Name:	Student number:	
Chemistry 1A03	FINAL EXAM	December, 2008
McMaster University	VERSION 1	
Instructors: Drs. P. Britz-Mck	Libbin, G. Goward, P. Lock	Duration: 3 hours

This test contains **28** numbered pages printed on both sides. There are **35** multiple-choice questions appearing on pages numbered 3 to 25. Page 26 is extra space for rough work. Page 27 includes some useful data and equations, and there is a periodic table on page 28. You may tear off the last page to view the periodic table and the data provided.

You must enter your name and student number on this question sheet, as well as on the answer sheet. Your invigilator will be checking your student card for identification. You are responsible for ensuring that your copy of the question paper is complete. Bring any discrepancy to the attention of your invigilator.

Questions 1 to 25 are each worth 2 marks, questions 26 - 35 are each worth 3 marks; the total marks available are 80. There is **no** additional penalty for incorrect answers.

BE SURE TO ENTER THE CORRECT VERSION OF YOUR TEST (shown near the top of page 1), IN THE SPACE PROVIDED ON THE ANSWER SHEET.

#### ANSWER ALL QUESTIONS ON THE ANSWER SHEET, IN PENCIL.

Instructions for entering multiple-choice answers are given on page 2.

**SELECT ONE AND ONLY ONE ANSWER FOR EACH QUESTION** from the answers **(A)** through **(E). No work written on the question sheets will be marked**. The question sheets may be collected and reviewed in cases of suspected academic dishonesty.

Academic dishonesty may include, among other actions, communication of any kind (verbal, visual, *etc.*) between students, sharing of materials between students, copying or looking at other students' work. If you have a problem please ask the invigilator to deal with it for you. Do not make contact with other students directly. Try to keep your eyes on your own paper – looking around the room may be interpreted as an attempt to copy.

Only Casio FX 991 electronic calculators may be used; but they must NOT be transferred between students. Use of periodic tables or any aids, other than those provided, is not allowed.

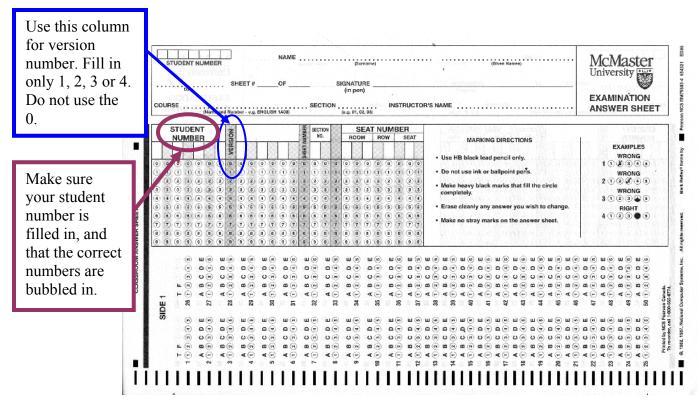
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#### OMR EXAMINATION – STUDENT INSTRUCTIONS

# NOTE: IT IS YOUR RESPONSIBILITY TO ENSURE THAT THE ANSWER SHEET IS PROPERLY COMPLETED: YOUR EXAMINIATION RESULT DEPENDS UPON PROPER ATTENTION TO THESE INSTRUCTIONS.

The scanner, which reads the sheets, senses the bubble shaded areas by their non-reflection of light. A heavy mark must be made, completely filling the circular bubble, with an HB pencil. Do not use pen to bubble answers. Erasures must be thorough or the scanner will still sense a mark. Do **NOT** use correction fluid on the sheets. Do **NOT** put any unnecessary marks or writing on the sheet.

- 1. On SIDE 1 (**red side**) of the form, in the top box, *in pen*, print your student number, name, course name, (section number, instructor name) and the date in the spaces provided. Then you **MUST** write your signature, in the space marked SIGNATURE.
- 2. In the second box, *with a pencil*, mark your student number, **exam version number** (mark "1", "2", "3" or "4" and **do not** use the "0" bubble) (and course section number) in the space provided and fill in the corresponding bubble numbers underneath.
- 3. Answers: mark only **ONE** choice from the alternatives (1,2,3,4,5 or A,B,C,D,E) provided for each question. If there is a True/False question, enter response o 1 (or A) as True, and 2 (or B) as False. The question number is to the left of the bubbles. Make sure that the number of the question on the scan sheet is the same as the number on the test paper.
- 4. Pay particular attention to the Marking+ Directions on the form.
- 5. Begin answering the question using the first set of bubbles, marked "1".



