



2003 U. S. NATIONAL CHEMISTRY OLYMPIAD

NATIONAL EXAM—PART I



Prepared by the American Chemical Society Olympiad Examinations Task Force

OLYMPIAD EXAMINATIONS TASK FORCE

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DIRECTIONS TO THE EXAMINER—PART I

Part I of this test is designed to be taken with a Scantron® answer sheet on which the student records his or her responses. Only this Scantron sheet is graded for a score on **Part I**. Testing materials, scratch paper, and the Scantron sheet should be made available to the student *only* during the examination period. All testing materials including scratch paper should be turned in and kept secure until April 27, 2003, after which tests can be returned to students and their teachers for further study.

Allow time for the student to read the directions, ask questions, and fill in the requested information on the Scantron sheet. The answer sheet must be completed using a pencil, not pen. When the student has completed **Part I**, or after **one hour and thirty minutes** has elapsed, the student must turn in the Scantron sheet, **Part I** of the testing materials, and all scratch paper.

There are three parts to the National Olympiad Examination. You have the option of administering the three parts in any order, and you are free to schedule rest-breaks between parts.

Part I	60 questions	single-answer multiple-choice	1 hour, 30 minutes
Part II	8 questions	problem-solving, explanations	1 hour, 45 minutes
Part III	2 lab problems	laboratory practical	1 hour, 30 minutes

A periodic table and other useful information are provided on page 2 for student reference. Students should be permitted to use non-programmable calculators.

DIRECTIONS TO THE EXAMINEE—PART I

DO NOT TURN THE PAGE UNTIL DIRECTED TO DO SO. Answers to questions in **Part I** must be entered on a Scantron answer sheet to be scored. Be sure to write your name on the answer sheet; an ID number is already entered for you. **Make a record of this ID number because you will use the same number on both Parts II and III.** Each item in **Part I** consists of a question or an incomplete statement that is followed by four possible choices. Select the single choice that best answers the question or completes the statement. Then use a pencil to blacken the space on your answer sheet next to the same letter as your choice. You may write on the examination, but the test booklet will not be used for grading. Scores are based on the number of correct responses. When you complete **Part I** (or at the end of one hour and 30 minutes), you *must* turn in all testing materials, scratch paper, and your Scantron answer sheet. Do not forget to turn in your U.S. citizenship statement before leaving the testing site today.

Not valid for use as an USNCO National Exam after April 27, 2003.

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ABBREVIATIONS AND SYMBOLS			
amount of substance	<i>n</i>	Faraday constant	<i>F</i>
ampere	A	formula molar mass	<i>M</i>
atmosphere	atm	free energy	<i>G</i>
atomic mass unit	u	frequency	<i>v</i>
atomic molar mass	A	gas constant	<i>R</i>
Avogadro constant	<i>N_A</i>	gram	g
Celsius temperature	°C	heat capacity	<i>C_p</i>
centi- prefix	c	hour	h
coulomb	C	joule	J
electromotive force	<i>E</i>	kelvin	K
energy of activation	<i>E_a</i>	kilo- prefix	k
enthalpy	<i>H</i>	liter	L
entropy	<i>S</i>	measure of pressure mmHg	
equilibrium constant	<i>K</i>	milli- prefix	m
		molal	<i>m</i>
		molar	M
		molar mass	<i>M</i>
		mole	mol
		Planck's constant	<i>h</i>
		pressure	<i>P</i>
		rate constant	<i>k</i>
		retention factor	<i>R_f</i>
		second	s
		speed of light	<i>c</i>
		temperature, K	<i>T</i>
		time	<i>t</i>
		volt	V

CONSTANTS
$R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$R = 0.0821 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$1 F = 96,500 \text{ C}\cdot\text{mol}^{-1}$
$1 F = 96,500 \text{ J}\cdot\text{V}^{-1}\cdot\text{mol}^{-1}$
$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$
$c = 2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}$
$0^\circ\text{C} = 273.15 \text{ K}$

EQUATIONS		
$E = E^\circ - \frac{RT}{nF} \ln Q$	$\ln K = \left(\frac{-\Delta H}{R} \right) \left(\frac{1}{T} \right) + c$	$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

