FORM GR0027

# 27

### GRADUATE RECORD EXAMINATIONS®

## CHEMISTRY TEST

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GRE

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Material in the tables on pages 10 and 11 may be useful in answering the questions in this examination.

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### TABLE OF INFORMATION

Electron rest mass	$m_e = 9.11 \times 10^{-31}$ kilogram
Proton rest mass	$m_p = 1.672 \times 10^{-27}$ kilogram
Neutron rest mass	$m_n = 1.675 \times 10^{-27}$ kilogram
Magnitude of the electron charge	$e = 1.60 \times 10^{-19}$ coulomb
Bohr radius	$a_0 = 5.29 \times 10^{-11} \text{ meter}$
Avogadro number	$N_A = 6.02 \times 10^{23}$ per mole
Universal gas constant	R = 8.314  joules/(mol • K) = 0.0821  L • atm/(mol • K) = 0.08314  L • bar/(mol • K)
Boltzmann constant	$k = 1.38 \times 10^{-23}$ joule/K
Planck constant	$h = 6.63 \times 10^{-34}$ joule • second
Speed of light	$c = 3.00 \times 10^8 \text{ m/s} = 3.00 \times 10^{10} \text{ cm/s}$
1 atmosphere pressure	1 atm = $1.0 \times 10^5$ newtons/meter <sup>2</sup> = $1.0 \times 10^5$ pascals (Pa)
Faraday constant	$\mathcal{F} = 9.65 \times 10^4$ coulombs/mol
1 atomic mass unit (amu)	$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kilogram}$
1 electron volt (eV)	$1 \text{ eV} = 1.602 \times 10^{-19} \text{ joule}$
Volume of 1 mole of ideal gas at 0° C, 1 atmosphere	= 22.4 liters

### CHEMISTRY TEST Time—170 minutes 136 Questions

**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 then fill in the corresponding space on the answer sheet.

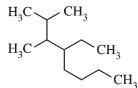
Note: Solutions are aqueous unless otherwise specified.

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

T = temperature	M = molar
P = pressure	m = molal
V = volume	mL = milliliter(s)
S = entropy	g = gram(s)
H = enthalpy	nm = nanometer(s)
U = internal energy	L = liter(s)
R = molar gas constant	kg = kilogram(s)
n = number of moles	atm = atmosphere(s)

1. THIS ITEM WAS NOT SCORED.

- 3. Which of the following has the largest radius?
  - (A) Ca<sup>2+</sup>
    (B) K<sup>+</sup>
    (C) Ar
    (D) Cl<sup>-</sup>
    (E) S<sup>2-</sup>



- 4. According to IUPAC nomenclature, which of the following is the name for the compound shown above?
  - (A) 3-butyl-2-(1-methylethyl)pentane
  - (B) 2-isopropyl-3-butylpentane
  - (C) 2-isopropyl-3-ethylheptane
  - (D) 4-ethyl-2,3-dimethyloctane
  - (E) 2-isododecane

- 2. The third ionization energy of titanium is required to carry out which of the following processes?
  - (A)  $\operatorname{Ti}^{3+}(g) + e^- \rightarrow \operatorname{Ti}^{2+}(g)$
  - (B)  $\text{Ti}^{2+}(g) \rightarrow \text{Ti}^{3+}(g) + e^{-}$
  - (C)  $3 \operatorname{Ti}(g) \rightarrow 3 \operatorname{Ti}^+(g) + 3 \mathrm{e}^-$
  - (D)  $\operatorname{Ti}(g) \rightarrow \operatorname{Ti}^{3+}(g) + 3e^{-}$
  - (E)  $Ti(s) \rightarrow Ti^+(g) + e^-$

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- 5. Of the following, which corresponds to a compound with exactly one ring or double bond?
  - (A)  $C_5H_{10}O$
  - (B) C<sub>5</sub>H<sub>10</sub>Cl<sub>2</sub>O
  - (C)  $C_5H_{11}Cl$
  - (D) C<sub>5</sub>H<sub>11</sub>ClO
  - (E)  $C_5H_{12}O_2$
- 6. If 4.0 g of a gas occupies 11.2 L at 0.0°C and 0.25 atmosphere, then the molecular mass of the gas is
  - (A) 8.0 g
  - (B) 16 g
  - (C) 32 g
  - (D) 48 g
  - (E) 64 g
- 7. Solutions of the following compounds, all at the same molality, were prepared. Which solution has the lowest freezing point?
  - (A) KBr
  - (B)  $Al(NO_3)_3$
  - (C) CH<sub>3</sub>COONa
  - (D) NaNO<sub>2</sub>
  - (E) MgCl<sub>2</sub>
    - $(P + n^2 a/V^2)(V nb) = nRT$
- 8. Which of the following gases has the largest value of *b* in the van der Waals equation shown above?
  - (A)  $CH_4$
  - (B) CCl<sub>4</sub>
  - (C) HCl
  - (D) H<sub>2</sub>O
  - (E) N<sub>2</sub>
- 9. The solubility product expression,  $K_{sp}$ , for the slightly soluble salt Pb(IO<sub>3</sub>)<sub>2</sub> is equal to
  - (A) [Pb<sup>2+</sup>][IO<sub>3</sub><sup>-</sup>]
    (B) [Pb<sup>2+</sup>]<sup>2</sup>[IO<sub>3</sub><sup>-</sup>]
  - (C)  $[Pb^{2+}][IO_3^{-}]^2$
  - (C)  $[Pb^{2+}]^2[IO_3^{-}]^2$
  - (D)  $[PD^{-1}]^{-}[IO_3]^{-}$
  - (E)  $[Pb^{2+}][2 IO_3^{-}]^2$

- 10. Which of the following is the pH of a solution obtained by mixing 50.0 mL of 0.100 *M* HA and 50.0 mL of 0.100 *M* NaOH ?
  - I. Neutral if HA is a strong acid
  - II. Basic if HA is a weak acid
  - III. Neutral if HA is a weak acid
  - (A) I only
  - (B) II only
  - (C) III only
  - (D) I and II
  - (E) I and III

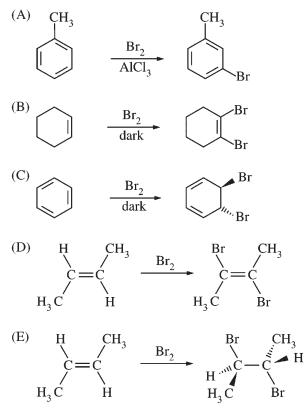
$$X^+ + e^- \rightarrow X(s)$$
  $E^\circ = -2.174 V$ 

- 11. For the half-reaction above, which of the following is a correct statement?
  - (A)  $X^+$  is readily reduced.
  - (B)  $X^+$  is a good oxidizing agent.
  - (C) X is a poor reducing agent.
  - (D) X is a good oxidizing agent.
  - (E) X is readily oxidized.

$$H \sim CO_{2}H \qquad CO_{2}H \qquad H \sim CO_{2}H \qquad H \sim$$

- 12. The structures shown above are
  - (A) identical
  - (B) different conformations of the same compound
  - (C) enantiomers
  - (D) diastereomers
  - (E) constitutional isomers

13. Which of the following reactions yields the indicated compound as a major product?



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$$CH_{3}$$

$$\downarrow$$

$$CH_{3}CHCH_{2}CH_{2}CH_{3} + Br_{2} - hv$$

14. In the reaction shown above, the intermediate that is formed at the fastest rate is which of the following?

$$\overset{(A)}{\underset{c}{\overset{}H_{2}CHCH_{2}CH_{2}CH_{2}CH_{3}}} \overset{CH_{3}}{\underset{c}{\overset{}H_{2}CHCH_{2}CH_{2}CH_{3}}}$$

$$\stackrel{(B)}{\underset{CH_{3} \leftarrow CH_{2}CH_{2}CH_{2}CH_{3}}{CH_{3} \leftarrow CH_{2}CH_{2}CH_{3}}}$$

(D) 
$$CH_3$$
  
|  
CH\_3CHCH\_2CHCH\_3

- 15. A high equivalent weight is desirable for compounds used as primary standards because
  - (A) such compounds are generally easier to purify
  - (B) such compounds are generally hygroscopic
  - (C) such compounds generally react with 1:1 stoichiometry
  - (D) larger compounds generally contain less surface water
  - (E) weighing errors are minimized
- 16. Given that a certain organic compound absorbs light in the visible region, it CANNOT be true that it
  - (A) is aromatic
  - (B) is an alkane
  - (C) is colored
  - (D) contains a nitro group
  - (E) contains a chlorine atom

- 17. What is the oxidation state of chromium in (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> ?
  - (A) +7
  - (B) +6
  - (C) +5
  - (D) +4
  - (E) +3
- 18. Which of the following transmutations entails an absorption of an alpha particle and release of a proton?
  - (A)  $^{238}_{92}$ U  $\rightarrow ^{234}_{90}$ Th
  - (B)  $^{14}_{7}N \rightarrow ^{17}_{8}O$
  - (C)  $^{238}_{92}$ U  $\rightarrow ^{234}_{91}$ Pa
  - (D)  $^{27}_{13}\text{Al} \rightarrow ^{30}_{15}\text{P}$
  - (E)  ${}^{2}_{1}H \rightarrow {}^{1}_{1}H$
- 19. The azide ion,  $N_3^-$ , is isoelectronic with which of the following?
  - (A)  $NO_2^-$ (B)  $NO_2$ (C)  $CO_2$ (D)  $SO_2$ (E)  $O_2^-$
  - (E) O<sub>3</sub>
- 20. For which of the following sets of values of  $\Delta H$  and  $\Delta S$  will a reaction be spontaneous only at high temperature?