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See pages 1 and 2 of the exam for instructions.

Questions 1-25 are worth two (2) marks each.

- 1. Which ONE of the following choices lists the halogen and halide species in order of **increasing size** (from smallest to largest)?
- $(\mathbf{A}) \qquad \mathbf{F}^{-} < \mathbf{F} < \mathbf{C}\mathbf{1}$
- **(B)**  $F < F^- < Cl^-$
- (C)  $I^- < I < Br$
- $(\mathbf{D}) \qquad \mathbf{F}^{-} < \mathbf{C}\mathbf{l}^{-} < \mathbf{C}\mathbf{l}$
- $(\mathbf{E}) \qquad \operatorname{Cl}^{+} < \operatorname{Cl}^{-} < \operatorname{Cl}$
- 2. In the upper atmosphere ozone can be destroyed with help from Cl radicals. These radicals can be generated from photolytic dissociation of Cl bonds in various molecules, including  $\text{Cl}_2(g)$ .

From the Cl-Cl bond energy (243 kJ mol<sup>-1</sup>), calculate the **minimum frequency of light (in Hz, or s<sup>-1</sup>)** which will dissociate a Cl<sub>2</sub> molecule into Cl atoms.

- (A)  $3.67 \times 10^{38}$
- **(B)**  $7.63 \times 10^{-38}$
- (C)  $9.06 \times 10^{15}$
- **(D)**  $5.62 \times 10^{-19}$
- **(E)**  $6.09 \times 10^{14}$

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3. You are put in charge of designing a system to filter Cd<sup>2+</sup>(aq) cations from solution. Using the data below, which of the following salts would **be best suited to remove** Cd<sup>2+</sup> from solution?

$$K_{sp} \text{ Cd}_3(\text{PO}_4)_2 = 1.2 \times 10^{-33}; \ K_{sp} \text{ CdF}_2 = 6.44 \times 10^{-3}; \ K_{sp} \text{ Cd}(\text{OH})_2 = 17.2 \times 10^{-15}$$

(A) 
$$Cu_3(PO_4)_2$$
;  $K_{sp} = 1.2 \times 10^{-37}$ 

**(B)** MgF<sub>2</sub>; 
$$K_{sp} = 5.16 \times 10^{-11}$$

(C) 
$$Zn(OH)_2$$
;  $K_{sp} = 17.2 \times 10^{-17}$ 

**(D)** LiF; 
$$K_{sp} = 1.84 \times 10^{-3}$$

**(E)** Ag<sub>3</sub>PO<sub>4</sub>; 
$$K_{\rm sp} = 8.89 \times 10^{-17}$$

4. The production of chlorine (Cl<sub>2</sub>) by the chloralkali process is a key industrial reaction that is widely used in water disinfection programs. However, chlorine must be isolated from hydroxide generated as a by-product in the reaction in order to avoid the following disproportionation reaction involving Cl<sub>2</sub>:

$$Cl_2(aq) \rightarrow Cl^-(aq) + OCl^-(aq)$$

Determine the **smallest whole number coefficients** for the following species based on a **balanced** reaction under **alkaline** (**basic**) conditions: **Cl<sub>2</sub>**, **OCl<sup>-</sup> and OH<sup>-</sup>**.

	$Cl_2$	OCI <sup>-</sup>	OH
<b>(A)</b>	2	1	1
<b>(B)</b>	3	2	1
<b>(C)</b>	1	1	2
<b>(D</b> )	2	5	9
<b>(E)</b>	1	3	6

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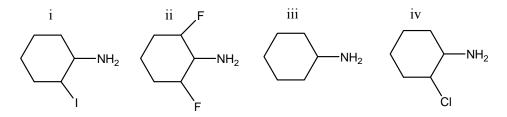
- 5. A major source of **fluoride** in natural ground water supplies in many countries is derived from the **dissolution** of calcium fluoride,  $CaF_2$  (s) that is found in the bedrock. Calculate the **equilibrium concentration** (**mM**) of **fluoride** in water if  $K_{sp}$  (CaF<sub>2</sub>) is 5.3 x 10<sup>-9</sup> assuming that there are no other ions present in solution.
- **(A)** 0.056
- **(B)** 0.34
- **(C)** 120
- **(D)** 2.2
- **(E)** 25