PERIODIC TABLE OF THE ELEMENTS

1											18																																	
1A											8A																																	
1 H 1.008											2 He 4.003																																	
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18																											
11 Na 22.99	12 Mg 24.31	3 B	4 C	5 N	6 O	7 F	8 Ne	9 Na	10 Mg	11 Al 26.98	12 Si 28.09	13 P 30.97	14 S 32.07	15 Cl 35.45	16 Ar 39.95																													
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80																											
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3																											
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)																											
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)	114 (???)																																
<table border="1" style="width: 100%; text-align: center;"> <tbody> <tr> <td>58 Ce 140.1</td> <td>59 Pr 140.9</td> <td>60 Nd 144.2</td> <td>61 Pm (145)</td> <td>62 Sm 150.4</td> <td>63 Eu 152.0</td> <td>64 Gd 157.3</td> <td>65 Tb 158.9</td> <td>66 Dy 162.5</td> <td>67 Ho 164.9</td> <td>68 Er 167.3</td> <td>69 Tm 168.9</td> <td>70 Yb 173.0</td> <td>71 Lu 175.0</td> </tr> <tr> <td>90 Th 232.0</td> <td>91 Pa 231.0</td> <td>92 U 238.0</td> <td>93 Np (237)</td> <td>94 Pu (244)</td> <td>95 Am (243)</td> <td>96 Cm (247)</td> <td>97 Bk (247)</td> <td>98 Cf (251)</td> <td>99 Es (252)</td> <td>100 Fm (257)</td> <td>101 Md (258)</td> <td>102 No (259)</td> <td>103 Lr (262)</td> </tr> </tbody> </table>																	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)
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11. Which change increases the solubility of a gas in water?
- | |
|-------------------------------------|
| 1. an increase in water temperature |
| 2. a decrease in gas pressure |

- (A) 1 only (B) 2 only
(C) both 1 and 2 (D) neither 1 nor 2

12. Benzene melts at 5.50 °C and has a freezing point depression constant of 5.10 °C·m⁻¹. Calculate the freezing point of a solution that contains 0.0500 mole of acetic acid, CH₃COOH, in 125 g of benzene if acetic acid forms a dimer in this solvent.

- (A) 3.46 °C (B) 4.48 °C
(C) 5.24 °C (D) 6.01 °C

13. A 200. mL sample of a gaseous hydrocarbon has a density of 2.53 g·L⁻¹ at 55 °C and 720 mmHg. What is its formula?

- (A) C₂H₆ (B) C₄H₁₀ (C) C₅H₁₂ (D) C₆H₆

14. A liquid has a vapor pressure of 40 mmHg at 19.0 °C and a normal boiling point of 78.3 °C. What is its enthalpy of vaporization in kJ·mol⁻¹?

- (A) 42.4 (B) 18.4 (C) 5.10 (D) 1.45

15. Sulfur and fluorine form SF₆ and S₂F₁₀, both of which are gases at 30 °C. When an equimolar mixture of them is allowed to effuse through a pinhole, what is the ratio SF₆/S₂F₁₀ in the first sample that escapes?

Molar Mass g·mol ⁻¹	
SF ₆	146
S ₂ F ₁₀	254

- (A) 1.32/1 (B) 1.74/1 (C) 3.03/1 (D) 3.48/1

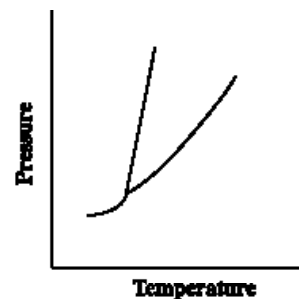
16. The volumes of real gases often exceed those calculated by the ideal gas equation. These deviations are best attributed to the

- (A) attractive forces between the molecules in real gases.
(B) dissociation of the molecules in real gases.
(C) kinetic energy of the molecules in real gases.
(D) volumes of the molecules in real gases.

17. The electrical conductivity of a solid is slight at 25 °C and much greater at 125 °C. The solid is most likely a(n)

- (A) ionic compound (B) insulator
(C) metal (D) semiconductor

18. According to the phase diagram, what would be the effect of increasing the pressure on this substance?



- (A) decrease both the melting and boiling points
(B) increase both the melting and boiling points
(C) increase the melting point and decrease the boiling point
(D) decrease the melting point and increase the boiling point

19. When the substances below are arranged in order of increasing entropy values, S°, at 25 °C which is the correct order?

- (A) CO₂(s) < CO₂(aq) < CO₂(g)
(B) CO₂(g) < CO₂(aq) < CO₂(s)
(C) CO₂(s) < CO₂(g) < CO₂(aq)
(D) CO₂(g) < CO₂(s) < CO₂(aq)

20. When 50. mL of 0.10 M HCl is mixed with 50. mL of 0.10 M NaOH the temperature of the solution increases by 3.0 °C. Calculate the ΔH_{neutralization} per mole of HCl. (The solution has a density = 1.0 g·mL⁻¹ and C_p = 4.2 J·g⁻¹·°C⁻¹)

- (A) 1.3 × 10³ kJ (B) -1.3 × 10² kJ
(C) -2.5 × 10² kJ (D) -1.3 × 10³ kJ

21. The combustion of 0.200 mol of liquid carbon disulfide, CS₂, to give CO₂(g) and SO₂(g) releases 215 kJ of heat. What is ΔH_f° for CS₂(l) in kJ·mol⁻¹?

