## 1. Which of the following statements is(are) TRUE?

- (i)  $TeCl_2$  is a bent molecule.
- (ii) All of the atoms of TeCl<sub>3</sub><sup>+</sup> are in the same plane.
- (iii) TeCl<sub>4</sub> has one nonbonding pair of electrons on tellurium.
- A) iii
- B) i
- C) i, iii
- D) ii
- E) i, ii
- (i) True. It is AX<sub>2</sub>E<sub>2</sub>
- (ii) False. It is trigonal pyramidal (AX<sub>3</sub>E) which is not planar.
- (iii) True. It is AX<sub>4</sub>E

- 2. Choose the **FALSE** statement about the Lewis structure of the peroxide anion,  $O_2^{2-}$ :
- A) Two resonance forms are required to describe bonding in this anion.
- B) The oxygen-oxygen bond is a single bond.
- C) Each oxygen atom has 3 nonbonding electron pairs.
- D) Each oxygen atom carries a formal charge of -1.
- E) Each oxygen atom obeys the octet rule.

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

- (i) Br atoms are smaller than As atoms.
- (ii) O has a higher first ionization energy than N.
- (iii) Li has a higher magnitude of electron affinity than O.
- (iv) Ba is easier to ionize than Sr.
- (v)  $Cl^-$  is a larger ion than  $Ca^{2+}$ .

- A) i, iii, v
- B) all
- C) i, iv, v
- D) ii, iii, v
- E) i, ii, iv
- (i) True. Br is to the right of As in the fourth period.
- (ii) False. N has a half-filled subshell.
- (iii) False. O is to the right of Li in the second period.
- (iv) True. Ba is below Sr in group II. It has a lower ionization energy.
- (v) True. Cl<sup>-</sup> and Ca<sup>2+</sup> have the same number of electrons (same as Ar i.e., 18), while Ca<sup>2+</sup> has a higher nuclear charge (20 versus 17).

- 4. The O-H bond enthalpy in water is approximately 467 kJ mol<sup>-1</sup>. What is the wavelength of the photon with just enough energy to break one O-H bond?
- A) 23.7 nm
- B) 4130 nm
- C) 467 nm
- D) 256 nm
- E) 213 nm

The energy required to break one O-H bond is  $E = 467 \text{ kJ mol}^{-1} / 6.022 \times 10^{23} \text{ mol}^{-1} = 7.755 \times 10^{-19} \text{ J}$ The frequency of light that can break this bond is

$$v = E/h = 7.755 \times 10^{-19} \text{ J} / 6.626 \times 10^{-34} \text{ J s} = 1.170 \times 10^{15} \text{ s}^{-1}$$

The associated wavelength is  $\lambda = c / v = 2.9979 \times 10^8 \text{ m s}^{-1} / 1.170 \times 10^{15} \text{ s}^{-1} = 2.56 \times 10^{-7} \text{ m} = 256 \text{ nm}$ 

| Name: Student number: |  |
|-----------------------|--|
|-----------------------|--|

- 5. Identify the **incorrect** combination of quantum numbers  $(n, \ell, m_{\ell})$  for the given atomic orbitals:
- A) 4s (4, 0, 0)
- B) 2p (2, 1, 0)
- C) 2p (2, 1, -1)
- D) 3s (3, 0, 1)
- E) 3d (3, 2, -2)

 $m_{\ell}$  cannot be 1, if  $\ell = 0$ 

6. During experiment 2, Cycles of Copper, a student obtains a percent yield of 108%. What is the most likely source of error?

A) Copper oxide was lost during the decanting step.

- B) 108% is a valid yield as the atomic weight of copper at the end of the experiment is higher than at the start.
- C) There was residual solvent left within the copper precipitate at the end of the experiment.
- D) Not all of the zinc reacted with the  $Cu^{2+}$  (aq) to yield Cu(s).
- E) The student accidently added too much nitric acid in the first step.
- A. Losing copper oxide will give too low a yield.
- B. 108% is not a valid yield.
- C. Water in the final stage copper powder gives an anomalously high mass of copper.
- D. Zinc is in excess not all of it will react anyway.
- E. Nitric acid is in excess.