6. Which of the following substances will form **acidic solutions** when placed into water?

NaF CH<sub>3</sub>COOLi (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>Br KNO<sub>3</sub> SO<sub>3</sub>

- (A) NaF, CH<sub>3</sub>COOLi
- **(B)** CH<sub>3</sub>COOLi, SO<sub>3</sub>
- (C)  $(CH_3)_2NH_2Br$ ,  $KNO_3$
- (**D**) KNO<sub>3</sub>, NaF
- (E)  $SO_3$ ,  $(CH_3)_2NH_2Br$

7. For the following **weak bases**, select the correct order of **INCREASING** base strength from **weakest base**  $\rightarrow$  **strongest base** (or high pK<sub>b</sub>  $\rightarrow$  low pK<sub>b</sub>):



- (A) ii < iii < iv < i
- **(B)** iii < ii < i < iv
- (C) iv < i < iii < ii
- **(D)** i < iv < ii < iii
- (E) ii < iv < i < iii
- 8. Dissolving 3.90 g of CaF<sub>2</sub> in 50.0 mL of pure water (density = 1.00 g mL<sup>-1</sup>) causes the temperature of the solution to decrease from 20.00 to 16.79 °C. What is the **molar enthalpy of dissolution of CaF<sub>2</sub> (in kJ mol<sup>-1</sup>)?** Assume that the specific heat of the solution equals 4.184 J g<sup>-1</sup> K<sup>-1</sup>, and that there is no solution volume change upon dissolution of the salt.
- **(A)** -6.81
- **(B)** -2.40
- **(C)** +13.4
- **(D)** +6.05
- **(E)** +11.7

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- 9. 0.40 mol of a gas is heated at constant pressure, so that its temperature increases from  $21.00^{\circ}\text{C}$  to  $79.83^{\circ}\text{C}$ . As a result, the gas expands from 10.0 L to 12.0 L against an external pressure of 0.965 atm. The molar heat capacity of the gas, at constant pressure, is  $20.8 \text{ J mol}^{-1} \text{ K}^{-1}$ . What is the total energy change,  $\Delta U$  (in J), for the gas?
- **(A)** -470
- **(B)** -210
- **(C)** +290
- **(D)** +590
- **(E)** +785

- 10. Which one of the following statements is FALSE?
- (A) The reaction  $CO(g) \rightarrow C(g) + O(g)$  causes work to be done on the surroundings.
- (B) For the process  $H_2O(g) \rightarrow H_2O(l)$ , heat flows from system to surroundings.
- (C) If excess gas is produced in a reaction occurring at constant temperature, then  $\Delta H$  is greater than  $\Delta U$ , (where greater means more positive, or less negative).
- (**D**) In any process, the change of enthalpy depends on the path taken by the system to go from the initial to the final state.
- (E) The enthalpy change for  $O_2(g) \rightarrow 2 O(g)$  is positive.

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- 11. Which one of the following processes is **endothermic**?
- (A) Photosynthesis
- **(B)** Cellular respiration
- (C) Combustion of gasoline
- **(D)** Detonation of an airbag in a car
- (E) A body cooling down in frigid water
- 12. Calculate the standard enthalpy of formation of liquid benzene,  $C_6H_6$ , in kJ mol<sup>-1</sup>, from its standard enthalpy of combustion which equals -3268 kJ mol<sup>-1</sup>. Data:

$$\Delta H_f^{\circ}(H_2O,l) = -285.8 \text{ kJ mol}^{-1} \qquad \Delta H_f^{\circ}(CO_2,g) = -393.5 \text{ kJ mol}^{-1}$$
 
$$\Delta H_f^{\circ}(C, \text{ diamond}) = 1.90 \text{ kJ mol}^{-1} \qquad \Delta H_f^{\circ}(CO,g) = -110.5 \text{ kJ mol}^{-1}$$

- (A) -62 kJ mol<sup>-1</sup>
- **(B)**  $53 \text{ kJ mol}^{-1}$
- **(C)**  $-48 \text{ kJ mol}^{-1}$
- **(D)**  $-42 \text{ kJ mol}^{-1}$
- **(E)**  $50 \text{ kJ mol}^{-1}$