ΔH _f °	kJ·mol ⁻¹
CO ₂ (g)	-393.5
SO ₂ (g)	-296.8

- (A) 385 (B) 87.9 (C) -385 (D) -475

22. For the reaction: 2NO₂(g) ⇌ N₂O₄(g) ΔH < 0. What predictions can be made about the sign of ΔS and the temperature conditions under which the reaction would be spontaneous?

- | ΔS _{rxn} | Temperature Condition |
|-------------------|-----------------------|
| (A) negative | low temperatures |
| (B) negative | high temperatures |
| (C) positive | high temperatures |

23. As ΔG° for a reaction changes from a large negative value to a large positive value, K for the reaction will change from
- (A) a large positive value to a large negative value.
 (B) a large positive value to a small positive value.
 (C) a large negative value to a large positive value.
 (D) a large negative value to a small negative value.
24. ΔE° is measured at constant volume and ΔH° is measured at constant pressure. For the reaction;
 $2C(s) + O_2(g) \rightarrow 2CO(g) \quad \Delta H^\circ < 0 \text{ kJ}$
 How do the ΔE° and ΔH° compare for this reaction?
- (A) $\Delta E^\circ < \Delta H^\circ$ (B) $\Delta E^\circ > \Delta H^\circ$
 (C) $\Delta E^\circ = \Delta H^\circ$ (D) Impossible to tell from this information.
25. Which statement about second order reactions is correct?
- (A) Second order reactions require different reactants.
 (B) Second order reactions are faster than first order reactions.
 (C) Second order reactions are unaffected by changes in temperature.
 (D) The half-life of a second order reaction depends on the initial reactant concentration.
26. A first order reaction has a rate constant of 0.0541 s^{-1} at 25°C . What is the half-life for this reaction?
- (A) 18.5 s (B) 12.8 s
 (C) 0.0781 s (D) 0.0375 s
27. The reaction between NO and I_2 is second-order in NO and first-order in I_2 . What change occurs in the rate of the reaction if the concentration of each reactant is tripled?
- (A) 3-fold increase (B) 6-fold increase
 (C) 18-fold increase (D) 27-fold increase
28. For the rate equation,

$$\text{Rate} = k[A][B]^2,$$
 what are the units for the rate constant, k , if the rate is given in $\text{mol}\cdot\text{L}^{-1}\cdot\text{sec}^{-1}$?
- (A) $\text{L}\cdot\text{mol}\cdot\text{sec}$ (B) $\text{L}\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$
 (C) $\text{L}^2\cdot\text{mol}^{-2}\cdot\text{sec}^{-1}$ (D) $\text{L}^3\cdot\text{mol}^{-3}\cdot\text{sec}^{-2}$
29. For the reaction
 $2A + 2B \rightarrow \text{Product}$
 the rate law is $\text{Rate} = k[A][B]^2$. Which mechanism is consistent with this information?
- (A) $B + B \rightleftharpoons C$ (B) $A + B \rightarrow C$ (slow)
 $C + A \rightarrow \text{Product}$ (slow) $C + B \rightarrow \text{product}$
 (C) $A + A \rightleftharpoons C$ (D) $A + B \rightleftharpoons C$
 $B + B \rightleftharpoons D$ $B + C \rightarrow D$ (slow)
 $C + D \rightarrow \text{Product}$ (slow) $D + A \rightarrow \text{product}$
30. Which straight line gives the activation energy for a reaction?
- (A) rate constant vs T (B) $\ln(\text{rate constant})$ vs T
 (C) rate constant vs T^{-1} (D) $\ln(\text{rate constant})$ vs T^{-1}
31. Based on the equilibrium constant for the reaction below,
 $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \quad K = 1.8 \times 10^{-5}$
 what is the equilibrium constant for the reaction
 $SO_2(g) + 1/2O_2(g) \rightleftharpoons SO_3(g) \quad K = ?$
- (A) 2.1×10^{-3} (B) 4.2×10^{-3}
 (C) 2.4×10^2 (D) 5.6×10^4
32. $CO(g) + Cl_2(g) \rightleftharpoons COCl(g) + Cl(g) \quad K_{eq} = 1.5 \times 10^{-39}$
 If the rate constant, k , for the forward reaction above is $1.4 \times 10^{-28} \text{ L}\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$ what is k (in $\text{L}\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$) for the backward reaction?
- (A) 2.1×10^{-67} (B) 1.0×10^{-11}
 (C) 9.3×10^{10} (D) 7.1×10^{27}
33. Calculate the $[H^+]$ in a 0.25 M solution of methylamine, CH_3NH_2 ($K_b = 4.4 \times 10^{-4}$).
- (A) 1.1×10^{-4} (B) 1.0×10^{-2}
 (C) 9.1×10^{-11} (D) 9.5×10^{-13}
34. A 0.010 M solution of a weak acid, HA, is 0.40% ionized. What is its ionization constant?
- (A) 1.6×10^{-10} (B) 1.6×10^{-7}
 (C) 4.0×10^{-5} (D) 4.0×10^{-3}