	$\Delta H(\rm kJ)$	$\Delta S(J/K)$
(A)	+60	+19
(B)	+60	-19
(C)	-60	-19
(D)	-60	+19
(E)	0	-19

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$$\operatorname{Cu}_2\operatorname{O}(s) + \frac{1}{2}\operatorname{O}_2(g) \rightleftharpoons 2\operatorname{CuO}(s) \qquad \Delta H^\circ = -11.3 \text{ kJ}$$

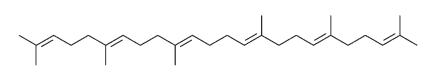
- 21. At 298 K and 1 atmosphere, the closed system shown above is at equilibrium. If the equilibrium is perturbed by isothermally decreasing the volume of the system, which of the following is NOT correct?
  - (A) More product will be present after equilibrium is reestablished.
  - (B)  $\Delta G$  is less than zero for the process of reestablishing equilibrium.
  - (C) The equilibrium constant,  $K_{eq}$ , will decrease.
  - (D) The temperature will remain constant.
  - (E)  $\Delta G^{\circ}$  will remain unchanged.
- 22. Which of the following is NOT accompanied by an increase in the entropy of the system?
  - (A) Discharging a battery
  - (B) Boiling water at atmospheric pressure
  - (C) Very slow mixing of hot and cold water in a well-insulated container
  - (D) Very slow expansion of a gas into an evacuated flask
  - (E) Rapid expansion of a gas and recompression to its original temperature, pressure, and volume
- 23. Which of the following comparisons of the average kinetic energies and the average molecular speeds of H<sub>2</sub> and N<sub>2</sub> gases at 300 K is correct?

	Average <u>Kinetic Energy</u>	Average <u>Molecular Speed</u>
(A)	$H_2 = N_2$	$H_2 = N_2$
(B)	$H_2 = N_2$	$H_2 > N_2$
(C)	$H_2 = N_2$	$H_2 < N_2$
(D)	$H_2 > N_2$	$H_2 = N_2$
(E)	$H_2 < N_2$	$H_2 = N_2$

- 24. For a triprotic acid, H<sub>3</sub>A,  $K_{a1}$  is  $1.0 \times 10^{-2}$ ,  $K_{a2}$  is  $1.0 \times 10^{-6}$ , and  $K_{a3}$  is  $1.0 \times 10^{-10}$ . The pH range in which H<sub>2</sub>A<sup>-</sup> is the predominant form is a pH between
  - (A) 1 and 3
  - (B) 3 and 5
  - (C) 5 and 7
  - (D) 7 and 9
  - (E) 9 and 11
- 25. Which of the following is another way to express the concentration of a glucose solution that is 0.01 percent by weight?
  - (A) 1.0 ppb
  - (B) 100 ppm
  - (C) 10 ppt
  - (D) 1.0 ppt
  - (E) 1.0%

- 26. The molecular geometry of  $XeF_4O$  is
  - (A) trigonal
  - (B) octahedral
  - (C) trigonal bipyramidal
  - (D) square pyramidal
  - (E) tetrahedral
- 27. The structure of cesium metal at 25°C and 1 atmosphere is body-centered cubic. At the same temperature but at high pressure, cesium undergoes a phase transition to yield a structure much more dense than body-centered cubic. Which of the following is the likely structure at high pressure?
  - (A) Cubic close-packed
  - (B) Amorphous
  - (C) Primitive cubic
  - (D) Primitive tetragonal
  - (E) Primitive orthorhombic

- 28. Which of the following does NOT have a threefold rotational symmetry axis?
  - (A) BCl<sub>3</sub>
  - (B)  $CH_4$
  - $(C) \operatorname{NH}_3$
  - (D)  $CClF_3$
  - (E)  $ClF_3$



- 29. The compound shown above is a
  - (A) triglyceride
  - (B) trinucleotide
  - (C) tripeptide
  - (D) trisaccharide
  - (E) triterpene

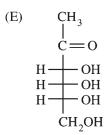
30. A pyranose form is a cyclic hemiacetal with a six-membered ring. Which of the following compounds CANNOT exist in a pyranose form?

(A) 
$$CH = O$$
  
H  $OH$   
H  $OH$   
H  $OH$   
H  $OH$   
CH<sub>2</sub>OH

(B) 
$$CH_{2}OH$$
  
 $C=O$   
 $H \rightarrow OH$   
 $H \rightarrow OH$   
 $CH_{2}OH$ 

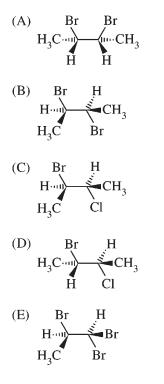
(C) 
$$CH = O$$
  
 $H \rightarrow OH$   
 $H \rightarrow OH$   

(D) 
$$CH_2OH$$
  
 $C=O$   
 $H \rightarrow OH$   
 $H \rightarrow OH$   
 $H \rightarrow OH$   
 $CH_2OH$ 

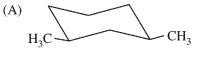


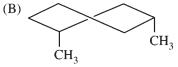
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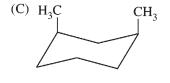
31. Which of the following substances is achiral?

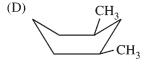


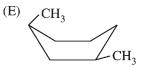
32. Which of the following structures is the most stable conformation of *cis*-1,3-dimethylcyclohexane?

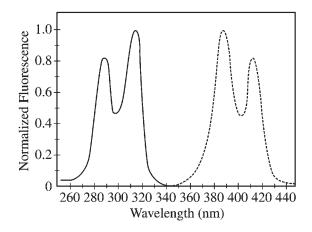




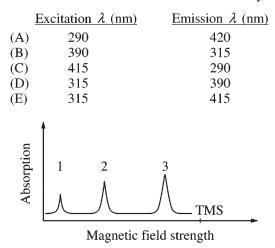








33. Based on the excitation and emission spectra for compound Y shown above, what excitation and emission wavelengths should be chosen to maximize the measured fluorescence intensity?



- 34. Based on the low-resolution proton NMR spectrum of a particular compound shown above, which of the following is(are) true?
  - I. There are at least three different types of protons in this compound.
  - II. There are more protons of the type corresponding to peak 3 than the type corresponding to peak 1.
  - III. Protons of the type corresponding to peak 2 are more shielded than those corresponding to peak 1.
  - (A) I only
  - (B) II only
  - (C) III only
  - (D) I and II only
  - (E) I, II and III

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- 35. Which of the following is classified as an indeterminate (random) error in analytical measurements?
  - (A) A colorimetric reaction has not reached completion before the absorbance of the product is measured.
  - (B) An arithmetic mistake is made in computing the concentration of a measured substance.
  - (C) A balance is incorrect by a constant amount of 0.10 g.
  - (D) A blank used to correct for background interference is accidentally contaminated with the analyte.
  - (E) A pipet is not handled in quite the same way during the repetitions of a determination.

 $2 \operatorname{NO}(g) + 2 \operatorname{H}_2(g) \rightarrow \operatorname{N}_2(g) + 2 \operatorname{H}_2\operatorname{O}(g)$ 

36. The method of initial rates is used to determine the rate law for the reaction shown above. The following initial rates were determined.

$P_{\rm NO}({\rm torr})$	$P_{\rm H_2}(\rm torr)$	Initial Rate (torr/s)
200	400	0.46
400	200	0.92
400	400	1.85

These data imply which of the following rate laws?