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- 13. Choose the **FALSE** statement about phase changes. (Recall "fusion" = melting).
- (A) The phase transition for the melting of paraffin wax requires energy, and therefore temperature decreases during the transition.
- **(B)** In a phase change material energy is released by the material upon freezing and absorbed upon melting.
- (C) The heat capacity of a material is determined by, for example, the vibrational and rotational degrees of freedom available to the molecules.
- (**D**) The greater the amount of material, the greater the energy available as it freezes.
- (E) At pressure = 1 atm, freezing occurs when  $T < \Delta H^{o}(fus) / \Delta S^{o}(fus)$ .
- 14. Your body can extract all the energy from glucose ( $C_6H_{12}O_6$ ) by aerobic metabolism (using oxygen; the net reaction is combustion). However, (without oxygen, when under stress) *anaerobic metabolism* converts one mole of glucose into two moles of lactic acid ( $C_6H_{12}O_6 \rightarrow 2C_3H_6O_3$ ). How much **energy (in kJ) does the body extract** from the **anaerobic metabolism of one mole of glucose**? The energy of combustion of lactic acid is -321 kJ mol<sup>-1</sup> and the energy of combustion for glucose is -2808 kJ mol<sup>-1</sup>.
- **(A)** 1183
- **(B)** 2166
- **(C)** 2287
- **(D)** 3116
- **(E)** 3050

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- 15. A galvanic electrochemical cell (like those seen in experiment # 5) is constructed with both half-cell reactions involving the same metal (M) and different concentrations of M<sup>+</sup>(aq). Choose the **CORRECT** statement about the cell.
- (A) The half-cell with the lower  $[M^+]$  will contain the anode.
- **(B)** A salt bridge is not needed in this cell.
- (C) The weight of the cathode will decrease over time.
- (**D**) A voltage of twice  $E^{\circ}_{red}$  for  $M^{+}(aq)/M(s)$  will be observed.
- (E) Electrons will flow from the half-cell of higher  $[M^+]$  to the half-cell with lower  $[M^+]$ .

16. Given the following half-reactions, identify the **strongest reducing agent**.

$$E^{o}_{red}$$

$$Al^{3+} + 3e^{-} \rightarrow Al(s)$$

$$AgBr(s) + e^{-} \rightarrow Ag(s) + Br^{-} + 0.07$$

$$Sn^{4+} + 2e^{-} \rightarrow Sn^{2+} + 0.14$$

$$Fe^{2+} + 2e^{-} \rightarrow Fe$$

$$-0.44$$

- (A)  $\operatorname{Sn}^{4+}(\operatorname{aq})$
- $(\mathbf{B})$  Al(s)
- (C) Fe(s)
- **(D)**  $Br^{-}(aq)$
- (E)  $Al^{3+}(aq)$

17. Calculate  $E_{cell}^0$  (in volts) for the reaction as written:

$$4 \text{ Al(s)} + 3 \text{ O}_2(g) + 12 \text{ H}^+(aq) \rightarrow 4 \text{ Al}^{3+}(aq) + 6 \text{ H}_2\text{O}$$

Data: 
$$O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$$
  $E_{red}^0 = +1.22 V$ 

$$Al^{3+} + 3 e^{-} \rightarrow Al$$
  $E^{0}_{red} = -1.66 V$ 

- **(A)** +5.98
- **(B)** +2.88
- **(C)** +1.22
- **(D)** -0.56
- **(E)** -1.98

- 18. What is the value of the equilibrium constant, K, at 25 °C for the electrochemical cell described by the reaction Fe(s) + Cu<sup>2+</sup>(aq)  $\rightarrow$  Fe<sup>2+</sup>(aq) + Cu(s) for which E°<sub>cell</sub> = 0.78 V?
- **(A)**  $3.0 \times 10^5$
- **(B)**  $1.9 \times 10^{13}$
- (C)  $2.4 \times 10^{26}$
- **(D)**  $7.2 \times 10^{-3}$
- **(E)**  $9.1 \times 10^{-16}$

