

Name: _____ Student Number: _____

CARLETON UNIVERSITY

Final Examination April 2015

DURATION: 3 HOURS

No. of Students: _____

Department Name & Course Number: CHEM 1002 A, N and V**Instructor** Bob Burk

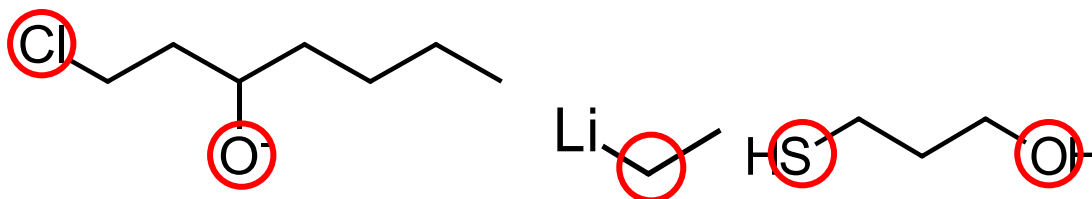
AUTHORIZED MEMORANDA CALCULATOR ONLY

Students MUST count the number of pages in this examination question paper before beginning to write, and report any discrepancy immediately to a proctor. This question paper has 12 pages. This examination paper MAY NOT be taken from this examination room.

Some useful data appear on pages 13 and 14. You may tear those pages if you wish.

Part A. Answer all twelve questions with a few sentences or equations (5 marks each).

1. Circle any nucleophilic centres in the following three molecules:



Marks	
Total	
A	
B1	
B2	
B3	
C1	
C2	
C3	
C4	
C5	
Total	

2. Are the entropy changes for the following processes positive or negative?

- (a) $2 \text{CH}_3\text{OH}_{(l)} + 3 \text{O}_{2(g)} \rightarrow 2 \text{CO}_{2(g)} + 4 \text{H}_2\text{O}_{(g)}$ **Positive** ($\Delta n > 0$)
- (b) $\text{Br}_{2(l)}$ is cooled from at 10°C to 5°C **Negative** (The system is losing energy)
- (c) $\text{K}_{(g)}^+ \xrightarrow{\text{H}_2\text{O}} \text{K}_{(aq)}^+$ **Negative** (bonds are being formed)
- (d) $\text{Na}_{(l)} \rightarrow \text{Na}_{(s)}$ **Negative** (freezing)
- (e) $\text{Cl}_{2(g)}$ at 1 bar, $25^\circ\text{C} \rightarrow \text{Cl}_{2(g)}$ at 2 bar, 25°C **Negative** (compression of a gas)

3. What three factors, related to molecular collisions, contribute to the value of a kinetic rate constant?

Frequency of collisions

Energy of collisions

Orientation of collisions

4. For the reaction $\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)$, which way (left or right) will the equilibrium shift if we double the volume of the container at constant temperature? Why?

For this reaction, $Q = \frac{P_{\text{PCl}_5}}{P_{\text{PCl}_3} P_{\text{Cl}_2}}$. If we double the volume, all three partial pressures will decrease by

half. The denominator of this expression will therefore decrease more than the numerator, Q will increase, and so the equilibrium will move to the left until $Q = K$.

5. Rank the following acids in order of strength (1 = strongest, 5 = weakest):

Acetic acid 5

Hydrochloric acid 1

Chloroacetic acid 4

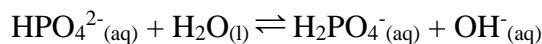
Dichloroacetic acid 3

Difluoroacetic acid 2

6. Does the solubility of $\text{Na}_2\text{HPO}_4(\text{s})$ increase or decrease as the pH is increased? Why? NaOH is a very strong base. $K_{\text{a}3}$ for H_3PO_4 is 4.8×10^{-13} .



Because NaOH is a strong base, $\text{Na}^+(\text{aq})$ is a weak acid and has no acid-base properties. But $K_{\text{a}2}$ for H_3PO_4 is small, meaning $\text{H}_2\text{PO}_4^-(\text{aq})$ is a weak acid, so its conjugate base, $\text{HPO}_4^{2-}(\text{aq})$, is relatively strong base. Thus in solution,



Increasing the pH increases $[\text{OH}^-(\text{aq})]$, pushing this equilibrium to the left, increasing $[\text{HPO}_4^{2-}(\text{aq})]$, which pushes the first equilibrium to the left, i.e. the solubility decreases.