- (A) Rate =  $k P_{NO}$
- (B) Rate =  $k P_{NO} P_{H_2}$
- (C) Rate =  $k P_{\text{NO}} P_{\text{H}_2}^2$
- (D) Rate =  $k P_{NO}^2 P_{H_2}$
- (E) Rate =  $k P_{\text{NO}}^2 P_{\text{H}_2}^2$

$$^{64}Cu \rightarrow {}^{64}Zn + \beta^{-}$$

- 37. A radioactive isotope of copper, <sup>64</sup>Cu, decays via the reaction shown above. The half-life for the reaction is 12.8 hours. Starting with 100 g of <sup>64</sup>Cu, how much <sup>64</sup>Zn is produced in 25.6 hours?
  - (A) 12.5 g
    (B) 20.0 g
    (C) 50.0 g
    (D) 75.0 g
  - (E) 100. g
  - (L) 100. g

### GO ON TO THE NEXT PAGE.

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38. For the reaction A → B, with A and B not participating in any other reactions, the rate of formation of B is directly proportional to the molar concentration of A, [A]. Which of the following is the integrated rate equation for this reaction?

$$(A) [A] = kt$$

(B) 
$$\ln \frac{[A]_0}{[A]} = kt$$

(C) 
$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

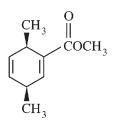
(D) 
$$[A]_0 - [A] = k$$

(E) 
$$\frac{[A]_0}{[A]} = kt$$

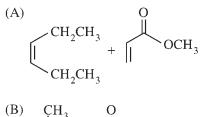
- 39. If the elementary step A → B has a reaction enthalpy of -50 kJ and an activation energy of 10 kJ, the activation energy for the reverse step B → A is
  - (A) 0 kJ
  - (B) 10 kJ
  - (C) 40 kJ
  - (D) 50 kJ
  - (E) 60 kJ
- 40. The reaction of nitrogen dioxide with water yields
  - (A) HNO<sub>3</sub> only
  - (B) HNO<sub>2</sub> only
  - (C) HNO3 and NO
  - (D)  $NH_3$  and  $H_2O_2$
  - (E)  $\rm NH_3$  and  $\rm O_2$

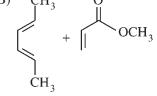
- 41. Which of the following compounds produces  $H_2$  gas when added to water?
  - (A) LiH
  - (B) CH<sub>4</sub>
  - (C)  $NH_3$
  - $(D) \ PH_3$
  - $(E) \ H_2S$
- 42. Which of the following is NOT true about the electrolysis of concentrated aqueous sodium chloride?
  - (A) Sodium metal is a final product.
  - (B)  $H_2$  is produced from  $H_2O$ .
  - (C) One mole of  $H_2$  is produced for each mole of  $Cl_2$  produced.
  - (D) It is a redox reaction.
  - (E) It yields products that are thermodynamically less stable than the reactants.

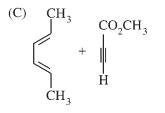
- (A) 0 NH<sub>2</sub> 1. LiAlH<sub>4</sub>, diethyl ether 2. H<sub>2</sub>O **(B)** 1. LiAlH<sub>4</sub>, diethyl ether 2. H<sub>2</sub>O н (C) 0 1.  $LiAlH_4$ , diethyl ether CH<sub>3</sub> 2. H<sub>2</sub>O (D) 0  $CH_3$ 1.  $LiAlH_4$ , diethyl ether 2. H<sub>2</sub>O (E) 0 CH<sub>3</sub> Ш 1.  $LiAlH_4$ , diethyl ether N 2. H<sub>2</sub>O Ĥ
- 43. Which of the following reactions will produce a secondary amine?

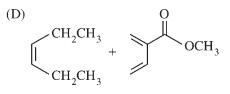


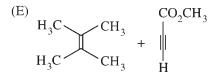
44. The best combination of reactants that will produce the product above via a Diels-Alder reaction is which of the following?

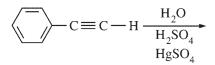




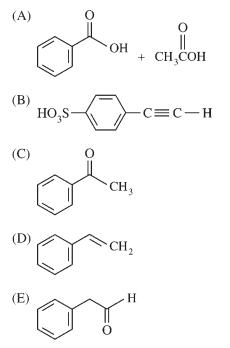








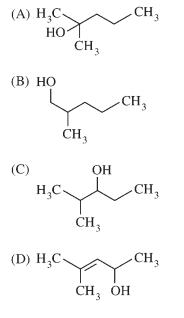
45. Which of the following is the major organic product of the reaction sequence shown above?

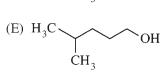


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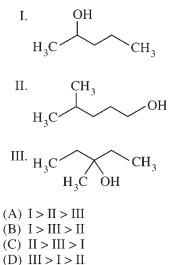
$$H_3C$$
  $CH_3$   $H_3 \bullet THF$   
 $CH_3$   $CH_2O_2$ , NaOH

46. Which of the following is the major organic product of the reaction sequence shown above?





47. Which of the following is the correct order of reactivity, from fastest to slowest, toward acid-catalyzed dehydration?



(E) III > II > I48. Which of the following partial derivatives is zero

(A) 
$$\left(\frac{\partial U}{\partial T}\right)_{V}$$
  
(B)  $\left(\frac{\partial H}{\partial T}\right)_{P}$   
(C)  $\left(\frac{\partial S}{\partial T}\right)_{P}$   
(D)  $\left(\frac{\partial U}{\partial V}\right)_{T}$   
(E)  $\left(\frac{\partial S}{\partial V}\right)_{T}$ 

for an ideal gas?

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- 49. Given that dU = TdS PdV and that H = U + PV, which of the following is true?
  - (A) dH = TdS + VdP
  - (B) dH = SdT VdP
  - (C) dH = -SdT PdV
  - (D) dH = dU + PdV
  - (E) dH = dU TdS

- 50. A reaction is at equilibrium in a closed rigid vessel at constant temperature when
  - (A)  $\Delta S = 0$
  - (B)  $\Delta H = 0$
  - (C)  $\Delta U = 0$
  - (D)  $\Delta G = 0$ (E)  $\Delta A = 0$

$$H \stackrel{CH_3}{\leftarrow} C \stackrel{0}{\leftarrow} C - CH_2 - CH_2 - CH_3 \xrightarrow{Na^{18}OH}_{H_2^{18}O}$$

51. The saponification of the optically active ester using isotopically labeled oxygen as shown above would most likely produce which of the following products?

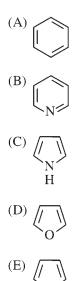
(A) 
$$H = CH_{3}$$
  
 $H = C = OH$   
 $CH_{2}$   
 $CH_{3}$   
(B)  $H = CH_{3}$   
 $H = CH_{3}$   

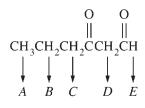
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52. Of the following, which is the strongest base?





- 53. A hydrogen in which position in the structure shown above is most acidic?
  - (A) *A*
  - (B) *B*
  - (C) *C*
  - (D) *D* (E) *E*
- 54. Of the following carboxylic acids, which is the most acidic?

(A) CH<sub>3</sub>CO<sub>2</sub>H

(B) HCO<sub>2</sub>H

$$(C)$$
  $CO_2H$ 

- (D) Cl<sub>3</sub>CCO<sub>2</sub>H
- (E)  $(CH_3)_3CCO_2H$

- 55. Of the following, which is the strongest Brønsted acid in aqueous solution?
  - (A) HClO<sub>3</sub>
  - (B) HClO<sub>2</sub>
  - (C) HOCl
  - (D) HOBr
  - (E) HOI
- 56. HF behaves as a base in which of the following solvents?
  - (A)  $NH_3(l)$
  - (B)  $H_2O(l)$
  - (C)  $CH_3COOH(l)$
  - (D)  $H_2SO_4(l)$
  - (E) Aqueous 0.10 M NaOH
- 57. Of the following materials, which contribute(s) most to the production of acid rain?
  - (A) Uranium hexafluoride
  - (B) Ozone
  - (C) Phosphate detergents
  - (D) Nitric oxide
  - (E) Chlorofluorocarbons

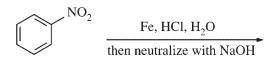
	Bond Enthalpy
Bond	(kJ/mol)
H–H	435
ClCl	243
H–C	414
H–Cl	431
C–Cl	331

- 58. Based on the bond enthalpies listed above, what is the value of  $\Delta H$  for the reaction CH<sub>4</sub> + Cl  $\rightarrow$  CH<sub>3</sub>Cl + H ?
  - (A) 275 kJ
    (B) 109 kJ
    (C) 83 kJ
  - (D) -83 kJ (E) -109 kJ