19. Knowing that  $E^{\circ}_{red} (Mg^{2+}/Mg) = -2.37 \text{ V}$ , calculate the standard free energy change  $(\Delta G^{\circ} \text{ in kJ})$  for the following reaction:

$$MgCl_2(aq) + H_2(g) \rightarrow Mg(s) + 2 HCl(aq)$$

- **(A)** +457
- **(B)** +209
- **(C)** +174
- **(D)** -269
- **(E)** -356

- 20. Calculate the **cell potential** (**in V**) at 25°C for a fuel cell using the combustion of hydrogen gas to form liquid water, when the pressure of H<sub>2</sub> gas is 0.50 atm and the pressure of O<sub>2</sub> gas is 0.25 atm. The standard cell potential for this fuel cell is 1.23 V. Hint: start by balancing the reaction.
- **(A)** 1.16
- **(B)** 1.21
- **(C)** 1.24
- **(D)** 1.27
- **(E)** 1.31

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21. The freezing point of ammonia (NH<sub>3</sub>(1)  $\rightarrow$  NH<sub>3</sub>(s)) is -78°C at 1 atm. Predict the signs of  $\Delta$ H,  $\Delta$ S,  $\Delta$ G (in that order) for the freezing of ammonia at -80°C and 1 atm.

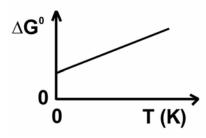
ΔH ΔS ΔG

- (A) + -
- **(B)** – –
- (C) + + -
- **(D)** - +
- (E) + +
- 22. Which of the following processes are likely to have  $\Delta S_{svs} > 0$ ?
  - (i)  $NaCl(s) \rightarrow NaCl(aq)$
  - (ii)  $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
  - (iii)  $SO_2(g) + H_2O(1) \rightarrow H_2SO_3(aq)$
  - (iv)  $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$
  - (v)  $HCl(aq) + NaHCO_3(aq) \rightarrow NaCl(aq) + H_2O(1) + CO_2(g)$
- (**A**) i, iii
- **(B)** i, v
- (C) ii, iii
- **(D)** ii, iii, iv
- **(E)** iv, v
- 23. The enthalpy of vaporization of HCN is  $20.0 \, \text{kJ J mol}^{-1}$ . The molar entropy of the gas is  $201.7 \, \text{J mol}^{-1} \, \text{K}^{-1}$ , and the molar entropy of the liquid is  $112.8 \, \text{J mol}^{-1} \, \text{K}^{-1}$ . Calculate the **normal boiling point** of HCN.
- (A)  $-48^{\circ}$ C
- **(B)** -3.6°C
- (C) +5.9°C
- **(D)**  $-78^{\circ}$ C
- **(E)**  $+22^{\circ}$ C

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24. The figure below shows  $\Delta G^{\circ}$  for a chemical reaction plotted against the absolute temperature. Select the **TRUE** statement below.

(Hint: Consider  $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$  as the equation of a line).



- (A) The reaction is spontaneous at all temperatures.
- **(B)** The reaction has a positive entropy.
- **(C)** The reaction reaches equilibrium at very low temperature.
- (**D**) The reaction is spontaneous at temperatures at  $T \le 0$ .
- **(E)** The reaction is endothermic.
- 25. Milk of magnesia, Mg(OH)<sub>2</sub>, is a widely used antacid for treatment of acid reflux. Although it is a sparingly soluble salt in aqueous solution at neutral pH, its solubility is greatly enhanced under acidic conditions. With use of the data below, determine the **free energy change** (ΔG°<sub>rxn</sub>) at 25°C for the dissolution of Mg (OH)<sub>2</sub> and neutralization of excess stomach acid based on the following equation:

$$K$$
 Mg(OH)<sub>2</sub> (s) + 2H<sup>+</sup> (aq)  $\longrightarrow$  Mg<sup>2+</sup> (aq) + 2H<sub>2</sub>O (l)

Species	$Mg(OH)_2(s)$	$Mg^{2+}$ (aq)	$H_2O(1)$	$H^+(aq)$
$\Delta G_f^{o} (kJ \text{ mol}^{-1})$	-833.5	-454.8	-237.1	0

- (A) -95.5 kJ
- **(B)** 126.1 kJ
- (C) -148.3 kJ
- **(D)** 17.6 kJ
- **(E)** -278.4 kJ

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## Questions 26-35 are worth three (3) marks each.

