Test 2

Nov. 12, 2010

McMaster University

VERSION 1

Instructor: Dr. R. Dumont, Dr. G. Goward, Dr. J. Landry and Dr. P. Lock

Duration: 120 minutes

This test contains 22 numbered pages printed on both sides. There are **29** multiple-choice questions appearing on pages numbered 3 to 18. Pages 19 and 20 are extra space for rough work. Page 21 includes some useful data and equations, and there is a periodic table on page 22. 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 23 are each worth 2 marks each, and questions 24 - 29 are worth 3 marks each; the total marks available are 64. 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.

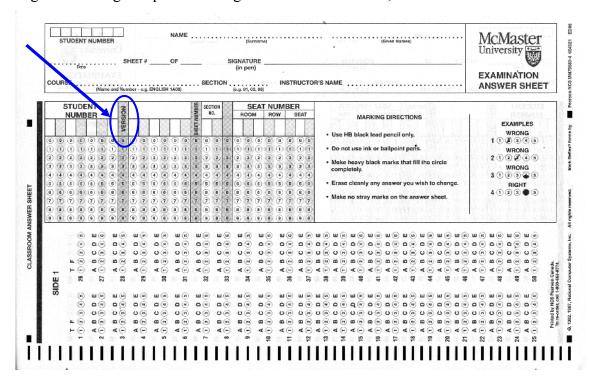
Only Casio FX 991 electronic calculators may be used; but they must NOT be transferred between students. Use of periodic tables or any aids, other than those provided, is not allowed.

OMR EXAMINATION – STUDENT INSTRUCTIONS

NOTE: IT IS YOUR RESPONSIBILITY TO ENSURE THAT THE ANSWER SHEET IS PROPERLY COMPLETED: YOUT 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. Marks made with a pen will **NOT** be sensed. 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** (and course section number) in the space provided and <u>fill in the corresponding bubble numbers</u> 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".



Questions 1-23 are worth 2 marks each.

1. What is the correct chemical formula for **calcium nitrate**?

- A) Ca₂NO₂
- B) CaNO₃
- C) Ca(NO₃)₂
- D) Ca₂NO₃
- E) $Ca(NO_2)_2$

Ca has a valence of 2. It appears as Ca²⁺ Nitrate is a singly charged anion – i.e. it is NO₃⁻

2. Which one of the following statements is **FALSE**?

- A) When the quantum number l = 2, the possible values of m_l are -2, -1, 0, 1, or 2.
- B) As the wavelength of light increases, the energy decreases.
- C) As the quantum number *n* of an orbital increases, so does the average distance between the nucleus and an electron in that orbital.
- D) The photoelectric effect occurs when sufficiently energetic light strikes the surface of a metal and electrons are ejected.
- E) Light is emitted when electrons are excited to higher energy levels.

Light is **absorbed** when "electrons are excited to higher energy levels". Light is emitted when electrons drop to lower energy levels.

3. Which of the following statements are **TRUE**?

(i) Br atoms are smaller than As atoms. TRUE

(ii) O has a higher first ionization energy than N. FALSE

(iii) Ba is easier to ionize than Sr. TRUE

(iv) Cl⁻ is a larger ion than Ca²⁺. TRUE

A) all statements are true

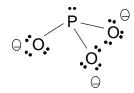
- B) i, iii, iv
- C) ii, iii, iv
- D) i, ii, iv
- E) i, ii, iii

Br and As are both in the 4 th row. Atomic size decreases to the right as Z_{eff} increases. Br is to the right of As and is therefore smaller. N has a half-filled valence subshell which is relatively stable, giving it a relatively high ionization energy. O is the next element to the right of N. A

half-filled subshell results after O is ionized. This makes O easier to ionize than expected. Thus, O has a lower ionization energy than N, though the general trend is for ionization energy to increase to the right in a row. Ba is below Sr in the alkaline earth metals group. Ionization energy decreases down a group, as the outer electrons are further from the nucleus. Thus, Ba is easier to ionize than Sr. Cl^- is larger than Ca^{2+} because it has a lower nuclear charge with the same number of electrons.