7. Identify the **oxidizing agent** in the following reaction.

16 
$$HCl(aq) + 2 KMnO_4(aq) \rightarrow 5 Cl_2(g) + 2 MnCl_2(aq) + 8 H_2O(l) + 2 KCl(aq)$$

- A) MnCl<sub>2</sub>(aq)
- B) K<sup>+</sup>(aq)
- C) H<sup>+</sup>(aq)
- D) Cl<sup>-</sup>(aq)
- E)  $MnO_4$  (aq)

The oxidation number of Mn in  $MnO_4^-$  is +7. It goes to +2 in  $Mn^{2+}$  - i.e., in  $MnCl_2(aq)$ .

- 8. Which statement is **FALSE** regarding the following three product-favored reactions?
  - (i)  $HCI(g) + NH_3(g) \rightarrow NH_4CI(s)$
  - (ii)  $H_2SO_3(aq) + NaOCI(aq) \rightarrow NaHSO_3(aq) + HOCI(aq)$
  - (iii)  $KH_2PO_4(aq) + KOH(aq) \rightarrow H_2O(I) + K_2HPO_4(aq)$
- A) All of these reactions are Brønsted-Lowry acid-base reactions.
- B) In reaction (ii), H<sub>2</sub>SO<sub>3</sub> is acting as a Brønsted-Lowry acid.
- C) NH<sub>4</sub><sup>+</sup> is the conjugate acid of NH<sub>3</sub>.
- D) HOCl is the conjugate acid of OCl<sup>-</sup>.
- E) HOCl is a stronger acid than H₂SO₃.

Equilibrium shifts away from the stronger acid. Therefore,

 $HCl > NH_4^+$  $H_2SO_3 > HOCl - i.e$ , statement E is false.

The other statements are true.

 $H_2PO_4^- > H_2O$ 

- 9. Dichromate ions,  $Cr_2O_7^{2-}(aq)$ , react with zinc metal in acid solution to produce  $Cr^{3+}(aq)$  and  $Zn^{2+}(aq)$  ions. When the reaction is balanced, such that the smallest possible integers appear as stoichiometric coefficients, what is the **coefficient** of  $Zn^{2+}$ ?
- A) 2
- B) 6
- C) 4
- D) 1
- E) 3

+6 +3 
$$Cr_2O_7^{2-}(aq) + 6 e^- \rightarrow 2 Cr^{3+}(aq)$$

0 +2  

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} \times 3$$

$$Cr_2O_7^{2-}(aq) + 3 Zn(s) \rightarrow 2 Cr^{3+}(aq) + 3 Zn^{2+}(aq)$$

We could balance the O's and H's. But, we already have the answer.

- 10. Which statement is **TRUE** regarding the following three reactions?
  - (i)  $Cd(s) + NiO_2(s) + 2 H_2O(I) \rightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$
  - (ii)  $2 \text{ MnO}_4^-(aq) + 5 \text{ H}_2\text{SO}_3(aq) \rightarrow 2 \text{ Mn}^{2+} + 5 \text{ SO}_4^{2-}(aq) + 4 \text{ H}^+(aq) + 3 \text{ H}_2\text{O}(I)$
  - (iii)  $KH_2PO_4(aq) + KOH(aq) \rightarrow H_2O(I) + K_2HPO_4(aq)$
- A) In reaction (iii),  $\mbox{HPO}_4{}^{2-}$  is the conjugate acid of  $\mbox{H}_2\mbox{PO}_4{}^-.$
- B) In reaction (i), NiO<sub>2</sub> is the reducing agent.
- C) In reaction (i), Cd(s) is oxidized.
- D) In reaction (ii), sulfur is reduced.
- E) In reaction (iii),  $H_2PO_4^-$  is acting as a Brønsted-Lowry base.
- A.  $HPO_4^{2-}$  is the conjugate *base* of  $H_2PO_4^{-}$ .
- B. NiO<sub>2</sub> is the *oxidizing* agent.
- D. Oxidation number of S increases (from 4 to 6). It is *oxidized*.
- E. H<sub>2</sub>PO<sub>4</sub><sup>-</sup> acts as a Brønsted-Lowry acid. It loses H<sup>+</sup>.