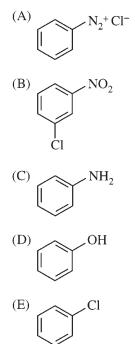
- 59. The quantity  $T\Delta S$  may be expressed in units of
  - (A) J
  - (B) K
  - (C) **J**•K
  - (D)  $J \cdot K^{-1}$
  - (E)  $L \cdot atm \cdot K^{-1}$
- 60. In which of the following processes is energy transferred into the substance by work (w > 0)?
  - (A) Expansion of a gas against the surroundings
  - (B) Expansion of a gas into a vacuum
  - (C) Vaporization of one mole of water at 50°C in an open container
  - (D) Melting of 100 g of ice on a laboratory benchtop
  - (E) Combustion of methane in a constant-volume container
- 61. If helium gas trapped in a cylinder with a movable piston undergoes an adiabatic expansion, which of the following statements is true for the expansion?  $(q = \text{heat}; w = \text{work}; \Delta U = \text{internal energy change})$ 
  - (A) q = w
  - (B) w = 2q
  - (C)  $\Delta U = 0$
  - (D)  $\Delta U = q$
  - (E)  $\Delta U = w$
- 62. One mole of an ideal gas expands isothermally until its volume is doubled. What is the change in Gibbs energy,  $\Delta G$ , for the process?
  - (A)  $R \ln \frac{1}{2}$
  - (B)  $R \ln 2$
  - (C)  $RT \ln \frac{1}{2}$
  - (D)  $RT \ln \frac{2}{2}$
  - (E)  $e^{-2/RT}$

- 63. In chromatography, the van Deemter equation relates the theoretical column-plate height (HETP) to which of the following?
  - I. Mobile-phase flow rate
  - II. Eddy diffusion
  - III. Longitudinal diffusion
  - IV. Mass transfer
  - (A) I only
  - (B) II only
  - $(C) \ \ I \ and \ II \ only$
  - (D) I, II, and III only
  - (E) I, II, III, and IV
- 64. The key components common to both a highperformance liquid and a gas chromatographic system include all of the following EXCEPT a
  - (A) detector
  - (B) mobile or eluent phase
  - (C) stationary phase
  - (D) device for temperature programming
  - (E) sample injector

- 65. The *trans*-2-bromo-1-cyclohexanol product of the reaction shown above is
  - (A) a mixture of equal quantities of diastereomers
  - (B) optically active
  - (C) not optically active, because it is achiral
  - (D) not optically active, because it is a meso form
  - (E) not optically active, because it contains equal quantities of enantiomers

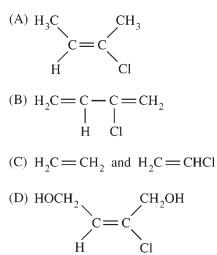


66. What is the major product of the reaction shown above?





67. Which of the following monomers or pair of monomers is used to make the addition polymer neoprene shown above?



(E)  $H_2C = O$  and  $HC \equiv CCl$ 

$$\begin{array}{c} O \\ C_6H_5 \end{array} \xrightarrow{O} OCH_3 \end{array} \xrightarrow{(1) CH_3CH_2MgBr (2 \text{ moles})} \\ \hline (2) H_3O^+ \end{array}$$

68. Which of the following is a product of the reaction shown above?

(A) 
$$C_6H_5$$
 —  $CH_2OH$ 

$$\stackrel{(B)}{\underset{C_{6}H_{5}}{\overset{OH}{\longrightarrow}}} \stackrel{OH}{\underset{CHCH_{2}CH_{3}}{\overset{H}{\longrightarrow}}}$$

(C) OH  

$$C_6H_5$$
—CCH<sub>2</sub>CH<sub>3</sub>  
 $CH_2CH_3$ 

$$\begin{array}{c} \text{(D)} & O \\ & & \parallel \\ & C_6H_5 - \text{COCH}_2CH_3 \end{array}$$

(E) 
$$C_6H_5$$
 — CHCH<sub>2</sub>CH<sub>3</sub>  
 $|$   
CH<sub>2</sub>CH<sub>3</sub>

- 69. Which of the following molecules will exhibit a pure rotational absorption spectrum?
  - I.  $Cl_2$
  - II. HCl
  - III. CH<sub>4</sub>
  - IV. PF<sub>3</sub>
  - (A) II only
  - (B) I and II only
  - (C) I and III only
  - (D) II and IV only
  - (E) I, II, III, and IV

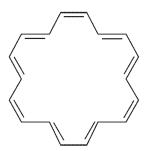
- 70. Which of the following hydrogen molecules has the highest vibrational frequency?
  - (D = deuterium; T = tritium)
  - $(A)~H_2$
  - (B) HD
  - (C)  $D_2$
  - (D) HT
  - $(E) \ T_2$
- 71. When gaseous HBr in the ground electronic state absorbs infrared radiation, which of the following changes in the vibrational quantum number, v, and the rotational quantum number, J, are allowed?
  - (A)  $\Delta v = 0$ ,  $\Delta J = 0$
  - (B)  $\Delta v = 1$ ,  $\Delta J = 0$
  - (C)  $\Delta v = 1$ ,  $\Delta J = \pm 1$
  - (D)  $\Delta v = 1$ ,  $\Delta J = \pm 2$
  - (E)  $\Delta v = 2$ ,  $\Delta J = 0$
- 72. Of the following metal ions, which has the largest magnetic moment in its low-spin octahedral complexes?
  - (A) Fe<sup>3+</sup>
  - (B) Co<sup>3+</sup>
  - (C)  $Co^{2+}$
  - (D)  $Sc^{3+}$
  - (E) Cr<sup>2+</sup>
- 73. A Jahn-Teller distortion of  $[Ti(H_2O)_6]^{3+}$  acts to
  - (A) raise its symmetry
  - (B) remove an electronic degeneracy
  - (C) cause loss of a H<sub>2</sub>O ligand
  - (D) promote a *d*-electron to an antibonding molecular orbital
  - (E) cause reduction of the metal to  $Ti^0$

74. Which of the following represents the correct distribution of electrons in the 3d orbitals of a ground-state  $[CoCl_4]^{2-}$  ion?

(A) 
$$E \begin{bmatrix} t & t & e_g \\ t & t & t & e_g \\ t & t & t & t & t_{2g} \end{bmatrix}$$

(B) 
$$E \begin{bmatrix} 1 & e_g \\ \hline t & t \end{bmatrix} = e_g$$
  
 $e_g = t_g$ 

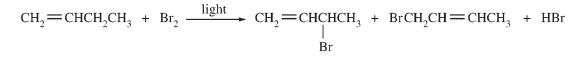
(D) 
$$E \begin{bmatrix} - & - & + & + \\ & - & - & + & + \\ & - & - & + & - & e \end{bmatrix}$$



- 75. What value of n in Huckel's rule applies to the aromatic compound shown above?
  - (A) 3

(A) 5
(B) 4
(C) 5
(D) 9

- (E) 18

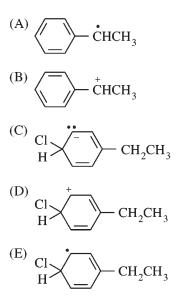


- 76. What kind of reactive intermediate is formed in the reaction shown above?
  - (A) Carbanion
  - (B) Carbocation
  - (C) Bromonium ion
  - (D) Bromide ion
  - (E) Free radical

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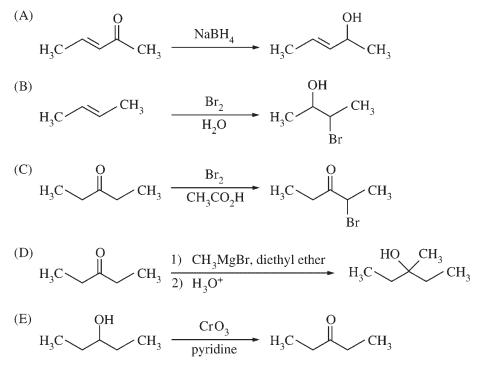
$$\begin{array}{c} & \\ \hline \end{array} \\ - CH_2CH_3 + Cl_2 \end{array} \xrightarrow{FeCl_3} Cl - \begin{array}{c} \\ \hline \end{array} \\ - CH_2CH_3 \end{array}$$

77. Which of the following is a key intermediate in the reaction shown above?



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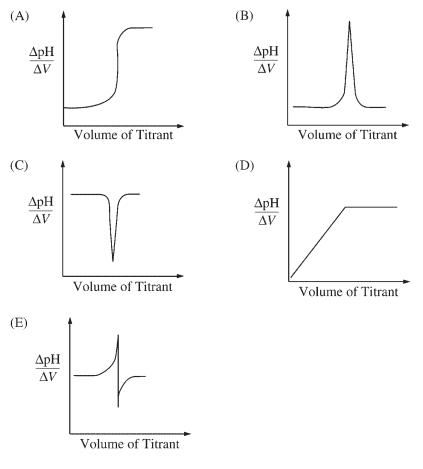
78. In which of the following reactions is an enol an important intermediate?