35. 1.0 L of an aqueous solution in which $[\text{H}_2\text{CO}_3] = [\text{HCO}_3^-] = 0.10 \text{ M}$, has $[\text{H}^+] = 4.2 \times 10^{-7}$. What is the $[\text{H}^+]$ after 0.005 mole of NaOH has been added?
- (A) $2.1 \times 10^{-9} \text{ M}$ (B) $2.2 \times 10^{-8} \text{ M}$
 (C) $3.8 \times 10^{-7} \text{ M}$ (D) $4.6 \times 10^{-7} \text{ M}$
36. A solution of $\text{Pb}(\text{NO}_3)_2$ is added dropwise to a second solution in which $[\text{Cl}^-] = [\text{F}^-] = [\text{I}^-] = [\text{SO}_4^{2-}] = 0.001 \text{ M}$. What is the first precipitate that forms?
- (A) PbCl_2 ($K_{\text{sp}} = 1.5 \times 10^{-5}$)
 (B) PbF_2 ($K_{\text{sp}} = 3.7 \times 10^{-8}$)
 (C) PbI_2 ($K_{\text{sp}} = 8.5 \times 10^{-9}$)
 (D) PbSO_4 ($K_{\text{sp}} = 1.8 \times 10^{-8}$)
37. $\text{Cl}_2 + \text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}_3^-$
 What is the coefficient for OH^- when this equation is balanced with the smallest integer coefficients?
- (A) 2 (B) 3 (C) 4 (D) 6
38. Use the standard reduction potentials;
 $\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s}) \quad E^\circ = -0.141 \text{ V}$
 $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) \quad E^\circ = 0.800 \text{ V}$
 to calculate E° for the reaction;
 $\text{Sn}(\text{s}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$
- (A) 0.659 V (B) 0.941 V
 (C) 1.459 V (D) 1.741 V
39. Which of the processes happen during the discharging of a lead storage battery?
- | |
|--|
| 1. $\text{H}_2(\text{g})$ is produced |
| 2. PbO_2 is converted to PbSO_4 |
| 3. The density of the electrolyte solution decreases |
- (A) 1 only (B) 2 only
 (C) 1 and 3 only (D) 2 and 3 only
40. What is the value of ΔG° for the reaction?
- $$2\text{Al}(\text{s}) + 3\text{Cu}^{2+}(\text{aq}) \rightarrow 2\text{Al}^{3+}(\text{aq}) + 3\text{Cu}(\text{s}) \quad E^\circ = 2.02 \text{ V}$$
- (A) -1170 kJ (B) -585 kJ
 (C) -390 kJ (D) -195 kJ
41. The voltage for the cell $\text{Fe} | \text{Fe}^{2+}(0.0010 \text{ M}) || \text{Cu}^{2+}(0.10 \text{ M}) | \text{Cu}$ is 0.807 V at 25 °C. What is the value of E° ?
- (A) 0.629 V (B) 0.689 V
 (C) 0.748 V (D) 0.866 V
42. A current of 2.0 A is used to plate Ni(s) from 500 mL of a 1.0 M $\text{Ni}^{2+}(\text{aq})$ solution. What is the $[\text{Ni}^{2+}]$ after 3.0 hours?
- (A) 0.39 M (B) 0.46 M (C) 0.78 M (D) 0.89 M
43. Which region of the electromagnetic spectrum is capable of inducing electron transitions with the greatest energy?
- (A) infrared (B) microwave
 (C) ultraviolet (D) visible
44. All of the following possess complete d shells EXCEPT
- (A) Ag^+ (B) Cu^{2+} (C) Ga^{3+} (D) Zn^{2+}
45. Which orbital fills completely immediately before the 4f?
- (A) 6s (B) 5p (C) 5d (D) 4d
46. Which set of quantum numbers (n, l, m_l, m_s) is permissible for an electron in an atom?
- (A) 1, 0, 0, -1/2 (B) 1, 1, 0, +1/2
 (C) 2, 1, 2, +1/2 (D) 3, 2, -2, 0
47. When the elements Li, Be, and B, are arranged in order of increasing ionization energy, which is the correct order?
- (A) Li, B, Be (B) B, Be, Li
 (C) Be, Li, B (D) Li, Be, B
48. Which forms the most alkaline solution when added to water?
- (A) Al_2O_3 (B) B_2O_3 (C) CO_2 (D) SiO_2
49. What is the total number of valence electrons in the peroxydisulfate, $\text{S}_2\text{O}_8^{2-}$, ion?
- (A) 58 (B) 60 (C) 62 (D) 64