- 11. An unknown aqueous solution contains either KNO<sub>3</sub> or K<sub>3</sub>PO<sub>4</sub>. Addition of which **one** of the following aqueous solutions provides a simple visual test that identifies the unknown?
- A) CaBr<sub>2</sub>
- B) Na<sub>2</sub>SO<sub>4</sub>
- C) RbOH
- D) LiBr
- E) NaCl

 $Ca_3(PO_4)_2(s)$  precipitates.

12. Select the one **false** statement concerning the equilibrium,

$$MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$$

for which  $\Delta H^{\circ} = 100.6 \text{ kJ}.$ 

.

- A) Adding MgO(s) does not change the amount of MgCO<sub>3</sub>(s).
- B) Removing CO<sub>2</sub>(g) increases the amount of MgO(s).
- C) Doubling the amount of all three species (with the volume of the reaction vessel fixed) has no effect on the equilibrium.
- D) Halving the size of the reaction vessel increases the amount of MgCO<sub>3</sub>(s).
- E) Increasing the temperature increases the amount of MgO(s).

Doubling the amount of all species with volume fixed doubles the partial pressure of CO<sub>2</sub>. Net reverse reaction ensues.

13. For the heterogeneous reaction,

$$CaCO_3(s)$$
  $\Longrightarrow$   $CaO(s) + CO_2(g)$ ,

the equilibrium constant at 112°C is  $K_p = 0.220$ . If the partial pressure of  $CO_2(g)$  is 0.50 bar at this same temperature, which one of the following statements is **TRUE**?

.

- A) Q > K, the reaction will proceed to the right.
- B) Q < K, the reaction will proceed to the left.
- C) Q < K, the reaction will proceed to the right.
- D) Q = K, the system is at equilibrium.
- E) Q > K, the reaction will proceed to the left.

 $Q = P[CO_2] = 0.50 > K_p = 0.220$ . There will be net reverse reaction.

14. 1.41 bar of PCl<sub>5</sub>(g), 7.95 bar of PCl<sub>3</sub>(g) and 7.95 bar of Cl<sub>2</sub>(g) are at equilibrium in a reaction vessel. Calculate the **equilibrium constant**  $K_p$  for

$$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$$

at the temperature of the equilibrium mixture.

A) 9.71

- B) -1.30
- C) 28.6
- D) 51.8
- E) 44.8

$$K_p = P[PCl_3] P[Cl_2] / P[PCl_5] = 7.95 \times 7.95 / 1.41 = 44.8$$

15. The equilibrium constant  $K_p$  for

$$C(s) + CO_2(g) \implies 2 CO(g)$$

is 1.52 at 700°C. If the partial pressure of CO in an equilibrium mixture at 700°C is 1.30 bar, what is the partial pressure of CO<sub>2</sub> (in bar)?

- A) 1.30
- B) 1.11
- C) 0.900
- D) 0.860
- E) 1.17

$$K_p = P^2[CO] / P[CO_2] = 1.52 = 1.30^2 / P[CO_2]$$

Therefore, 
$$P[CO_2] = 1.30^2 / 1.52 = 1.11$$
 bar

- 16. A student creates a calibration curve relating the absorbance of FeSCN<sup>2+</sup>(aq) to the concentration of FeSCN<sup>2+</sup>(aq). The slope of this plot is 1.68. If a student mixes 10.0 mL of 0.20 M Fe<sup>3+</sup>(aq) with 10.0 mL of 0.40 M SCN<sup>-</sup>(aq) an absorbance of 0.084 is observed. What is the **equilibrium constant** for the reaction?
- A) 3.2
- B) 6.7
- C) 12
- D) 120
- E) 44
- $1.68 [FeSCN^{2+}] = 0.084 \rightarrow [FeSCN^{2+}] = 0.084 / 1.68 = 0.05$

Fe<sup>3+</sup>(aq) + SCN<sup>-</sup>(aq) FeSCN<sup>2+</sup>(aq)