- 4. What is the molecular shape of the phosphite ion, PO₃³⁻?
 - A) tetrahedral
 - B) seesaw
 - C) trigonal pyramidal
 - D) trigonal planar
 - E) T-shaped

Lewis structure:



AX₃E trigonal pyramidal

- 5. How many **grams** of calcium oxide, **CaO**, can be produced from 4.20 g of calcium metal and 1.60 g of oxygen gas?
 - A) 5.88
 - B) 5.80
 - C) 2.90
 - **D)** 5.61
 - E) 2.94

Write the balanced reaction:

$$2 \text{ Ca} + \text{O}_2 \rightarrow 2 \text{ CaO}$$

Moles of Ca = $4.20 \text{ g} / 40.078 \text{ g mol}^{-1} = 0.104_8 \text{ mol}$

 $0.0502 \text{ mol } O_2$ are needed to consume the Ca

Moles of $O_2 = 1.60 \text{ g} / 31.999 \text{ g mol}^{-1} = 0.0500_0 \text{ mol}$

0.100 mol Ca are needed to consume the O₂

O₂ is the limiting reactant. Therefore, 0.100 mol of CaO is produced.

Mass of CaO = $0.100 \text{ mol} \times 56.078 \text{ g mol}^{-1} = 5.61 \text{ g}$

6. Select the one **FALSE** statement concerning the equilibrium,

$$MgCO_3(s) \implies MgO(s) + CO_2(g)$$
 $\Delta H^{\circ} = 100.6 \text{ kJ}.$

- A) Increasing the temperature increases the amount of MgO(s).
- B) Removing $CO_2(g)$ increases the amount of MgO(s).
- C) Adding MgO(s) does not change the amount of MgCO₃(s).
- D) Halving the size of the reaction vessel increases the amount of MgCO₃(s).
- E) Doubling the amount of all three species (with the volume of the reaction vessel fixed) has no effect on the equilibrium.

Increasing the temperature shifts the equilibrium to the right – i.e. more MgO(s) is produced – because the reaction is endothermic. Removing $CO_2(g)$, a product, shifts the equilibrium to the right – again, more MgO(s) is produced. Adding MgO(s) has no effect on the equilibrium because it is a pure solid. Halving the size of the reaction vessel shifts the equilibrium to the side with the fewest moles of gas – the reactant side – i.e. more $MgCO_3(s)$ will result from the reverse reaction.

Doubling the amount of all three species with fixed volume increases the partial pressure of $CO_2(g)$, shifting the reaction to the left – i.e. there **is** an effect.

7. The K_{ow} value of substance, S, is the equilibrium constant for the partitioning of S between water and octanol;

$$S(aq) \implies S(octanol)$$

Which of the following substances is **most** lipophilic, and therefore most likely to accumulate in fatty tissue?

A) hexamethylbenzene $K_{\text{ow}} = 4.1 \times 10^4$ B) 2,2',4,4',5-pentachlorobiphenyl $K_{\text{ow}} = 2.6 \times 10^6$ C) methanol $K_{\text{ow}} = 0.15$ D) diethyl ether $K_{\text{ow}} = 6.8$ E) p-dichlorobenzene $K_{\text{ow}} = 2.3 \times 10^3$

The most lipophilic substance is that with the greatest K_{ow} value. Here, that is 2,2',4,4',5-pentachlorobiphenyl.

8. At 25°C, the following reactions have the equilibrium constants shown:

$$2 \text{ CO (g)} + \text{ O}_2 \text{ (g)} \implies 2 \text{ CO}_2 \text{ (g)}$$
 $K_p = 1.33 \times 10^{88}$
 $2 \text{ H}_2 \text{ (g)} + \text{ O}_2 \text{ (g)} \implies 2 \text{ H}_2 \text{ O (g)}$ $K_p = 3.67 \times 10^{77}$

Use these data to **calculate** K_p for the reaction:

$$H_2O(g) + CO(g) \rightleftharpoons CO_2(g) + H_2(g)$$

- A) 2.3×10^5
- B) 8.1×10^{10}
- (1.9×10^5)
- D) 6.8×10^{10}
- E) 3.5×10^{-6}

Express the "target reaction", $H_2O(g) + CO(g) \rightleftharpoons CO_2(g) + H_2(g)$ in terms of the two reactions for which equilibrium constants are known.

$$V_2$$
 2 CO (g) + O₂ (g) = 2 CO₂ (g)
 V_2 2 H₂O (g) = 2 H₂ (g) + O₂ (g) reverse of the 2nd rxn $K_p = (3.67 \times 10^{77})^{-1/2}$
 V_3 V_4 V_5 V_6 V_7 V_8 V_9 V_8 V_9 V