50. For which species are both bonds of equal length?

1. ClO_2^-
2. NO_2^-

- (A) 1 only (B) 2 only
(C) both 1 and 2 (D) neither 1 nor 2

51. Which compound has the highest melting point?

- (A) MgO (B) KCl (C) NaCl (D) CaO

52. Which molecular geometry is least likely to result from a trigonal bipyramidal electron geometry?

- (A) trigonal planar (B) see-saw
(C) linear (D) t-shaped

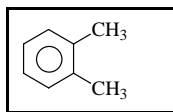
53. Which diatomic species has the greatest bond strength?

- (A) NO (B) NO^+ (C) O_2 (D) O_2^-

54. During the complete combustion of methane, CH_4 , what change in hybridization does the carbon atom undergo?

- (A) sp^3 to sp (B) sp^3 to sp^2
(C) sp^2 to sp (D) sp^2 to sp^3

55. What is the formula for the compound?



- (A) C_8H_{10} (B) C_8H_{12}
(C) C_8H_{14} (D) C_8H_{16}

56. Which is most likely to react by an $\text{S}_{\text{N}}1$ mechanism?

- (A) CH_3Cl (B) $\text{CH}_3\text{CHClCH}_3$
(C) $(\text{CH}_3)_3\text{CCl}$ (D) $\text{C}_6\text{H}_5\text{Cl}$

57. Which substance will react most rapidly with $\text{Br}_2(\text{aq})$?

- (A) benzene (B) chloropropane
(C) propanone (D) propene

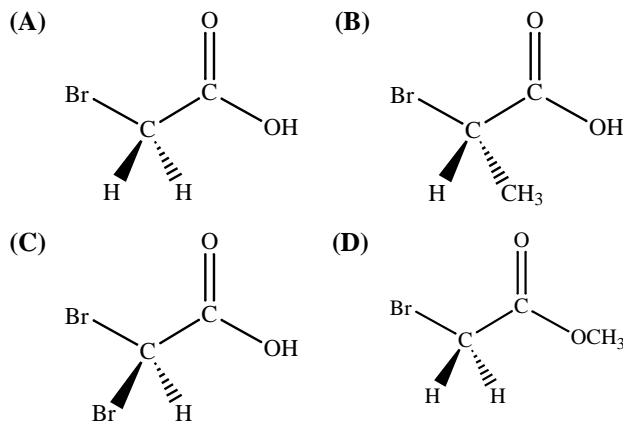
58. Which compound includes a carbon atom with an sp hybridized orbital?

- (A) benzene (B) butyne
(C) methyl chloride (D) phenol

59. Which compound has the highest vapor pressure at 25°C ?

- (A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (B) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3$
(C) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (D) $(\text{CH}_3)_3\text{COH}$

60. Which of the molecules can exist as optical isomers?



END OF TEST

**CHEMISTRY OLYMPIAD 2003
NATIONAL EXAM
PART 1— KEY**

Number	Answer	Number	Answer
1.	D	31.	C
2.	B	32.	C
3.	B	33.	D
4.	C	34.	B
5.	D	35.	C
6.	A	36.	D
7.	B	37.	D
8.	D	38.	B
9.	C	39.	D
10.	B	40.	A
11.	D	41.	C
12.	B	42.	C
13.	C	43.	C
14.	A	44.	B
15.	A	45.	A
16.	D	46.	A
17.	D	47.	A
18.	B	48.	A
19.	A	49.	C
20.	C	50.	C
21.	B	51.	A
22.	A	52.	A
23.	B	53.	B
24.	A	54.	A
25.	D	55.	A
26.	B	56.	C
27.	D	57.	D
28.	C	58.	B
29.	D	59.	B
30.	D	60.	B