- 79. Which of the following ligands forms complexes that are examples of linkage isomers?
  - (A) NH<sub>3</sub>
  - (B) NO<sub>2</sub><sup>-</sup>
  - (C) PF<sub>3</sub>
  - (D) H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>
  - (E) SO<sub>4</sub><sup>2-</sup>

- 80. A Ziegler-Natta catalyst for the polymerization of ethylene or propene consists of TiCl<sub>3</sub> and
  - (A) an aluminum alkyl
  - (B) titanium acetylacetonate
  - (C) a gold cluster
  - (D) ferrocene, [Fe( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]
  - (E) an amino acid

81. In plotting data from the potentiometric titration of a strong acid with a strong base, a plot of the change in pH per change in volume of titrant ( $\Delta pH/\Delta V$ ) versus volume of titrant will have which of the following shapes?



- 82. A weak acid, HA, has a  $K_a$  of  $1.00 \times 10^{-5}$ . If 0.100 mole of this acid is dissolved in one liter of water, the percentage of acid dissociated at equilibrium is closest to
  - (A) 0.100%
  - (B) 1.00%
  - (C) 99.0 %
  - (D) 99.9 %
  - (E) 100. %

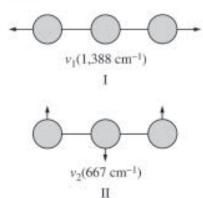
- 83. If 99.1% of a substance dissolved in 25.0 mL of water is extracted into 25.0 mL of organic solvent, then the distribution coefficient for the substance between the organic solvent and the water is
  - (A)  $1.01 \times 10^{-4}$ (B)  $1.10 \times 10^{-2}$ (C) 1.00(D)  $1.10 \times 10^{2}$ (E)  $1.10 \times 10^{4}$

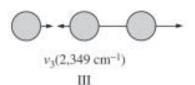
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- 84. Which of the following electronic transitions is forbidden for a hydrogen-like atom?
  - (A)  $2p \rightarrow 3p$ (B)  $2p \rightarrow 1s$ (C)  $2p \rightarrow 3s$ (D)  $2p \rightarrow 4s$
  - (E)  $2p \rightarrow 3d$

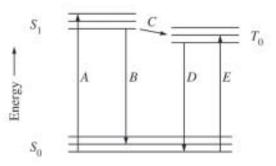
$$E_2 - E_1 = hcR\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

- 85. The Rydberg formula is given above. In the hydrogen atom emission spectrum, the Lyman series results from transitions in which the electron relaxes to the ground state (n = 1) from higher excited states. If the highest-energy transition in the series is 13.6 eV, the lowest transition is
  - (A) 0 eV
  - (B) 3.4 eV
  - (C) 6.8 eV
  - (D) 10.2 eV
  - (E) 13.6 eV





- 86. Of the vibrational normal modes of CO<sub>2</sub> depicted above, which are infrared active?
  - (A) None
  - (B) I and II only
  - (C) I and III only
  - (D) II and III only
  - (E) I, II, and III



- 87. Fluorescence is best represented by which of the processes indicated in the diagram above?
  - (A) A

(B) *B* 

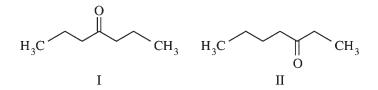
(C) C

(D) D

(E) E

- $\delta$  9.5 ppm, singlet, 1 H  $\delta$  6.5 ppm, quartet, 1 H  $\delta$  2.0 ppm, doublet, 3 H  $\delta$  1.8 ppm, singlet, 3 H
- 88. Which of the structures below is consistent with the <sup>1</sup>H NMR data above?

(A) 
$$CH_2 = CHCH_2CH_2CH$$
  
(B)  $CH_3CH_2CH = CHCH$   
(C)  $O$   $H$   
 $CH_3CH = CHCCH_3$   
(D)  $CH_2 = CHCCH_3$   
(E)  $CH_3CH = CHCH_3$   
(E)  $CH_3CH = CH$   
 $CH_3CH = CHCH$   
 $CHCH = CHCHCH$   
 $CHCH = CH$ 

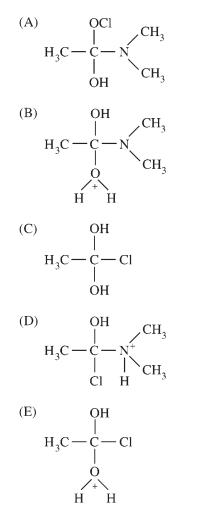


89. The isomeric ketones shown above can be distinguished from each other by the number of signals that they would show in their <sup>13</sup>C NMR spectra. These ketones should show which of the following numbers of signals?

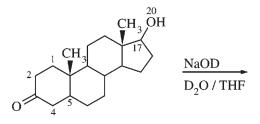
	Ī	II
(A)	3	5
(B)	3	7
(C)	4	7
(D)	4	3
(E)	5	7

$$\begin{array}{c} O \\ \parallel \\ CH_3CN(CH_3)_2 + H_2O + HCI \longrightarrow CH_3COH + (CH_3)_2NH_2CI^{-} \end{array}$$

90. Which of the following structures is an intermediate formed in the amide hydrolysis shown above?



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- 91. When the steroid shown above is treated with NaOD in  $D_2O/THF$ , several hydrogens are readily exchanged. The readily exchangeable hydrogens are on atoms numbered
  - (A) 2 and 20 only
  - (B) 2, 4, and 17 only
  - (C) 2, 4, and 20 only
  - (D) 1, 2, 17, and 20
  - (E) 2, 5, 17, and 20

$$\begin{array}{ccc} & & & & & \\ F_2 & & -187.9 \\ Cl_2 & & -34.0 \\ Br_2 & & +58.8 \\ I_2 & & +184.5 \end{array}$$

- 92. The increase in boiling points shown above is the result of an increase in which of the following from F<sub>2</sub> to I<sub>2</sub>?
  - (A) Ionic bonding
  - (B) Covalent bond strength
  - (C) Electron affinity
  - (D) Van der Waals forces
  - (E) Nuclear quadrupole moment

- 93. Which of the following compounds forms the strongest hydrogen bonds with itself?
  - (A) HF
  - (B) HCCl<sub>3</sub>
  - (C)  $PH_3$
  - $(D) \ H_2S$
  - (E)  $CH_4$
- 94. Of the following, which is the strongest oxidizing agent?
  - (A)  $O_2^+$
  - (B) O<sub>2</sub>
  - (C)  $O_2^-$
  - (D)  $O_2^{2-}$
  - (E) OH-
- 95. Which of the following reactions does NOT represent the formation of a Lewis acid-base adduct?
  - (A) (CH<sub>3</sub>)<sub>3</sub>N + BF<sub>3</sub>  $\rightarrow$  (CH<sub>3</sub>)<sub>3</sub>NBF<sub>3</sub>
  - (B)  $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$
  - (C) H<sub>2</sub>O + H<sup>+</sup>  $\rightarrow$  H<sub>3</sub>O<sup>+</sup>
  - (D)  $SnCl_2 + Cl^- \rightarrow SnCl_3^-$
  - (E)  $PF_3 + F_2 \rightarrow PF_5$

- 96. Although graphite is thermodynamically more stable than diamond at 25°C and 1 atmosphere, a diamond will not transform into graphite, even over a period of thousands of years. Which of the following correctly explains this observation?
  - (A)  $\Delta G$  for the reaction C(*diamond*)  $\rightarrow$  C(*graphite*) is greater than zero.
  - (B)  $\Delta H$  for the reaction C(*diamond*)  $\rightarrow$  C(*graphite*) is greater than zero.
  - (C)  $\Delta S$  for the reaction C(*diamond*)  $\rightarrow$  C(*graphite*) is less than zero.
  - (D) The reverse reaction  $C(graphite) \rightarrow C(diamond)$ would proceed relatively quickly.
  - (E) The reaction  $C(diamond) \rightarrow C(graphite)$  is not observed because it has a large activation energy.
- 97. Which of the following statements is generally true concerning the relationship between the rate constant, k, the Arrhenius activation energy,  $E_a$ , and the temperature?
  - (A) A plot of  $\ln k vs. T$  is a straight line with slope  $E_a/R$
  - (B) A plot of  $\ln k vs$ .  $\ln T$  is a straight line with slope  $E_a/R$
  - (C) A plot of  $\ln k$  vs.  $\ln T$  is a straight line with slope  $-E_a/R$
  - (D) A plot of  $\ln k vs. 1/T$  is a straight line with slope  $-E_a/R$
  - (E) A plot of  $\ln k \ vs. \ 1/T$  is a straight line with slope  $E_a/R$

$$A + M \stackrel{k_1}{\longleftrightarrow} A^* + M$$
$$A^* \stackrel{k_2}{\longrightarrow} P$$

