Chemistry 1B, Spring 2004

Midterm 3 April 22, 2004 (90 min, closed book)

Name:					

SID:_____

TA Name:_____

- This exam has 45 multiple choice questions.
- Fill in the Scantron form AND circle your answer on the exam.
- Each question is worth 4 points.

Note:

- The questions on the exam may be answered in any order.
- All the questions are equally weighted. Answer those you can quickly and go back to those that require more thought.
- Some questions may seem obvious or too simple. They are. There are no 'trick' questions.

• Potentially useful relations:

 $[A]_t = [A]_0 e^{-kt}$ $\ln[A]_t = \ln[A]_0 - kt$ $t_{1/2} = \ln 2/k$ $\frac{1/[A]_t = 1/[A]_0 + kt}{k = A e^{(-Ea/RT)}}$ $\ln(k_1/k_2) = E_a/R (1/T_2 - 1/T_1)$ $t_{1/2} = 1/[A]_0 k$ $t_{1/2} = [A]_0/kt$

$$PV = nRT$$
$$E_{kin} = \frac{3}{2}RT$$
$$\Delta E = q + w$$
$$w = -P_{ext}\Delta V$$
$$\Delta E = \frac{3}{2}nR\Delta T$$

$$N_{0} = 6.02214 \times 10^{23} \text{ mol}^{-1}$$

$$R_{\infty} = 2.179874 \times 10^{-18} \text{ J}$$

$$R_{\infty} = 3.28984 \times 10^{15} \text{ Hz}$$

$$k = 1.38066 \times 10^{-23} \text{ J K}^{-1}$$

$$h = 6.62608 \times 10^{-34} \text{ J s}$$

$$m_{e} = 9.101939 \times 10^{-31} \text{ kg}$$

$$c = 2.99792 \times 10^{8} \text{ m s}^{-1}$$
Gas Constant:

$$R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$R = 8.20578 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$T (K) = T (C) + 273.15$$

$$F = 96,485 \text{ C / mol}$$

$$1 \text{ V} = 1 \text{ J / C 1 nm} = 10^{-9} \text{ m}$$

$$1 \text{ kJ} = 1000 \text{ J}$$

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 $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$ $\Delta H^{\circ} = \sum \Delta H^{\circ}_{f}$ (products) - $\sum \Delta H^{\circ}_{f}$ (reactants) $\Delta S^{\circ} = \Sigma S^{\circ}$ (products) - ΣS° (reactants) $\Delta G^{\circ} = \sum \Delta G^{\circ}_{f} (\text{products}) - \sum \Delta G^{\circ}_{f} (\text{reactants})$ $S = k_B ln W$ $\Delta T = i k_{b,f} m$ $\prod = i RTc$

for
$$aA + bB \stackrel{\checkmark}{\leftarrow} cC + dD$$

 $Q = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$ At equilibrium, $Q = K$

$$\Delta G^{\circ} = - RT \ln K$$

$$\ln K = -\frac{\Delta H^{\circ}}{R} \frac{1}{T} + \frac{\Delta S^{\circ}}{R}$$

$$\Delta G^{\circ} = - nF\Delta C^{\circ}$$

$$\Delta C = \Delta C^{\circ} - RT/nF \ln Q$$

$$\ln K = nF\Delta C^{\circ}/RT$$

 $\Delta x \ \Delta p \sim h$ $p = h/\lambda$ Particle in a box: $E_n = h^2 n^2 / 8mL^2$; n = 1, 2, 3...harmonic oscillator: $E_v = (v + \frac{1}{2}) hA/2\pi; A = (k/m)^{1/2}; v = 0, 1, 2 \dots$ $m = m_a m_b / (m_a + m_b)$; rotation: $E_{\ell} = \ell(\ell+1)hB; B=h/8\pi^{2}I; I = mr^{2}; \ell = 0, 1, 2, 3...$ $m = m_a m_b / (m_a + m_b)$ H-Atom: $E_n = -Z^2/n^2 R; n = 1, 2, 3...$

SECTION 1: QUANTUM MECHANICS

1.) Calculate the velocity of an oxygen molecule if it has a de Broglie wavelength



- A) 890. m·s
- B) $3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1}$
- C) 1780 $\text{m} \cdot \text{s}^{-1}$
- D) 445 m·s⁻¹
- E) 8.90 m·s⁻¹
 - 2.) Which of the following experiments most directly supports de Broglie's hypothesis of the wave nature of matter?
- A) blackbody radiation
- B) the photoelectric effect
- \vec{C} alpha-particle scattering by a metal foil
- D) electron diffraction by a crystal
- E) the emission spectrum of the hydrogen atom
- 3.) In a one-dimensional particle in a box, for n = 6, how many wavelengths equals the size of the box?

B)	3	
\sim		
\mathbf{C}	1	

- D) 12
- E) 6
- 4.) In a one-dimensional particle in a box, for Ψ_4 , how many nodes are predicted?