9. Which one of the following equilibria is **unaffected** when the volume of the reaction vessel is doubled?

A)
$$N_2(g) + O_2(g) \implies 2 NO(g)$$

- B) $2 SO_2(g) + O_2(g) \implies 2 SO_3(g)$
- C) $Br_2(g) \implies 2 Br(g)$
- D) $2 \text{ NO}_2(g) + 7 \text{ H}_2(g) \implies 2 \text{ NH}_3(g) + 4 \text{ H}_2\text{O}(1)$
- E) $PC1_5(g) \Longrightarrow PC1_3(g) + C1_2(g)$

Doubling the volume of the vessel halves all partial pressures. A factor of $\frac{1}{2}$ is introduced in the numerator of the reaction quotient for each mole of product gas. A factor of $\frac{1}{2}$ is introduced in the denominator of the reaction quotient for each mole of reactant gas. The reaction quotient is unaffected if the number of moles of reactant gas equals the number of moles of product gas.

10. The equilibrium constant for the reaction

$$N_2(g) + O_2(g) \implies 2 NO(g)$$

is $K_p = 1.7 \times 10^{-1}$ at an elevated temperature. A reaction vessel at this temperature contains these gases with the following partial pressures:

Gas	Partial Pressure
$N_2(g)$	0.25 atm
$O_2(g)$	0.25 atm
NO(g)	4.2×10^{-1} atm

Select the one **TRUE** statement for this system.

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- A) The system is at equilibrium.
- **B**) Q > K, and the reaction proceeds to the reactants side.
- C) $Q \le K$, and the reaction proceeds to the reactants side.
- D) Q > K, and the reaction proceeds to the products side.
- E) $Q \le K$, and the reaction proceeds to the products side.

$$Q = \frac{(P(NO))^2}{P(N_2)P(O_2)} = \frac{(0.42)^2}{(0.25)(0.25)} = 2.82 > 1.7 \times 10^{-1} = K_p$$

Since $Q > K_p$, the reaction proceeds in the reverse direction – i.e. to the reactants side.

11. Identify the **FALSE** statement concerning the following reaction:

$$3 \text{ Cu(s)} + 8 \text{ HNO}_3(\text{aq}) \rightarrow 3 \text{ Cu(NO}_3)_2(\text{aq}) + 2 \text{ NO(g)} + 4 \text{ H}_2\text{O}$$

- A) Some of the nitrate ions are spectator ions.
- B) Each copper atom loses 2 electrons.
- C) Some of the nitrate ions are oxidizing agents.
- **D**) Each nitrogen atom gains 3 electrons.
- E) The reaction is an oxidation-reduction reaction.

This is a redox reaction. Copper goes from oxidation number = 0 to oxidation number = +2. Some of the reactant nitrate N atoms change from oxidation number = +5 to oxidation number = +2. Some of the nitrate ions on the reactants side remain as nitrate ions on the products side. D is false because only **some** of the N atoms gain 3 electrons.

- 12. Aqueous solutions of barium nitrate and ammonium sulfate are mixed, and a white precipitate is observed. The **balanced net ionic equation** for this reaction is:
 - A) $Ba^{2+}(aq) + 2 NH_4^+(aq) + SO_4^{2-}(aq) \rightarrow (NH_4)_2SO_4(s) + BaSO_4(s)$
 - B) $2 \text{ Ba}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{Ba}_2 \text{SO}_4(\text{s})$
 - C) $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$
 - D) $2 NH_4^+(aq) + SO_4^{2-}(aq) \rightarrow (NH_4)_2SO_4(s)$
 - E) $Ba^{2+}(aq) + 2 NH_4^+(aq) + SO_4^{2-}(aq) + 2 NO_3^-(aq) \rightarrow BaSO_4(s) + 2 NO_3^-(aq) + 2 NH_4^+(aq)$

Barium ions (Group 2) are always Ba^{2+} . The white precipitate is $BaSO_4(s)$. Ammonium salts are soluble. E shows spectator ions – it is not a net ionic equation.

- 13. Classify the reaction $KH(s) + H_2O(1) \rightarrow KOH(aq) + H_2(g)$ according to the following three **reaction types** (choose all that apply):
 - (i) acid-base
 - (ii) oxidation-reduction
 - (iii) precipitation
 - A) iii
 - **B**) i, ii
 - C) ii, iii
 - D) i, iii
 - E) ii 50% part mark

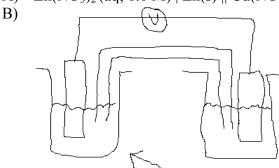
This reaction is an acid-base reaction with the base, hydride, accepting a proton from water (acting here as an acid). However, the hydride H (oxidation number = -1) becomes one of the two H's in a hydrogen molecule (oxidation number = 0). This H atom is oxidized. The H donated by water is correspondingly reduced (from oxidation number = +1 to 0). This is also an oxidation-reduction reaction.

