewis electron-dot diagram of the HNO_2 molecule in the box below, including any lone pairs of electrons.

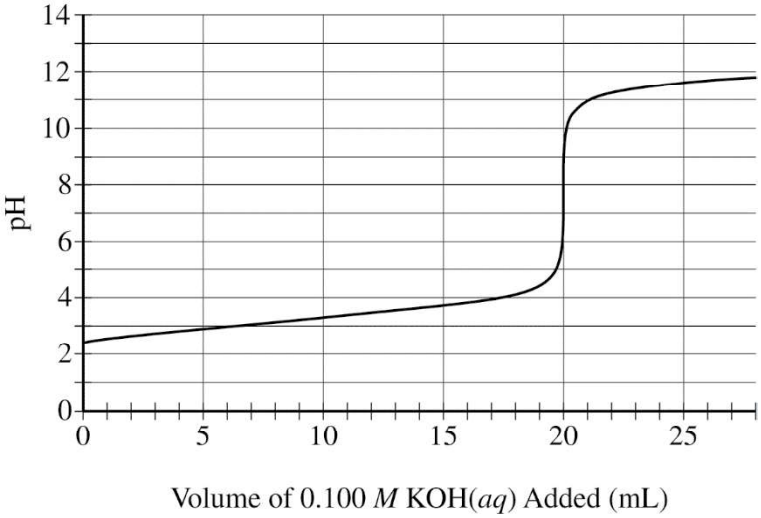
H O N O

(ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

To produce an aqueous solution of HNO_2, the student bubbles $N_2O_3(g)$ into distilled water. Assume that the reaction goes to completion and that HNO_2 is the only species produced. To determine the concentration of $HNO_2(aq)$ in the resulting solution, the student titrates a 100. mL sample of the solution with 0.100 *M* KOH(*aq*). The neutralization reaction is represented below.

$$HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$$

The following titration curve shows the change in pH of the solution during the titration.



(e) Use the titration curve and the information above to

(i) determine the initial concentration of the $HNO_2(aq)$ solution

(ii) estimate the value of pK_a for $HNO_2(aq)$

(f) During the titration, after a volume of 15 mL of 0.100 *M* KOH(*aq*) has been added, which species, $HNO_2(aq)$ or $NO_2^-(aq)$, is present at a higher concentration in the solution? Justify your answer.