I 0.10 0.20 0 note dilution of Fe<sup>3+</sup> and SCN<sup>-</sup>

C 
$$-x$$
  $-x$   $x$ 

E  $0.10-x$   $0.20-x$   $x$ 

$$K = [FeSCN^{2+}] / ([Fe^{3+}] [SCN^{-}]) = 0.05 / ((0.10 - 0.05) (0.20 - 0.05)) = 6.7$$

- 17. Heroin, a derivative of morphine, is a powerful analgesic and a powerful narcotic agent. **Calculate**  $K_b$  for heroin if the pH of a  $1.7 \times 10^{-3}$  M solution was found to be 9.60.
- A) 9.5 x 10<sup>-7</sup>
- B) 2.3 x 10<sup>-2</sup>
- C)  $8.3 \times 10^{-7}$
- D) 1.5 x 10<sup>-7</sup>
- E) 3.7 x 10<sup>-7</sup>

Heroin(aq) + 
$$H_2O(I)$$
  $\longrightarrow$  HHeroin<sup>+</sup>(aq) +  $OH^-(aq)$   
I 1.7 x  $10^{-3}$  0 0  
C  $-x$   $x$   $x$   
E 1.7 x  $10^{-3} - x$   $x$ 

pH = 9.60 
$$\rightarrow$$
 pOH = 4.40  $\rightarrow$  [OH<sup>-</sup>] = 10<sup>-4.40</sup> = 3.98 x 10<sup>-4</sup> = x

$$K_b = [HHeroin^+] [OH^-] / [Heroin] = 3.98 \times 10^{-4} \times 3.98 \times 10^{-4} / (1.7 \times 10^{-3} - 3.98 \times 10^{-4}) = 9.5 \times 10^{-7}$$

- 18. Your stomach (volume = 2.5 L) has a pH of 1.00 because of the presence of HCl. **How many** grams of  $Mg(OH)_2$  (58.3 g mol<sup>-1</sup>) do you need to add to completely neutralize the acid in your stomach?
- A) 7.3 g
- B) 15 g
- C) 21 g
- D) 2.9 g
- E) 5.8 g

 $[H^+]$  =  $10^{-1.00}$  mol L<sup>-1</sup> = 0.10 mol L<sup>-1</sup> in the stomach Number of moles of H<sup>+</sup> = n = 2.5 L × 0.10 mol L<sup>-1</sup> = 0.25 mol Number of moles of OH<sup>-</sup> to neutralize H<sup>+</sup> = 0.25 mol Number of moles of Mg(OH)<sub>2</sub> = 0.125 mol (two OH<sup>-</sup> for every Mg(OH)<sub>2</sub>)

Mass of Mg(OH)<sub>2</sub> =  $0.125 \text{ mol} \times 58.3 \text{ g mol}^{-1} = 7.3 \text{ g}$ 

- 19. A 2.60 g sample of propanoic acid (CH<sub>3</sub>CH<sub>2</sub>COOH, molar mass = 74.1 g mol<sup>-1</sup>,  $K_a$  = 1.40 x 10<sup>-5</sup>) was dissolved in water and made up to a final volume of 100. mL in water. What is the pH of this solution?
- A) 2.66
- B) 4.85
- C) 3.26
- D) 2.32
- E) 1.82

moles of  $CH_3CH_2COOH = 2.60 \text{ g} / 74.1 \text{ g mol}^{-1} = 0.0351 \text{ mol}$  $[CH_3CH_2COOH] = 0.0351 \text{ mol} / 0.100 \text{ L} = 0.351 \text{ mol L}^{-1}$ 

$$CH_3CH_2COOH(aq) + H_2O(I) \longrightarrow CH_3CH_2COO^-(aq) + H_3O^+(aq)$$
 $I = 0.351 = 0 = 0$ 
 $C = -x = x = x$ 
 $E = 0.351 - x = x = x$ 

$$K_a = 1.40 \times 10^{-5} = x^2 / (0.351 - x)$$

$$x = 0.00221 = [H_3O^+]$$

$$pH = -log_{10}(0.00221) = 2.66$$

20. Order the following species according to increasing acid dissociation constant,  $K_a$ :

 $\mathsf{CH_3COOH},\,\mathsf{CF_3COOH},\,\mathsf{CH_2FCOOH},\,\mathsf{CH_3CH_2OH}$ 