98. Based on the Lindemann mechanism shown above and the steady-state approximation for the intermediate A\*, the rate of formation of product P is given by

(A) 
$$\frac{d[P]}{dt} = \frac{k_1 k_2 [A][M]}{(k_{-1}[M] + k_2)}$$

(B) 
$$\frac{d[P]}{dt} = \frac{k_1[A][M]}{(k_{-1}[M] + k_1)}$$

(C) 
$$\frac{d[P]}{dt} = \frac{-k_1k_2[A][M]}{k_{-1}[M]}$$

(D) 
$$\frac{d[\mathbf{P}]}{dt} = \frac{k_1 k_2 [\mathbf{A}]}{[\mathbf{M}]}$$

(E) 
$$\frac{d[\mathbf{P}]}{dt} = k_1[\mathbf{A}][\mathbf{M}]$$

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$$2 CH_3 CH_2 CH \xrightarrow{NaOH} CH_3 CH_2 CHCHCHCH$$

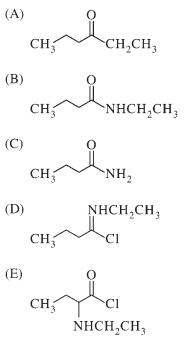
99. Which of the following species is an intermediate in the reaction shown above?

(A) 
$$O$$
  
 $\dot{C}H_2CH_2CH$   
(B)  $O$   
 $\bar{C}H_2CH_2CH$   
(C)  $O$   
 $CH_3CHCH$   
(D)  $O$   
 $CH_3CHCH$   
(E)  $CH_3CH_2C$ =0

~

$$CH_3 \xrightarrow{O} + CH_3CH_2NH_2 \xrightarrow{O}$$

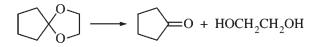
100. What is the major product of the reaction shown above?



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- 101. The conversion above can be accomplished with which of the following reagents?
  - (A) LiAlH<sub>4</sub>
  - (B) HCl,  $H_2O$ , heat
  - (C)  $H_2NNH_2$ , heat
  - (D) NaOH, H<sub>2</sub>O, heat
  - (E) H<sub>2</sub>, Pt catalyst

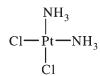
 $CH_3CH_2CH_2CH = NCH_3$ 

102. Of the following, which reacts with methylamine  $(CH_3NH_2)$  to form the imine shown above?

(A) O  $CH_3CH_2CH_2CH$ (B) O  $CH_3CH_2CH_2COH$ (C) O  $CH_3CH_2CH_2COCH_3$ (D) O  $CH_3CH_2CH_2CNH_2$ (E)  $CH_3CH_2CH_2C \equiv N$ 

- 103. Which of the following is the best method for preparing (CH<sub>3</sub>)<sub>3</sub>COCH<sub>3</sub> ?
  - (A) NaOCH<sub>3</sub> + (CH<sub>3</sub>)<sub>3</sub>CCl  $\rightarrow$
  - (B)  $(CH_3)_3COH + CH_3I \xrightarrow{H_2SO_4}$
  - (C)  $(CH_3)_3CH + CH_3OH \xrightarrow{H_2SO_4}$

(E)  $(CH_3)_3COK + CH_3I$ 



- 104. The systematic name of the compound shown above is
  - (A) platinum *cis*-ammoniumchloride
  - (B) cis-diammoniaplatinumdichloride
  - (C) cis-diamminedichloroplatinum(II)
  - (D) cis-dichlorodiammineplatinum(IV)
  - (E) platinum cis-dichloride cis-diammonia

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- 105. Which of the following complexes exists as a pair of enantiomers?
  - (A) trans-[Co(H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>
  - (B)  $[Co(NH_3)_4Cl_2]^+$
  - (C)  $[Co{P(C_2H_5)_3}_2ClBr]$
  - (D)  $[Pt{P(C_2H_5)_3}_2Cl_2]$
  - (E)  $[Cr(H_2NCH_2CH_2NH_2)_3]^{3+}$
- 106. Which of the following is true for the element xenon?
  - (A) It does not form chemical compounds.
  - (B) It exists as the diatomic molecule  $Xe_2$ .
  - (C) It has a lower first ionization energy than Na.
  - (D) It has an extensive organometallic chemistry.
  - (E) It forms compounds with some electronegative elements.
- 107. Boron-rich deposits on Earth appear to have formed by precipitation from an aqueous solution. In what form does boron exist in the deposits?
  - (A) Its elemental form
  - (B) A sulfide
  - (C) An oxide or hydroxide
  - (D) Diborane
  - (E) Boron nitride
- 108. According to the second law of thermodynamics, which of the following quantities represents the change in a state function?
  - (A)  $q_{rev}$
  - (B)  $q_{rev}/T$
  - (C)  $Tq_{rev}$
  - (D)  $w_{rev}$
  - (E) Tw<sub>rev</sub>
- 109. The function  $F(x) = c \sin(ax)$  is an eigenfunction of  $d^2/dx^2$ . The eigenvalue is
  - (A) *c*
  - (B) *a*
  - (C) -1
  - (D)  $a^2c$
  - (E)  $-a^2$

- 110. In quantum mechanics, the measurements of two different physical properties are represented by the operators  $\hat{A}$  and  $\hat{B}$ . It is possible to know, exactly and simultaneously, the values for both of these measured quantities only if the
  - (A) eigenfunctions of operator  $\hat{A}$  form an orthonormal set and the eigenfunctions of operator  $\hat{B}$  form an orthonormal set
  - (B) eigenfunctions for both operators  $\hat{A}$  and  $\hat{B}$  can be normalized
  - (C) eigenvalues for both operators  $\hat{A}$  and  $\hat{B}$  are real numbers
  - (D) operators  $\hat{A}$  and  $\hat{B}$  are both Hermitian
  - (E) operators  $\hat{A}$  and  $\hat{B}$  commute

$$E_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

- 111. The energy levels of a particle in a cubic box are given by the expression above, in which  $n_x$ ,  $n_y$ ,  $n_z = 1, 2, ...$  The degeneracy of the  $E = 14 h^2/8ma^2$  level is
  - (A) 2
  - (B) 3
  - (C) 4
  - (D) 5
  - (E) 6
- 112. Which of the following processes could be the termination step in a chain reaction?
  - $\begin{array}{rl} (A) \ C_2H_6 \rightarrow 2 \ CH_3 \cdot \\ (B) \ C_2H_6 + H \cdot \rightarrow H_2 + C_2H_5 \cdot \\ (C) \ C_2H_6 + CH_3 \cdot \rightarrow CH_4 + C_2H_5 \cdot \end{array}$
  - (D)  $CH_3 \cdot + CH_3 \cdot \rightarrow C_2H_6$
  - (E)  $C_2H_5 \cdot \rightarrow C_2H_4 + H \cdot$

### GO ON TO THE NEXT PAGE.

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- 113. The half-life of <sup>14</sup>C is 5,730 years. The <sup>14</sup>C activity of living material is approximately 920 decays/hr per gram of carbon. A fragment of wool fabric from an archaeological site has an activity of 680 decays/hr per gram of carbon. The approximate date of the sample is
  - (A) A.D. 1950
    (B) 500 B.C.
    (C) 3700 B.C.
  - (D) 5700 B.C.
  - (E) 10,000 B.C.