5.) In a one-dimensional particle in a box, the zero-point energy corresponds to

- A) a node.
- B) n=0.
- C) n = 1. D) a quantum state where the Uncertainty Principle is not valid.
- E) $\Psi^2 = 0.$

6.)	Which one of the following statements is incorrect?
A)	For a one-dimensional particle in a box, as the mass of the particle becomes
B)	larger the separation between neighboring energy levels increases. For a one-dimensional particle in a box, the separation between neighboring energy levels decreases as the length of the container increases.
C)	For a one-dimensional particle in a box, the separation between neighboring energy levels becomes zero when the walls of the box are infinitely far apart.
D)	Argon atoms in a cylinder can be treated as though their translational energy were not quantized.
E)	A billiard ball on a table has a completely negligible <i>zero-point energy</i> .
7.)	The total number of orbitals in a shell with principal quantum number 5 is
۸)	32

- A) 32B) 50
- B) 50C) 25
- $\frac{(1)}{(1)}$ $\frac{(2)}{(1)}$ $\frac{(2)}{(1)}$
- E) 5
- 8.) Which set of quantum numbers could correspond to a 4d orbital?
- A) $n = 3, l = 2, m_l = 0$ B) $n = 3, l = 2, m_l = +1$ C) $n = 4, l = 3, m_l = +2$ D) $n = 4, l = 2, m_l = -2$ E) $n = 4, l = 2, m_l = +3$

9.) Which set of quantum numbers could correspond to a 4f orbital?

A) $n = 4, l = 4, m_l = +3$ B) $n = 4, l = 3, m_l = +4$ C) $n = 4, l = 3, m_l = -3$ D) $n = 3, l = 2, m_l = +1$ E) $n = 3, l = 2, m_l = 0$

10.) How many total nodal planes are present in the 3d orbitals?

- A) 15
 B) 0
 C) 5
 D) 20
- E) 10

11.) How many nodal planes (angular nodes) are present in an f orbital?



12.) Which is the ground state electron configuration of a chromium atom?

- A) $[Ar]4s^23d^2$
- B) $[Ar]4s^{1}3d^{5}$
- C) $[Ar]3d^{5}4s^{1}$
- D) $[Ar]3d^{6}_{4}$
- E) [Ar] $3d^44s^2$
- 13.) All of the following can have the ground-state electron configuration $[Xe]4f^{14}5d^{10}$ except
- A) Pb⁴⁺
- B) Hg^{2+}
- C) Bi⁵⁻
- D) Tl^+
- E Au⁺

14.) Which of the following orbital groups cannot exist in an atom?

- A) 4d
- B) 5g
- C) 5f
- D) 4f E) 3f

15.) Which of the following has bond angles slightly less than 109°?

- A) NH_4^+ B) ClO_4^- C) BrO_3^- D) PO_4^{3-}
- E) BH₄⁻

16.) How many σ - and π -bonds, respectively, are there in acrolein, CH₂=CHCHO?

- A) 4 and 2
- B) 7 and 2
- C) 5 and 2
- D) 5 and 4
- E) 7 and 1
 - Identify the hybrid orbitals used by the underlined atom in acetone, CH₃COCH₃.



- C) Pure p_z orbitals are used in sigma bonding.
- D) sp^3
- E) sp

- 18.) The experimental observation that B₂ has two unpaired electrons indicates that, in molecular orbital ideas,
- A) the $2p_{\pi}$ orbitals lie above the $2p_{\sigma}$ orbital in energy.
- B) the $2p_{\pi}$ orbitals lie below the $2p_{\sigma}$ orbital in energy.
- C) the $2p_{\pi}^*$ orbitals lie below the $2p_{\sigma}^*$ orbital in energy.
- D) the $2p_{\pi}$ orbitals are nonbonding.
- E) the $2p_{\pi}^*$ orbitals lie above the $2p_{\sigma}^*$ orbital in energy.
- 19.) How many π molecular orbitals are formed in 1,3,5 hexatriene; CH₂=CH– CH=CH=CH₂?

A) 4

- B) 6
- C) 8
- D) 10
- E) 12
- 20.) Rank the possibilities for π MOs in 1,3,5 hexatriene from lowest to highest energy.



A)	A, B, C, D, E
B)	C, A~D, E, B
_C)	D, A, B~E, C
D)	C, A, D~E, B
E)	B, D, E, D, A

Consider the following ions trapped in a tiny box H^+ , He^+ , Li^{+2} , Be^{+3} so that each displays quantum particle in a box behavior for the next three questions.

21.) Which has the lowest ground state energy?