- 14. An unknown aqueous solution contains either KNO₃ or K₃PO₄. Addition of which **ONE** of the following aqueous solutions provides a simple visual test that identifies the unknown?
 - A) RbOH
 - B) NaCl
 - C) CaBr₂
 - D) NH₄Br
 - E) Na₂SO₄

Neither of the species, KNO₃ or K₃PO₄, is a good oxidizing or reducing agent (nitrate is only oxidizing under concentrated strong acid conditions). Only a precipitation reaction could produce a simple visual test. Nitrate salts are soluble. So, mixing a solution with a cation that precipitates with phosphate would provide the desired test. Alkali metal cations and ammonium

salts are soluble. Only calcium ion will precipitate with phosphate.

- 15. Which of the following cell diagrams is **correct**?
 - $Zn(NO_3)_2$ (aq; 1.0 M) | Zn(s) || $Cu(NO_3)_2$ (aq; 1.0 M) | Cu(s)



- Copper goes here
- C) $Zn(s) | Zn(NO_3)_2(aq; 1.0 M) | Cu(NO_3)_2(aq; 1.0 M) | Cu(s)$
- D) $Cu(NO_3)_2(aq; 1.0 M) | Zn(NO_3)_2(aq; 1.0 M) || Zn(s) | Cu(s)$
- $Cu(s) | Zn(NO_3)_2(aq; 1.0 M) | Cu(NO_3)_2(aq; 1.0 M) | Zn(s)$
- Zn(s) $| Zn(NO_3)_2 (aq; 1.0 M) | Cu(NO_3)_2 (aq; 1.0 M) | Cu(s)$ anode and ox. reactant | ox. product || red. reactant | red. product and cathode
 - 16. A concentration cell is created based on two half cells containing Co²⁺/Co. Which of the following statements is **FALSE**?
 - A) $E_{\text{cell}}^{\circ} = 0.0 \text{ V}$
 - Electrons are being transferred *from* the concentrated half-cell to the diluted half-
 - Co²⁺(aq) in the concentrated half-cell is being reduced.
 - The flow of electrons will stop when the concentrations of Co²⁺(aq) become equal in both half-cells.
 - Co(s) in the diluted half-cell is being oxidized. E)

Concentration cell based on Co²⁺/Co:

$$Co(s) | Co^{2+}(aq,anode) | Co^{2+}(aq,cathode) | Co(s)$$

The cell reaction is

$$\text{Co}^{2+}(\text{aq,cathode}) \rightarrow \text{Co}^{2+}(\text{aq,anode})$$

Under standard conditions, there is no net reaction – i.e. $E_{\text{cell}}^{\circ} = 0.0 \text{ V}$. The forward reaction is spontaneous if Co^{2+} is concentrated at the cathode and dilute at the anode. The net reaction is the spontaneous dilution of the concentrated solution and concentrating of the dilute solution – i.e. the concentration even out. Electrons are liberated at the anode where Co atoms become oxidized. They flow through wires to the cathode where they are taken up by Co²⁺ ions, reducing them to Co atoms plated on the cathode.

17. The following reactions are observed to proceed to near completion as written.

$$3 \operatorname{Sn}^{2+}(aq) + 2 \operatorname{Al}(s) \rightarrow 3 \operatorname{Sn}(s) + 2 \operatorname{Al}^{3+}(aq)$$

 $2 \operatorname{Ce}^{4+}(aq) + \operatorname{Sn}(s) \rightarrow 2 \operatorname{Ce}^{3+}(aq) + \operatorname{Sn}^{2+}(aq)$

Which species is the **strongest oxidizing agent**?

- A) $Ce^{3+}(aq)$
- $\stackrel{\frown}{B}$ $Ce^{4+}(aq)$
- C) Sn(s)
- D) $A1^{3+}(aq)$
- E) $\operatorname{Sn}^{2+}(\operatorname{aq})$

The first reaction tells us that $Sn^{2+}(aq)$ is a stronger oxidizing agent than $Al^{3+}(aq)$. The second reaction tells us that Ce^{4+} (aq) is a stronger oxidizing agent than Sn^{2+} (aq). Therefore, Ce⁴⁺(aq) is the strongest oxidizing agent.