26. Which of the following ions or molecules has the **fewest number of <u>equivalent</u> charge-minimized structures**?

- (A)  $ClO_4^-$
- **(B)**  $SO_3^{2-}$
- (C)  $ClO_2^-$
- **(D)**  $NO_3^-$
- **(E)**  $AsO_3^{3-}$

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- 27.  $K_P = 2.00$  for the reaction 2  $COF_2(g) = CO_2(g) + CF_4(g)$ . All three gases are placed in a 5.00 L flask at 298K. The initial amounts are 0.145 moles of  $COF_2$ , 0.074 moles of  $COF_2$  and 0.074 moles of  $CF_4$ . What is the **partial pressure** of  $COF_2(g)$  at equilibrium?
- (**A**) 0.529 atm
- **(B)** 0.0217 atm
- (**C**) 0.392 atm
- **(D)** 0.0573 atm
- **(E)** 0.118 atm

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28. "SO<sub>x</sub>" gases contribute to the production of acid rain. Consider the following equilibrium for production of SO<sub>3</sub>, and select the **TRUE statements** for the equilibrium in a constant volume container:

$$2 \text{ SO}_2(g) + \text{O}_2(g) = 2 \text{ SO}_3(g)$$
  $\Delta H = -198.2 \text{ kJ}; K_P = 1.02 \times 10^5 \text{ at } 425^{\circ}\text{C}.$ 

- (i) At 425 °C,  $\Delta G^{\circ}_{rxn} = -66.9 \text{ kJ}.$
- (ii) The concentration of SO<sub>2</sub>(g) will decrease if temperature is increased.
- (iii) Addition of water to form sulfuric acid  $(SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l))$  will lead to a decrease in the partial pressure of oxygen gas.
- (iv) At 425 °C, if  $P_{eq}(SO_2) = P_{eq}(SO_3) = 1.50$  atm, then  $P_{eq}(O_2) = 3.1 \times 10^{-3}$  atm.
- (v) Increasing the container volume will cause a decrease in the partial pressure of  $SO_3(g)$ .
- (**A**) i, ii
- **(B)** i, v
- (C) ii, iv
- **(D)** i, iii, v
- **(E)** ii, iii, iv

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- 29. Sodium monofluoroacetate (NaOOCCH<sub>2</sub>F) is a highly toxic chemical produced by some classes of plants. Calculate the **pH** of a solution containing 600 mg of sodium monofluoroacetate dissolved in 20 mL water. ( $pK_a$  for HOOCCH<sub>2</sub>F = 2.6)
- **(A)** 5.2
- **(B)** 7.0
- **(C)** 9.6
- **(D)** 6.5
- **(E)** 8.0

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30. One reaction in the creation of photochemical smog is  $O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$ . Use the following average bond enthalpies (BE) to estimate the enthalpy change,  $\Delta H$  (in kJ), for this reaction.

Bond	BE (kJ mol <sup>-1</sup> )
О-О	142
O=O	498
N-O	222
N=O	590

- **(A)** -468
- **(B)** −59
- **(C)** −80
- **(D)** +46
- **(E)** +82

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- 31. A calorimeter is designed to monitor the energy absorbed during the sublimation of  $CO_2$  (sublimation is  $CO_2(s) \rightarrow CO_2(g)$ , heat of sublimation = 570 J g<sup>-1</sup>) at a constant temperature of 194.7 K. The oxidation of calcium metal (0.268 g) by excess oxygen released enough heat to cause  $CO_2$  to sublime, producing a 2.34 atm pressure in a 1.00 L vessel. What is the **enthalpy of reaction in kJ mol**<sup>-1</sup> for the oxidation of calcium metal? (Disregard any work done during the process).
- **(A)** -550
- **(B)** -215
- (C) -75.6
- **(D)** −891
- **(E)** -348

32. Identify the **CORRECT** statements regarding the following electrochemical cell:

$$Pt(s)\mid Fe(NO_3)_2(aq),\, Fe(NO_3)_3(aq)\parallel AgNO_3(aq)\mid Ag(s).$$

Data: 
$$E_{red}^{\circ}(Ag^{+}/Ag) = +0.799 \text{ V}$$
  $E_{red}^{\circ}(Fe^{3+}/Fe^{2+}) = +0.771 \text{ V}$ 

- (i) The spontaneous cell reaction is  $Fe^{3+}(aq) + Ag(s) \rightarrow Fe^{2+}(aq) + Ag^{+}(aq)$ .
- (ii)  $E^{\circ}_{cell} = +0.028 \text{ V}.$
- (iii) In the outer circuit, the electrons flow from the Pt to the Ag electrode.
- (iv) Inside the cell, nitrate ions migrate from the Ag side to the Fe side.
- (v)  $\Delta G^{\circ} = -5.40 \text{ kJ}$  for the reaction  $\text{Fe}^{2+}(\text{aq}) + \text{Ag}^{+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{Ag}(\text{s})$ .
- (**A**) i, ii, v
- **(B)** ii, iii, iv
- (**C**) i, iv, v
- **(D)** ii, iii
- **(E)** ii, v