- .
- A)  $CH_3COOH < CF_3COOH < CH_2FCOOH < CH_3CH_2OH$
- B) CH<sub>3</sub>COOH < CH<sub>2</sub>FCOOH < CF<sub>3</sub>COOH < CH<sub>3</sub>CH<sub>2</sub>OH
- C) CH<sub>3</sub>CH<sub>2</sub>OH < CF<sub>3</sub>COOH < CH<sub>2</sub>FCOOH < CH<sub>3</sub>COOH
- D) CH<sub>3</sub>CH<sub>2</sub>OH < CH<sub>3</sub>COOH < CH<sub>2</sub>FCOOH < CF<sub>3</sub>COOH
- E) CF<sub>3</sub>COOH < CH<sub>2</sub>FCOOH < CH<sub>3</sub>CH<sub>2</sub>OH < CH<sub>3</sub>COOH

CH<sub>3</sub>CH<sub>2</sub>OH is weakest. The others are carboxylic acids with (1) the inductive effect of a second O bonded to C (it pulls harder on the O bearing the minus charge, in the conjugate base), and (2) two resonance structures of the conjugate base spreading out the minus charge. The three carboxylic acids are distinguished by the inductive effect due to F. Three F's have greater effect than one F.

- 21. Dissolving 4.24 g of CaF<sub>2</sub> in 50.0 mL of pure water at 20.00°C results in a solution with temperature 16.79°C. What is the **enthalpy of dissolution of CaF<sub>2</sub> (in kJ mol<sup>-1</sup>)?** Assume that the specific heat of the solution equals 4.18 J K<sup>-1</sup> g<sup>-1</sup>.
- A) +13.4
- B) +1.05
- C) -1.05
- D) -13.4
- E) -671

The solution has mass =  $4.24 \text{ g} + 50.00 \text{ mL} \times 1.00 \text{ g mL}^{-1} = 54.24 \text{ g}$ The solution has heat capacity, C =  $54.24 \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} = 226.7 \text{ J K}^{-1}$ The dissolution consumes heat, causing the temperature to decrease.

$$q = C(20.00 - 16.79) = 226.7 \text{ J K}^{-1} \times 3.21 \text{ K} = 727.8 \text{ J}$$

Note that, in calorimetry, q is the heat required to return the system to its initial temperature.

The enthalpy of dissolution of  $CaF_2$  is for dissolution of one mole of  $CaF_2$ . Moles of  $CaF_2 = 4.24 \, \text{g} / 78.07 \, \text{g mol}^{-1} = 0.0543 \, \text{mol}$ 

 $\Delta H = 727.8 \text{ J} / 0.0543 \text{ mol} = 13401 \text{ J} \text{ mol}^{-1} = 13.4 \text{ kJ mol}^{-1}$ 

Student number:

- <sup>22.</sup> A chemical reaction with an enthalpy change  $\Delta H^{\circ} = -400$  kJ is carried out in a calorimeter containing 1500 cm<sup>3</sup> of pure water initially at 25.0°C. What is the **final temperature** (in °C) of the water?
  - .
- A) 67.5
- B) -28.7
- C) 336.7
- D) 69.3
- E) 88.8

Since the reaction is exothermic, the temperature goes up.

$$\Delta T = 400 \text{ kJ} / C$$

where 
$$C = 1500 \text{ cm}^3 \times 1.00 \text{ g cm}^{-3} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} = 62700 \text{ J K}^{-1}$$

Therefore, 
$$\Delta T = 400 \times 10^3 \,\text{J} / 62700 \,\text{J} \,\text{K}^{-1} = 63.8 \,\text{K}$$

The final temperature is 25.0 + 63.8 °C = 88.8 °C

### 23. PCl₅(s) can be prepared by the reaction,

$$PCl_3(I) + Cl_2(g) \rightarrow PCl_5(s)$$
.