- 18. During experiment 2, Cycles of Copper, a student obtains a percent yield Cu(s) of 108%. The product obtained was unreactive with HCl. What is the **most likely** source of error?
 - A) Copper oxide was lost during the decanting step.
 - There was residual solvent left within the copper precipitate at the end of the experiment.
 - C) Not all of the zinc reacted with the Cu²⁺(aq) to yield Cu(s).
 - D) 108% is a valid yield, as the atomic weight of copper at the end of the experiment is higher than at the start.
 - E) The student accidentally added too much nitric acid in the first step.

A and C would reduce the yield of copper. E has no effect on the yield. Solvent or unreacted zinc would make the yield too high. However, the product is unreactive with HCl, so it cannot contain zinc.

- 19. What is the **equilibrium constant** for an electrochemical cell based on $I_2/2I^-$ and Pb^{2+}/Pb where $E_{cell}^{\circ} = 0.66 \text{ V}$ at 298.15 K?
 - A) 5.1×10^{-3}
 - B) 56

 - C) 2.1×10^{22} D) 7.2×10^4
 - E) 6.3×10^{12}

From
$$E^{\circ} = \frac{RT}{zF} \ln K$$
 (see information sheet), we get
$$K = e^{\frac{zFE^{\circ}}{RT}} = e^{\frac{2\times96485\times0.66 \text{ J/mol}}{8.314\times298.15 \text{ J/mol}}} = e^{\frac{2\times96485\times0.66 \text{ J/mol}}{8.314\times298.15 \text{ J/mol}}} = e^{51.379} = 2.1\times10^{22}$$

²⁰. Determine the **oxidizing agent** (OA) and **reducing agent** (RA) in the following reaction for the industrial production of bleach.

$$Cl_2(aq) + 2 NaOH(aq) \rightarrow NaCl(aq) + NaOCl(aq) + H_2O(1)$$

A) OA: Cl₂

RA: Na⁺

B) OA: Cl₂

RA: Cl₂

C) OA: OH

RA: Cl₂

D) OA: Na⁺

RA: OH

E) OA: Cl₂

RA: OH

ON:
$$Cl_2(aq) + 2 \text{ NaOH (aq)} \rightarrow \text{NaCl (aq)} + \text{NaOCl (aq)} + \text{H}_2O(1)$$

ON: $0 + 1$

Chlorine is both oxidizing and reducing agent in this disproportionation reaction.

21. What is $E_{cell}^{o}(V)$ for the reaction of Cu(I) with V(II)?

$$Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$$
 $E^{\circ}_{red} = 0.535 \text{ V}$
 $V^{3+}(aq) + e^{-} \rightarrow V^{2+}(aq)$ $E^{\circ}_{red} = -0.255 \text{ V}$

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A) -0.125 V

B) 0.790 V

C) -1.075 V

D) 0.285 V

E) -0.268 V

When Cu(I) reacts with V(II), the first half reaction proceeds in the forward direction (reduction), while the second reaction proceeds in the reverse direction (oxidation).

$$E_{\text{red}}^{\circ} = E_{\text{red}}^{\circ}(\text{Cu}^{+}) - E_{\text{red}}^{\circ}(\text{V}^{3+}) = 0.535 \text{ V} - (-0.255 \text{ V}) = 0.790 \text{ V}$$

 $E_{\text{red}}^{\circ} = E_{\text{red}}^{\circ}(\text{Cu}^{+}) + E_{\text{ox}}^{\circ}(\text{V}^{2+}) = 0.535 \text{ V} + (0.255 \text{ V}) = 0.790 \text{ V}$

- 22. Select the one **FALSE** statement about thermodynamics of reactions.
 - A) The heat flow q (from the surroundings to the system) must be positive for an endothermic reaction.
 - B) Cellular respiration, in which cells extract energy from glucose, is an example of combustion.
 - C) The temperature rise in a coffee-cup calorimeter is independent of the amounts of reagents added.
 - D) A calorimeter must be an isolated system, in order to determine the heat flow of the reaction
 - E) When measured in a bomb calorimeter, the heat released by the reaction is equal to that absorbed by the calorimeter.

The heat liberated in a coffee-cup calorimeter reaction is proportional to the amount of reagents (i.e. reactants). The temperature increase is proportional to the heat liberated. Therefore, the amount of reagents does affect the temperature increase.