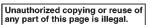
 $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad K_a = 5.0 \times 10^{-8}$ 

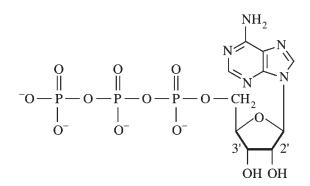
- 114. Given the information shown above, how many millimoles of  $K_2HPO_4$  must be added to 100. mL of a 0.100 *M* KH<sub>2</sub>PO<sub>4</sub> solution to obtain a solution with a pH of 7.0 ?
  - $(A) \quad 1.0 \text{ mmol}$
  - $\begin{array}{c} (B) \quad 5.0 \text{ mmol} \\ (C) \quad 10 \text{ mmol} \end{array}$
  - (C) 10. mmol (D) 20. mmol
  - (E) 25. mmol
    - $\begin{array}{rll} \mathrm{Hg}^{2+} + 2\mathrm{e}^{-} \rightarrow \mathrm{Hg} & E^{\circ} = 0.85 \mathrm{~V} \\ \mathrm{Zn}^{2+} + 2\mathrm{e}^{-} \rightarrow \mathrm{Zn} & E^{\circ} = -0.76 \mathrm{~V} \end{array}$
- 115. Given the cell potentials shown above, the equilibrium constant at 298 K for the reaction

 $Zn + Hg^{2+} \rightleftharpoons Zn^{2+} + Hg$ 

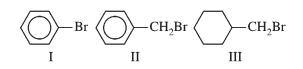
is closest to which of the following?

- (A)  $2.5 \times 10^{54}$
- (B) 54
- (C) 1.6
- (D)  $1.8 \times 10^{-2}$
- (E)  $4.1 \times 10^{-55}$
- 116. Which of the following isomers of  $C_6H_{12}$  has the highest heat of combustion?
  - (A) Cyclohexane
  - (B) Methylcyclopentane
  - (C) trans-1,2-dimethylcyclobutane
  - (D) Ethylcyclobutane
  - (E) 1,1,2-trimethylcyclopropane





- 117. Energy is released when adenosine triphosphate (ATP), shown above, undergoes an enzyme-catalyzed reaction involving
  - (A) conversion of ATP to adenosine diphosphate(ADP) by hydrolysis of the terminalP—O—P linkage
  - (B) conversion of C-2' from CHOH to  $CH_2$  by reduction in the presence of the coenzyme NADH
  - (C) conversion of C-3' from CHOH to C=O by oxidation in the presence of the coenzyme NAD<sup>+</sup>
  - (D) dehydration by loss of a proton at C-2' and of the hydroxyl group at C-3'
  - (E) inversion of configuration at C-3'

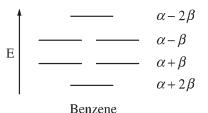


- 118. Which of the following correctly indicates the order of reactivity of the halides above with sodium iodide in acetone?

- 119. Of the following experimental observations, which best demonstrates the wavelike character of electrons?
  - (A) The photoelectric effect
  - (B) The ionization of an atom
  - (C) The flow of electrons in a metal wire
  - (D) The deflection of an electron beam by electrical plates
  - (E) The diffraction pattern of electrons scattered from a crystalline solid
- 120. Light of frequency v is found to eject electrons of velocity  $v_e$  from a clean potassium surface in vacuum. Which of the following is true concerning this phenomenon?
  - (A) The frequency v is most likely in the infrared region.
  - (B) This phenomenon is best explained theoretically by using the wave model of light.
  - (C) The minimum energy required to remove an electron from the metal is

$$hv - \frac{1}{2}mv_e^2$$

- (D) Light of frequency 2v will eject electrons of velocity  $2v_e$ .
- (E) A more intense light source of frequency vwill eject electrons with a velocity greater than  $v_{e}$ .
- 121. A system consists of N particles and behaves according to Boltzmann statistics. At temperature T, the number of particles that are found in a state having energy  $\varepsilon$  and a degeneracy g is directly proportional to
  - (A)  $g\varepsilon$
  - (B)  $\varepsilon/kT$
  - (C)  $g\varepsilon/kT$
  - (D)  $ge^{-\mathcal{E}/kT}$
  - (E)  $ge^{\mathcal{E}/kT}$

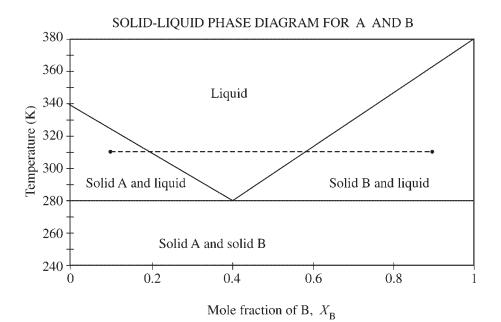


- 122. Shown above is the energy-level diagram for the  $\pi$  orbitals of benzene, calculated on the basis of Hückel molecular orbital theory. According to this theory, the total energy of the six  $\pi$  electrons of ground-state benzene is given by
  - (A)  $6\alpha + 8\beta$ (B)  $4\alpha + 6\beta$
  - (C)  $4\alpha + 4\beta$
  - (D)  $2\alpha + 3\beta$
  - (E)  $\alpha + 2\beta$

 $2 \operatorname{CN}^{-}(aq) + \operatorname{Ag}^{+}(aq) \rightleftharpoons \operatorname{Ag}(\operatorname{CN})_{2}^{-}(aq)$ 

- 123. Cyanide ion may be determined by a complexometric titration with silver nitrate that uses a color indicator to detect the endpoint. If 20.00 mL of a 0.100 *M* solution of silver nitrate is required to titrate a 5.00 mL aliquot of a  $CN^{-}$  solution, the concentration of the original  $CN^{-}$  solution is
  - (A) 0.100 M
    (B) 0.200 M
    (C) 0.400 M
    (D) 0.800 M
  - (E) 1.60 M
- 124. Which of the following statements is NOT true regarding glass-membrane pH electrodes?
  - (A) The electrodes are subject to both alkaline and acid errors.
  - (B) The electrodes are selective but not specific for measuring the activity of the hydrogen ion.
  - (C) The Nernst equation can usually be used to relate the activity of the hydrogen ion to the measured EMF in solution.
  - (D) The selectivity of glass-membrane electrodes is a function of their chemical composition.
  - (E) Hydrogen ions must migrate through the glass membrane to produce an EMF.

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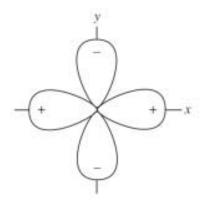
125. The phase diagram above shows the composition of mixtures of compounds A and B at different temperatures. A mixture at 310 K originally has  $X_{\rm B} = 0.10$ . Pure B is added to the mixture until  $X_{\rm B} = 0.90$ . A constant temperature is maintained throughout the process. Based on this information, which of the following is NOT true?

- (A) As B is initially added, it melts into the liquid phase.
- (B) When  $X_{\rm B} = 0.10$ , about half of the A is in the solid phase and half is in the liquid mixture.
- (C) When  $X_{\rm B} = 0.40$ , no solid exists.
- (D) When  $X_{\rm B} > 0.55$ , the liquid solution is nearly all A.
- (E) When  $X_{\rm B} = 0.90$ , most of the B is in the pure solid state.

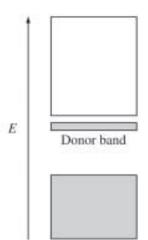
- 126. When a 0.001 M aqueous solution of each of the following compounds is prepared, which solution will have the greatest electrical conductivity?
  - (A) CH3COOH
  - (B) CH<sub>3</sub>OH
  - (C) NH3
  - (D) SO<sub>2</sub>
  - (E) HCl

$$H_2(g) + Cl_2(g) \xrightarrow{hv} 2 HCl(g)$$

- 127. The yield of HCl from the photochemical reaction shown above is found to be 3.0 × 10<sup>-3</sup> mol when 7.5 × 10<sup>16</sup> photons are absorbed. Which of the following statements explains this observation?
  - (A) The process requires multiphoton absorption.
  - (B) The process violates the Franck-Condon principle.
  - (C) The fluorescence quantum yield is 1.00.
  - (D) The reaction is an oscillating reaction.
  - (E) The reaction is a chain reaction.
- 128. According to molecular-orbital theory, which of the following species has the highest bond order?
  - (A) NO2-
  - (B) NO-
  - (C) NO
  - (D) NO<sup>+</sup>
  - (E) NO2+
- 129. According to the 18-electron rule, which of the following is NOT a correct formula for a stable metal carbonyl? (Atomic numbers: V = 23, Mn = 25, Fe = 26, Co = 27, Ni = 28)
  - (A) [V(CO)6]-
  - (B) [Mn(CO)<sub>5</sub>]-
  - (C) [Fe(CO)<sub>4</sub>]2-
  - (D) [Co(CO)<sub>4</sub>]<sup>+</sup>
  - (E) [Ni(CO)<sub>4</sub>]

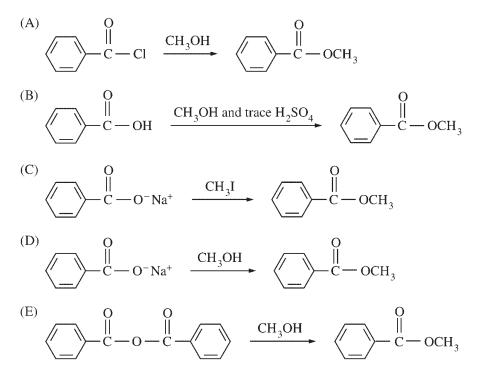


- 130. What type of orbital is shown above?
  - (A)  $3 p_x$ (B)  $3 p_y$ (C)  $3 d_{xy}$ (D)  $3 d_{x^2-y^2}$
  - (E) 3 d 2

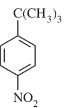


- 131. Which type of semiconductor is represented by the band structure shown above?
  - (A) An intrinsic semiconductor as in pure Si
  - (B) An n-type semiconductor as in Ga-doped Si
  - (C) An n-type semiconductor as in P-doped Si
  - (D) A p-type semiconductor as in Ga-doped Si
  - (E) A p-type semiconductor as in P-doped Si

132. Which of the following reactions would NOT be an acceptable method for the preparation of methyl benzoate?



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133. Of the following, which is the best synthesis of the compound shown above?