Calculate the **enthalpy change** (in kJ) that accompanies the production of 100.0 g of PCl<sub>5</sub>(s) by the above reaction, given the following data.

$$P_4(s) + 6 Cl_2(g) \rightarrow 4 PCl_3(I)$$
  $\Delta H^{\circ} = -1280 \text{ kJ mol}^{-1}$   
 $P_4(s) + 10 Cl_2(g) \rightarrow 4 PCl_5(s)$   $\Delta H^{\circ} = -1774 \text{ kJ mol}^{-1}$ 

- A) +124.7
- B) -258.1
- C) +59.31
- D) -124.7
- E) -59.31

Note

$$P_{4}(s) + 10 Cl_{2}(g) \rightarrow 4 PCl_{5}(s)$$

$$- P_{4}(s) + 6 Cl_{2}(g) \rightarrow 4 PCl_{3}(l)$$

 $4 \times PCl_3(I) + Cl_2(g) \rightarrow PCl_5(s)$ 

Therefore,  $\Delta H$  of the target reaction is

$$\Delta H = (-1774 + 1280)/4 \text{ kJ mol}^{-1} = -123.5 \text{ kJ mol}^{-1}$$

100.0 g of PCl<sub>5</sub>(s) produced  $\rightarrow$  100.0 g /208.24 g mol<sup>-1</sup> = 0.4802 mol of PCl<sub>5</sub>(s) produced = the extent of reaction

The desired change in enthalpy =  $-123.5 \text{ kJ mol}^{-1} \times 0.4802 \text{ mol} = -59.31 \text{ kJ}$ .

24. Determine the **enthalpy of formation** (in kJ mol<sup>-1</sup>) of hydrogen chloride gas using the following bond enthalpy data:

 $\begin{array}{lll} \text{CI-CI} & 243 \text{ kJ mol}^{-1} \\ \text{H-H} & 436 \text{ kJ mol}^{-1} \\ \text{H-CI} & 431 \text{ kJ mol}^{-1} \\ \end{array}$ 

- .
- A) 17.1 B) -91.5
- C) 91.5
- D) -17.1
- E) -53.4

The formation reaction of HCl(g) is

$$\frac{1}{2}$$
 H<sub>2</sub>(g) +  $\frac{1}{2}$  Cl<sub>2</sub>(g)  $\rightarrow$  HCl(g)

For this reaction,

$$\Delta H = \frac{1}{2}D(H-H) + \frac{1}{2}D(Cl-Cl) - D(H-Cl) = \frac{1}{2}436 + \frac{1}{2}243 - 431 \text{ kJ mol}^{-1}$$
  
= -91.5 kJ mol<sup>-1</sup>

### 25. Considering the reaction

$$2 B(s) + 3 F_2(g) \rightarrow 2 BF_3(g)$$

and the data below, identify the **FALSE** statement(s). enthalpy of formation of B(g) =  $563 \text{ kJ mol}^{-1}$  bond enthalpy of F-F bond =  $159 \text{ kJ mol}^{-1}$  bond enthalpy of B-F bond =  $646 \text{ kJ mol}^{-1}$ 

- (i) The reaction is a redox reaction.
- (ii) The reaction of boron and fluorine is endothermic.
- (iii) The sublimation of boron is an endothermic process.
- (iv)  $F_2(g)$  is a highly reactive species.

# A) <mark>ii</mark>

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

### (i) True. Oxidation numbers change: B (0 to +3) and F (0 to -1)

(ii) False

$$2 B(g) + 3 F_2(g) \rightarrow 2 BF_3(g)$$

 $2 B(s) \rightarrow 2 B(g)$ 

$$2 B(s) + 3 F_2(g) \rightarrow 2 BF_3(g)$$

Therefore,

 $\Delta H = 2 \Delta H_f[B(g)] + \Delta H[gas phase reaction]$ 

$$= 2 \times 563 \text{ kJ mol}^{-1} + 3 D(F-F) + 2 \times 3 D(B-F)$$

 $= -2273 \text{ kJ mol}^{-1}$ 

The reaction is exothermic.

- (iii) True. Sublimation (solid  $\rightarrow$  gas) is always endothermic bonds are only broken.
- (iv) True. Fluorine is the most reactive element.