- 23. How much **heat**, in **kJ**, is required to warm 63.0 g of liquid ethylene glycol (specific heat = $2.20 \text{ J g}^{-1} \text{ K}^{-1}$) from 20.0°C to 40.0°C ?
 - A) 3.91
 - B) 1.64
 - C) 5.14
 - D) 7.12
 - **E**) 2.77

$$q = m \text{ (specific heat) } \Delta T = 63.0 \text{ g} \times 2.20 \text{ J g}^{-1} \text{ K}^{-1} \times (40.0^{\circ}\text{C} - 20.0^{\circ}\text{C})$$

= 138.6 J K⁻¹ × 20.0 C° = 2772 J = 2.77 kJ

Note that temperature differences (ΔT) in °C are the same as those in absolute temperature – i.e. for temperature differences, 1 C° = 1 K. You do NOT add 273.15 to $\Delta T = 20.0$ C° to convert to K. You could add 273.15 K to each T in °C and then compute $\Delta T = 313.15$ K – 293.15 K = 20 K, however since the ΔT values are the same, there is no need for such a conversion.

Questions 24-29 are worth 3 marks each.

- 24. A 20. g sample of a metal, initially at 200.0°C, was placed in 20. mL of water, initially at 20.0°C. The final temperature of the water and the metal was 37.1°C. Ignore the heat capacity of the container. Water has a specific heat of 4.184 J g⁻¹ K⁻¹, and density 1.00 g/mL. What is the **specific heat** of the metal (in J g⁻¹ K⁻¹)?
 - A) 0.59
 - B) 7.7
 - C) 2.6
 - **D**) 0.44
 - E) 1.0

Heat flows from the hot metal to the cool water:

$$q_{
m metal} = -q_{
m water}$$
 $m_{
m metal} \ c_{
m metal} \ \Delta T_{
m metal} = -m_{
m water} \ c_{
m water} \ \Delta T_{
m water}$

The mass of water is $m_{\text{water}} = \text{volume} \times \text{density} = 20. \text{ mL} \times 1.00 \text{ g/mL} = 20. \text{ g}$ So

$$(sp. heat)_{metal} \times 3258 \text{ g K} = 1431 \text{ J}$$

or

$$(sp. heat)_{metal} = 1431 \text{ J} / (3258 \text{ g K}) = 0.44 \text{ J g}^{-1} \text{ K}^{-1}$$

- 25. A student creates a calibration curve relating the absorbance of FeSCN²⁺(aq) to the concentration of FeSCN²⁺(aq). The slope of this plot is 1.68. If a student mixes 10 ml of 0.2 M Fe³⁺(aq) with 10 mL of 0.4 M SCN⁻(aq) an absorbance of 0.084 is observed. What is the **equilibrium constant** for the reaction, according to the student's data?
 - **A**) 6.7
 - B) 12
 - C) 44
 - D) 3.2
 - E) 120

The calibration curve tells us that the measured absorbance is related to the concentration of $FeSCN^{2+}(aq)$ (in mol L⁻¹) by

Absorbance =
$$1.68 \text{ [FeSCN}^{2+}$$
]

If the measured absorbance is 0.084, then

$$[FeSCN^{2+}] = 0.084 / 1.68 = 0.050 \text{ mol } L^{-1}$$

at equilibrium. Since we only know the initial concentrations of Fe³⁺(aq) and SCN⁻(aq), we must set up an ICE table.

10 mL of each solution are combined to make 20 mL solutions. Initial concentrations of Fe³⁺(aq) and SCN⁻(aq):

$$[Fe^{3+}] = 0.2 \text{ mol } L^{-1} \times 0.010 \text{ L} / 0.020 \text{ L} = 0.1 \text{ mol } L^{-1}$$

 $[SCN^{-}] = 0.4 \text{ mol } L^{-1} \times 0.010 \text{ L} / 0.020 \text{ L} = 0.2 \text{ mol } L^{-1}$

	Fe ³⁺ (aq)	+ SCN ⁻ (aq)	\Rightarrow FeSCN ²⁺ (aq)
Initial	0.1	0.2	0
Change	-x	-x	x
Equilibrium	0.1 - x	0.2 - x	x = 0.050
	= 0.1 - 0.050 = 0.05	= 0.2 - 0.050 = 0.15	

Therefore,

$$K = \frac{\left[\text{FeSCN}^{2+}\right]}{\left[\text{Fe}^{3+}\right]\left[\text{SCN}^{-}\right]} = \frac{0.05}{0.05 \times 0.15} = 6.7$$