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#### 33. Identify the **TRUE** statement(s):

- (i) A spontaneous endothermic reaction is driven by entropy.
- (ii)  $P_4(s) + 5 O_2(g) \rightarrow P_4O_{10}(s)$  is an entropy-driven reaction.
- (iii) For a (reactants + products) mixture at equilibrium,  $\Delta G_{rxn} = 0$ .
- (iv) The reaction C(graphite) + CO<sub>2</sub>(g)  $\rightarrow$  2 CO(g) is spontaneous at temperatures below 600 °C. ( $\Delta H_{rxn}$  = +172.5 kJ,  $\Delta S_{rxn}$  = +175.7 J K<sup>-1</sup>).
- (v) At T = 0 K, a perfect crystal has zero entropy.
- (vi) In a cold pack, the dissolution of ammonium nitrate is an exothermic process that leads to an increase in entropy, thus it is a spontaneous process.
- (A) i, iii, iv, vi
- **(B)** i, v
- (C) ii, iii, vi
- **(D)** i, iii, v
- (E) ii, iv, vi

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34. The **Haber Bosch** process is an important industrial chemical process for the synthesis of **ammonia** that is performed under high temperature and high pressure conditions for optimum performance. Calculate  $K_P$  at 400°C for the reaction based on the standard state thermodynamic parameters below, assuming that the  $\Delta H_f^{\circ}$  and S° terms are unchanged from 25°C to 400°C

$$N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$$
 
$$\Delta H_f^{\circ} [NH_3] = -46.11 \text{ kJ mol}^{-1}; \qquad S^{\circ} [NH_3] = 192.5 \text{ J mol}^{-1} \text{ K}^{-1}$$
 
$$S^{\circ} [N_2] = 191.6 \text{ J mol}^{-1} \text{ K}^{-1}$$
 
$$S^{\circ} [H_2] = 130.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

- **(A)**  $3.09 \times 10^5$
- **(B)**  $6.00 \times 10^{-4}$
- (C)  $1.27 \times 10^{-10}$
- **(D)**  $2.28 \times 10^{12}$
- **(E)**  $4.20 \times 10^{-1}$

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35. The formation of **ATP** is a major way that energy is stored chemically during metabolism based on the reaction below:

$$ADP(aq) + H_2PO_4^-(aq) + H^+(aq) \longrightarrow ATP(aq) + H_2O(1)$$

If  $\Delta G^{\circ} = -9.2 \text{ kJ mol}^{-1}$  for this reaction under standard conditions, what is the apparent **free energy** ( $\Delta G$ ) for the same reaction **inside a cell** under normal biological conditions, assuming [ADP] = 50  $\mu$ M, [H<sub>2</sub>PO<sub>4</sub><sup>-</sup>] = 10 mM, [ATP] = 5.0 mM, pH = 7.4 at 37°C?

- **(A)**  $+58 \text{ kJ mol}^{-1}$
- **(B)**  $-25 \text{ kJ mol}^{-1}$
- (C)  $-0.48 \text{ kJ mol}^{-1}$
- **(D)**  $+130 \text{ kJ mol}^{-1}$
- **(E)**  $+26 \text{ kJ mol}^{-1}$

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This page is for rough work only.

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# Some general data are provided on this page and the next page. Other data appear with the questions.