A) H^+ B) He^+ \dot{C} Li⁺² D) Be^{+3} E) all are equal 22.) Which has the lowest translational n=1 to n = 2 transition energy? A) H^+ B) He^+ \vec{C} Li^{+2} D) Be⁺³ all are equal E) 23.) Which has the highest n=1 to n=2 electronic transition energy? A) H^+ B) He⁺ \vec{C} Li^{+2} \dot{D} Be^{+3} all are equal E)

Continue with the next question:

Match the following molecular phenomenon with the appropriate regions of the electromagnetic spectrum in the next three questions.



Each absorbance in the following spectrum is produced by a C-O stretching mode in A) CH_3OH , B) CO, or C) CO₂. Assign each peak in the next three questions.



Continue with the next question:

SECTION 2: THERMODYNAMICS

30.) Consider the following reaction NO(g) + $\frac{1}{2}O_2(g) \rightarrow NO_2(g)$. If $\Delta H^\circ = -56.52$ kJ and $\Delta S^\circ = -72.60 \text{ J} \cdot \text{K}^{-1}$ at 298 K, calculate the equilibrium constant for the reaction at 298 K.

A)
$$1.31 \times 10^6$$

B)
$$7.63 \times 10^{-7}$$

- C) 660
- D) 1.22×10^{14}
- E) 8.08×10^9
- 31.) Given: C(s) + CO₂(g) → 2CO(g). At equilibrium at a certain temperature, the partial pressures of CO (g) and CO₂ (g) are 1.22 atm and 0.780 atm, respectively. Calculate the value of K for this reaction.

A)	3.13
B)	2.00
C)	1.91
D)	1.56
E)	0.640

- 32.) Write the equilibrium constant for $2NaBr(aq) + Pb(ClO_4)_2(aq) \rightarrow PbBr_2(s) + 2NaClO_4(aq)$.
- A) $K = [Pb^{2+}][Br^{-}]^2$
- B) $K = 1/([Pb^{2+}][Br^{-}]^2)$ C) $K = [N_{12}Clo_{12}^{12}/([N_{12}Br^{-}]^2)]$
- C) $K = [NaClO_4]^2/([NaBr]^2[Pb(ClO_4)_2])$ D) $K = [PbBr_2]/([Pb^{2+}][Br^{-}]^2)$
- E) $K = \frac{[PDD1_2]}{[PD(ClO_4)_2][NaBr]^2}$
- 33.) Consider the reaction: $4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g)$, $K = 10^{80}$ at a certain temperature. Initially, all reactants and products have concentrations equal to 12 M. At equilibrium, the approximate concentration of oxygen is
- A) 6 M.
 B) 0 M.
 C) 3 M.
 D) 12 M.
- E) 18 M.

Continue with the next question:

Consider the following for the next five questions: Two products are formed in the reaction of 1,3,5-hexatriene with HBr, 2-Bromohexadiene with K = 10 and 1-Bromohexadiene with K = 35. The following plot of concentration vs. time is obtained starting with 1 M of each reactant and product.



34.) Which is the correct ranking of the components in terms of free energy of formation?

A hexatriene	B hexatriene	C 1-Bromo	D 2-Bromo	E 1-Bromo
1-Bromo	2-Bromo	hexatriene	1-Bromo	2-Bromo
2-Bromo	1-Bromo	2-Bromo	hexatriene	hexatriene

- 35.) Which of the following is true of this reaction?
- A) 1-Bromo is kinetically favored
- B) 2-Bromo is kinetically favored
- C) 2-Bromo is thermodynamically favored
- D) 1-Bromo and 2-Bromo are thermodynamically similar
- E) 1-Bromo and 2-Bromo are kinetically equivalent

36.) Which of the following is true of this reaction?

- A) $\Delta G^{\circ} = 0$ for the formation of hexatriene
- B) $\Delta G^{\circ} > 0$ for the formation of 2-Bromo
- C) $\Delta G^{\circ} < 0$ for the formation of 2-Bromo

- D) $\Delta G^{\circ} > 0$ for the formation of 1-Bromo E) ΔG° is the same for 1-Bromo and 2-Bromo

Match the plots for the course of reaction to the appropriate product of the hexatriene reaction



Consider the following plot of free energy vs. activity (P/P_0) for the gas phase reaction A $(g) \rightarrow B$ (g) for the following four questions.



- 43.) Which is true when A and B are placed in a container at partial pressures of 4 atm?
- A) $\Delta G^{\circ} > 0$ B) $\Delta G > 0$ C) $\Delta G = \Delta G^{\circ}$ D) $\Delta G = 0$
- E) $\Delta G < 0$

Continue with the next question:

44.) Pure liquids and solids

A) never appear as variables in an equilibrium constant

- B) are always in the numerator of an equilibrium constant
- C) are always in the denominator of an equilibrium constant
- D) have activities that are sensitive to pressure
- E) have activities that are sensitive to concentration
- 45.) At the triple point of a substance
- A) the gas phase is the highest free energy
- B) the liquid to gas transition is favored
- C) the liquid to solid transition is favored
- D) solid has the lowest free energy
- E) all phases have equal free energy