- 26. Rank the species CO₂, CO and HCO₂⁻ in order of **increasing bond energy** of the carbon-oxygen bonds. HCO₂⁻ is the formate ion; H is bonded to C.
 - A) $HCO_2^- < CO < CO_2$
 - B) $CO_2 < HCO_2^- < CO$
 - C) $CO < HCO_2^- < CO_2$
 - D) $CO_2 < CO < HCO_2^-$
 - $\mathbf{E)} \quad \mathrm{HCO}_{2}^{-} < \mathrm{CO}_{2} < \mathrm{CO}$

Draw the Lewis structures:

CO

Triple CO bond; the highest bond energy

 CO_2

Two double CO bonds; the next highest bond energies

Formate, HCO₂

Average bond order = 1.5; the lowest bond energies

27. Complete and balance the following redox reaction *in acidic solution* using the smallest whole-number coefficients. What is **the coefficient for water**?

$$HI + HNO_3 \rightarrow I_2 + NO$$

- A) 2
- B) 6
- C) 5
- **D**) 4
- E) 3

ON:
$$HI + HNO_3 \rightarrow I_2 + NO$$

ON: $-1 + 5 0 + 2$

Half reactions:

Oxidation - balance the I atoms

$$2~HI \rightarrow I_2 + 2~e^-$$

Reduction - balance the N atoms

$$HNO_3 + 3 e^- \rightarrow NO$$

You can balance H and O atoms at the end – to save time.

Balance the electrons:

$$3 \times [2 \text{ HI} \rightarrow I_2 + 2 \text{ e}^-]$$

 $2 \times [\text{HNO}_3 + 3 \text{ e}^- \rightarrow \text{NO}]$
 $-----$
 $6 \text{ HI} + 2 \text{ HNO}_3 \rightarrow 3 \text{ I}_2 + 2 \text{ NO}$

Balance the O's in acid by adding 4 H₂O to the right:

$$6 \text{ HI} + 2 \text{ HNO}_3 \rightarrow 3 \text{ I}_2 + 2 \text{ NO} + 4 \text{ H}_2\text{O}$$

The H's are balanced – no additional H⁺'s are required.

Alternatively, use the method suggested in Petrucci, or the method suggested in class.

28. In an insulated bomb calorimeter, 0.568 g of solid citric acid ($C_6H_8O_7$, molar mass 192.12 g/mol) was completely combusted, at 25.00 °C. The calorimeter contained 1032 g of water, initially at 25.00 °C. The temperature of the water was observed to rise to 26.36 °C. Assume all the heat of the reaction went into heating the water, and that the specific heat capacity of water is 4.184 J $g^{-1}K^{-1}$.

Calculate the molar energy change (in kJ mol⁻¹) for combustion of citric acid.

- A) -386
- **B**) −1990
- C) -103
- D) -91.2
- E) -774

$$q_{\text{rxn}} = -q_{\text{calorimeter}}$$

= $-m_{\text{water}} (specific heat)_{\text{water}} \Delta T_{\text{water}} = -1032 \text{ g} \times 4.184 \text{ J g}^{-1} \text{ K}^{-1} \times (26.36 \text{ }^{\circ}\text{C} - 25.00 \text{ }^{\circ}\text{C})$
= -5872 J

To get the heat per mole of citric acid, we divide by the moles of citric acid combusted:

Heat per mole of citric acid combusted = $-5872 \text{ J} / (0.568 \text{ g} / 192.12 \text{ g mol}^{-1})$

- = -1990000 J (to 3 significant digits)
- = -1990 kJ
- 29. A cell is made using $Zn(NO_3)_2(aq) (1.0 \times 10^{-2} \text{ M})$ /Zn and $AgNO_2(aq)$ /Ag (with excess $AgNO_2(s)$). When the cell first begins to operate, at 298.15 K, its voltage is 1.527 V. The excess $AgNO_2(s)$ in the cathode half-cell results because this solid has a low solubility. What is the $\textbf{\textit{K}}_{sp}$ of $AgNO_2$?