#### A periodic table is provided on the next page.

$$\begin{split} \text{STP} &= 273.15 \text{ K, 1 atm} & \text{F} = 96485 \text{ C/mol} \\ \text{R} &= 8.3145 \text{ J/K} \cdot \text{mol} = 0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol} & \text{N}_{\text{A}} = 6.022 \times 10^{23} \text{ mol}^{-1} \\ 1 \text{ atm} &= 760 \text{ mm Hg} = 101.325 \text{ kPa} & 0^{\circ}\text{C} = 273.15 \text{ K} \\ 1 \text{ J} &= 1 \text{ kg m}^{2} \text{ s}^{-2} = 1 \text{ kPa} \cdot \text{L} = 1 \text{ Pa} \cdot \text{m}^{3} & 1 \text{ m} = 10^{9} \text{ nm} = 10^{10} \text{ Å} \\ 1 \text{ cm}^{3} &= 1 \text{ mL} & 1 \text{ g} &= 10^{3} \text{ mg} = 10^{-3} \text{ kg} \\ \text{µM} &= 10^{-6} \text{ M} & \text{mM} &= 10^{-3} \text{ M} \\ 1 \text{ Hz} &= 1 \text{ cycle/s} & \text{c} &= 2.9979 \times 10^{8} \text{ m/s} \\ \text{h} &= 6.6256 \times 10^{-34} \text{ J} \cdot \text{s} & \text{m}_{e} &= 9.10 \times 10^{-31} \text{ kg} \\ \lambda &= \text{h} / \text{mu} &= \text{h} / \text{p} \\ E_{\text{n}} &= -\text{R}_{\text{H}} / \text{n}^{2} &= -2.179 \times 10^{-18} \text{J} / \text{n}^{2} & \text{(R}_{\text{H}} \text{ is the energy form of the Rydberg constant for H)} \\ K_{\text{w}} &= 1.0 \times 10^{-14} \text{ (25 °C)} \\ \Delta G &= \Delta G^{\circ} + RT \ln Q \end{split}$$

### **Solubility guidelines for Common Ionic Solids**

 $E_{cell} = E_{cell}^{o} - \frac{RT}{nE} \ln Q = E_{cell}^{o} - \frac{0.0592}{n} \log_{10} Q$ 

Follow the lower-numbered guideline when two guidelines are in conflict. This leads to the correct prediction in most cases.

- 1. Salts of group 1 cations (with some exceptions for Li<sup>+</sup>) and the NH<sub>4</sub><sup>+</sup> cation are soluble.
- 2. Nitrates, acetates, and perchlorates are soluble.
- 3. Salts of silver, lead, and mercury(I) are insoluble.
- 4. Chlorides, bromides, and iodides are soluble.
- 5. Carbonates, phosphates, sulfides, oxides, and hydroxides are insoluble (sulfides of group 2 cations and hydroxides of  $Ca^{2+}$ ,  $Sr^{2+}$ , and  $Ba^{2+}$  are slightly soluble).
- 6. Sulfates are soluble except for those of calcium, strontium, and barium.

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6.941	9.0122											10.811	12.011	14.007	15.999	18.998	20.180
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39.098	40.078	44.956	47.88	50.942	51.996	54.938	55.847	58.933	58.69	63.546	62:39	69.723	72.61	74.922	78.96	79.904	83.80
	38	39	40	41	42	43	44	45	46	47	48	49	20	51	52	53	54
8	รั	>	Ž	2	ŝ	Tc	Ru	뜐	Pd	Ag	ၓ	므	S	Sb	<u>P</u>	_	Xe
85.468	87.62	88.906	91.224	92.906	95.94	[98]	101.07	102.91	105.42	107.87	112.41	114.82	118.71	121.75	127.60	126.90	131.29
	99	25	72	73	74	75	9/	77	78	79	80	81	85	83	48	85	98
ပ္ပ	Ba	‡	Ξ	Ta	≥	æ	SO	<b>=</b>	ద	Au	H	F	В	窗	Po	At	絽
132.91	137.33	138.91	178.49	180.95	183.85	186.21	190.2	192.22	195.08	196.97	200.59	204.38	207.2	208.98	[509]	[210]	[222]
	88	68	104	105	106												
<u>i</u>	Ra	**Ac	**AcUng Unp	Unp	Unh		c weights a	re based o	Atomic weights are based on <sup>12</sup> C = 12 and conform to the 1987 IUPAC report values rounded to 5 significant digits.	and conform	n to the 198	37 IUPAC n	eport value	s rounded	to 5 signific	ant digits.	
[223]	226.03	227.03	[261]	[262]	[263]	QWN	ers in [] inc	dicate the n	Numbers in [] indicate the most stable isotope.	sotope.							
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				59	09	19	62	63	49	92	99	29	89	69	20	7	
*	Lanth	* Lanthanides   Ce	ဦ	4	ž		Pm Sm	品	පු	2	δ	운	ш	ᄪ	Ϋ́	3	
			140.12	140.91	144.24	[145]	150.36	151.97	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97	
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