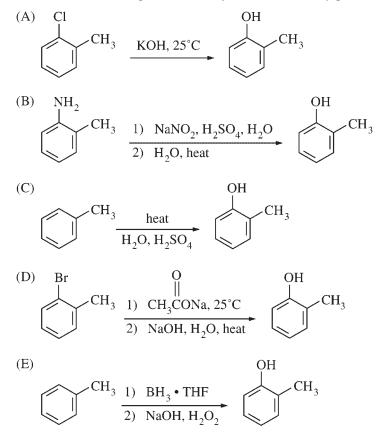
$$(CH_3)_2C = CH_2 \qquad HNO_3 \\ H_2SO_4 \qquad H_2SO_4$$

(E) Cl  

$$(CH_3)_3CH$$
  $HNO_3$   
 $H_2SO_4$ 

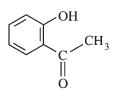
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134. Which of the following is a suitable synthesis of *o*-methylphenol?



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- 135. What is the primary advantage of a hollow-cathode lamp used in atomic absorption spectroscopy?
  - (A) It has high intensity.
  - (B) It emits a complete ultraviolet spectrum.
  - (C) It has a narrow line width.
  - (D) It allows direct application to nonmetal analysis.
  - (E) It eliminates the need for an ionization suppressor.



- 136. What infrared absorptions are most affected by intramolecular hydrogen bonding in the compound shown above?
  - (A) Methyl group C—H stretching
  - (B) Hydroxyl group O—H stretching

  - (C) Aromatic ring C—H bending(D) Aromatic ring C—H stretching
  - (E) Aromatic ring C-C stretching

If you finish before time is called, you may check your work on this test.

NOTE: To ensure prompt processing of test results, it is important that you fill in the blanks <u>exactly</u> as directed. SUBJECT TEST

A. Print and sign your full name in this box:	your full name PRINT:	(FIRST) (MIDDLE)	
your answer she fill in the corres	et. Then sponding	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Copy the Test Name and Form Code in box 7 on your answer sheet TEST NAME Chemistry FORM CODE GROO27

### GRADUATE RECORD EXAMINATIONS SUBJECT TEST

B. The Subject Tests are intended to measure your achievement in a specialized field of study. Most of the questions are concerned with subject matter that is probably familiar to you, but some of the questions may refer to areas that you have not studied.

Your score will be determined by subtracting one-fourth the number of incorrect answers from the number of correct answers. Questions for which you mark no answer or more than one answer are not counted in scoring. If you have some knowledge of a question and are able to rule out one or more of the answer choices as incorrect, your chances of selecting the correct answer are improved, and answering such questions will likely improve your score. It is unlikely that pure guessing will raise your score; it may lower your score.

You are advised to use your time effectively and to work as rapidly as you can without losing accuracy. Do not spend too much time on questions that are too difficult for you. Go on to the other questions and come back to the difficult ones later if you can.

YOU MUST INDICATE ALL YOUR ANSWERS ON THE SEPARATE ANSWER SHEET. No credit will be given for anything written in this examination book, but you may write in the book as much as you wish to work out your answers. After you have decided on your response to a question, fill in the corresponding oval on the answer sheet. BE SURE THAT EACH MARK IS DARK AND COMPLETELY FILLS THE OVAL. Mark <u>only one</u> answer to each question. No credit will be given for multiple answers. Erase all stray marks. If you change an answer, be sure that all previous marks are erased completely. Incomplete erasures may be read as intended answers. Do not be concerned that the answer sheet provides spaces for more answers than there are questions in the test.

Example:	Sample Answer	
What city is the capital of France?	$\mathbb{A} \bullet \mathbb{C} \oplus \mathbb{E}$	CORRECT ANSWER
(A) Rome		
(B) Paris	AVCDE	
(C) London		IMPROPER MARKS
(D) Cairo (E) Oslo		

#### DO NOT OPEN YOUR TEST BOOK UNTIL YOU ARE TOLD TO DO SO.



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Ι

### Scoring Your Subject Test

Chemistry Test scores typically range from 490 to 910. The range for different editions of a given test may vary because different editions are not of precisely the same difficulty. The differences in ranges among different editions of a given test, however, usually are small. This should be taken into account, especially when comparing two very high scores. The score conversion table on page 53 shows the score range for this edition of the test only.

The worksheet on page 52 lists the correct answers to the questions. Columns are provided for you to mark whether you chose the correct (C) answer or an incorrect (I) answer to each question. Draw a line across any question you omitted, because it is not counted in the scoring. At the bottom of the page, enter the total number correct and the total number incorrect. Divide the total incorrect by 4 and subtract the resulting number from the total correct. This is the adjustment made for guessing. Then round the result to the nearest whole number. This will give you your raw total score. Use the total score conversion table to find the scaled total score that corresponds to your raw total score.

Example: Suppose you chose the correct answers to 80 questions and incorrect answers to 46. Dividing 46 by 4 yields 11.5. Subtracting 11.5 from 80 equals 68.5, which is rounded to 69. The raw score of 69 corresponds to a scaled score of 690.



### Worksheet for the Chemistry Test, Form GR0027 Only Answer Key and Percentages\* of Examinees Answering Each Question Correctly

QUES Number	TION Answer	P+	TO C	TAL I	N	QUES	TION Answer	P +	TOT C	TAL I	QUE Number	STION Answer	P+	T01 C	TAL I
1 2 3 4 5	** B E D A	** 80 55 95 86				51 52 53 54 55	A B D D A	53 52 83 56 70			101 102 103 104 105	B A E C E	56 59 48 60 33	-	
6 7 8 9 10	C B C D	58 53 57 84 85				56 57 58 59 60	D D C A D	75 77 47 74 18			106 107 108 109 110	E C B E E	76 48 55 47 33		
11 12 13 14 15	E C B E	47 56 75 81 63				61 62 63 64 65	E C D E	68 34 15 64 53			111 112 113 114 115	E D B A	36 94 50 30 19		
16 17 18 19 20	B B C A	63 82 63 52 72				66 67 68 69 70	C B C D A	41 47 70 22 50			116 117 118 119 120	E A C E C	48 77 41 69 56		
21 22 23 24 25	C E B B B	53 63 68 56 66				71 72 73 74 75	C E C B	44 33 42 47 58			121 122 123 124 125	D A D E D	57 58 39 31 26		
26 27 28 29 30	D A E B	63 52 49 75 57				76 77 78 79 80	E D C B A	82 62 53 15 24			126 127 128 129 130	E D D D	78 35 40 46 57		
31 32 33 34 35	A A D E E	67 90 68 63 73				81 82 83 84 85	B D A D	61 45 39 33 27			131 132 133 134 135	C D A B C	30 53 60 42 35		
36 37 38 39 40	D D B E C	73 81 57 77 30				86 87 88 89 90	D B C B	51 54 77 79 63			136	В	85		
41 42 43 44 45	A E C C	81 30 57 67 41				91 92 93 94 95	C D A E	69 63 68 70 55							
46 47 48 49 50	C D D A E	66 80 38 70 12				96 97 98 99 100	E D A D B	62 68 33 60 79							

Correct (C)

Incorrect (I)

Total Score:

**C** – I/4 = \_

Scaled Score (SS) = \_

\* The P+ column indicates the percent of CHEMISTRY Test examinees who answered each question correctly; it is based on a sample of November 2000 examinees selected to represent all CHEMISTRY Test examinees tested between October 1, 1998 and September 30, 2001. \*\* Item 1 was not scored when this form of the test was originally administered.

### CHEMISTRY TEST **PRACTICE BOOK**