Data:

$$Ag^+ + e^- \rightarrow Ag$$
 $E^{\circ}_{red} = 0.800 \text{ V}$
 $Zn^{2^+} + 2e^- \rightarrow Zn$ $E^{\circ}_{red} = -0.763 \text{ V}$

- A) 1.3×10^{-4}
- B) 2.1×10^{-3}
- C) 1.8×10^{-5}
- D) 7.8×10^{-2}
- E) 6.1×10^{-4}

Cell reaction:

$$Zn(s) + 2 Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2 Ag(s)$$

The measured voltage allows us to determine the Ag⁺ concentration via the Nernst equation:

$$E = E^{\circ} - \frac{0.0592 \text{ V}}{z} \log_{10}(Q)$$

$$= (0.800 - (-0.763)) \text{ V} - (0.0296 \text{ V}) \log_{10} \left(\frac{1.0 \times 10^{-2}}{[\text{Ag}^{+}]^{2}}\right)$$

$$= 1.563 \text{ V} - (0.0296 \text{ V}) \log_{10} \left(\frac{1.0 \times 10^{-2}}{[\text{Ag}^{+}]^{2}}\right)$$

$$= 1.527 \text{ V}$$

or

$$\log_{10}\left(\frac{1.0\times10^{-2}}{\left[Ag^{+}\right]^{2}}\right) = \frac{1.563 \text{ V} - 1.527 \text{ V}}{0.0296 \text{ V}} = 1.216$$

or

$$\frac{1.0 \times 10^{-2}}{\left[Ag^{+}\right]^{2}} = 10^{1.216} = 16.45$$

or

$$[Ag^+]^2 = \frac{1.0 \times 10^{-2}}{16.45} = 6.1 \times 10^{-4}$$

Note that we only need the squared silver concentration – see below.

The excess AgNO₂(s) tells us that the solid is in equilibrium with its solvated ions:

$$AgNO_2(s) \implies Ag^+(aq) + NO_2^-(aq)$$

Since the silver and nitrate ions both arise from the dissolution of $AgNO_2(s)$, they must be present in equal concentrations:

$$K_{\rm sp} = [{\rm Ag}^+] [{\rm NO}_2^-] = [{\rm Ag}^+]^2 = 6.1 \times 10^{-4} \text{ (from above)}$$

Some general data are provided on this page.

• A Periodic Table with atomic weights is provided on the next page.

STP = 273.15 K, 1 atm F = 96485 C/mol $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$ $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ $N_A = 6.6256 \times 10^{-34} \text{ Js}$ $N_A = 6.6256 \times 10^{-34} \text{ Js}$

1 atm = 101.325 kPa = 760 mm Hg 1 J = 1 kg m² s⁻² = 1 kPa L = 1 Pa m³ 1 cm³ = 1 mL 1 Hz = 1 cycle/s 0°C = 273.15 K 1 m = 10^9 nm = 10^{10} Å 1 g = 10^3 mg

De Broglie wvaelength:

 $\lambda = h / mv = h / p$

Hydrogen atom energy levels:

$$E_{\rm n} = -R_{\rm H}/n^2 = -2.178 \times 10^{-18} \,{\rm J}/n^2$$

Nernst Equation:

$$E = E^{\circ} - \frac{RT}{zF} \ln Q = E^{\circ} - \frac{0.0257 \text{ V}}{z} \ln Q = E^{\circ} - \frac{0.0592 \text{ V}}{z} \log_{10} Q$$

$$E^{\circ} = \frac{RT}{zF} \ln K \qquad \Delta G^{\circ} = -RT \ln K \qquad \Delta G^{\circ} = -zFE^{\circ}$$

Solubility Guidelines for Common Ionic Solids

TABLE 5.1 Solubility Guidelines for Common Ionic Solids

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⁺) and the NH₄⁺ 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 Ca²⁺, Sr²⁺, and Ba²⁺ are slightly soluble).
- 6. Sulfates are soluble except for those of calcium, strontium, and barium.

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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	65.39	69.723	72.61	74.922	78.96	79.904	83.80
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		29	72	73	74	22	92	11	78	79	80	81	82	1	84		98
Cs	Ba	*La	Ξ	Та	>	Re	SO	=	ద	Au	된	F	Pb	窗	Po	At	R
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]
7	88	68	104	105	106												
止	Ra	**AcUnd	Ung	<u>5</u>	Unh	Atomi	Atomic weights are based on "2C = 12 and conform to the 1987 IUPAC report values rounded to 5 significant digits.	re based o	n 12C = 126	and conform	n to the 198	37 IUPAC re	sport value	s rounded t	o 5 signific	ant digits.	
[223]	226.03	227.03	[261]	126	[263]	Num	Numbers in [] indicate the most stable isotope.	icate the r	ost stable	isotope.							
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			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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