7. Explain using Hard Soft Acid Base theory, why gold is commonly found as the metal, not as the oxide or sulphide.

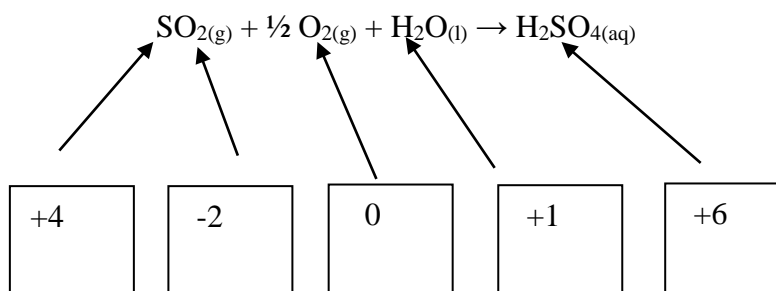
Gold is a relatively large atom, and is thus considered a soft acid. Oxide and sulphide ions are small, and therefore hard bases. A soft acid will not readily combine with a hard base.

8. Would you expect $\text{K}_2\text{Ni}(\text{NO}_2)_2$ to be diamagnetic or paramagnetic? Why?

Ni is s^2d^8 . In this compound, the nickel is Ni^0 , which is d^8 . Six electrons will be paired in the t_{2g} level, and the other two unpaired in the e_g level. The compound is therefore paramagnetic.

Even though it was not required, I forgot to supply the spectrochemical series, so this question will be marked, but the exam will be graded out of 175 instead of 180.

9. Write the oxidation numbers for each of the indicated atoms:



10. The decay series beginning with ^{238}U includes the isotope ^{222}Rn . What is the significance of this fact, with respect to human health?

Radon is a gas, and so it is easily inhaled, and it is radioactive. This increases our exposure to ionizing radiation, which causes cancer.

11. Which of the acids in the table below should you use to prepare a buffer of pH 7.0? Why?

Acid	K_a
H_3AsO_3	0.0055
Carbonic	4.5×10^{-7}
H_2PO_4^-	6.2×10^{-8}
CH_3COOH	1.8×10^{-5}
HF	6.3×10^{-4}

To make a buffer with the greatest buffer capacity, we use an acid with a $\text{p}K_a$ value as close to the desired pH as possible. The $\text{p}K_a$ values are -1.26, 6.35, 7.21, 4.74 and 3.20, respectively. That of H_2PO_4^- (7.20) is the closest.

12. In order to manufacture fluorine gas, $\text{F}_{2(\text{g})}$, why do we not simply electrolyze a solution of $\text{NaF}_{(\text{aq})}$?

If we did so, water would be preferentially oxidized to O_2 instead of F^- to F_2 at the anode, because the oxidation potential of water is more positive than that of $\text{F}^-_{(\text{aq})}$.

Part B. Answer both questions B1 and B2 (20 marks each).

- B1. (a) [10 marks] An automotive part is to be electroplated with chromium metal from a solution of $\text{CrO}_3(\text{aq})$. If the surface area of the part is 0.75 m^2 , the current used is 0.125 A , and the desired thickness of chromium metal is $0.050 \times 10^{-6} \text{ m}$, how long (in minutes) must the electrolysis be carried out for? The density of $\text{Cr}_{(\text{s})}$ is 7.14 g cm^{-3} .

$$0.75 \text{ m}^2 \times (0.050 \times 10^{-6} \text{ m}) \left(\frac{10^6 \text{ cm}^3}{\text{m}^3} \right) = 0.0375 \text{ cm}^3 \text{ Cr}_{(\text{s})}$$

$$0.0375 \text{ cm}^3 \left(\frac{7.14 \text{ g}}{\text{cm}^3} \right) = 0.268 \text{ g Cr}_{(\text{s})}$$

$$\frac{0.268 \text{ g Cr}_{(\text{s})}}{52 \text{ g mol}^{-1}} = 5.15 \times 10^{-3} \text{ mol Cr}_{(\text{s})}$$

The Cr in $\text{CrO}_3(\text{s})$ is at a 6+ oxidation state. Thus,

$$n = \frac{6 \text{ mol e}^-}{\text{mol Cr}} (5.15 \times 10^{-3} \text{ mol Cr}) = 0.0309 \text{ mol e}^-$$

$$it = nF \quad t = \frac{nF}{i} = \frac{0.0309 \text{ mol}(96487 \text{ C mol}^{-1})}{0.125 \text{ C s}^{-1}} \left(\frac{1 \text{ min}}{60 \text{ s}} \right) = 397 \text{ min}$$

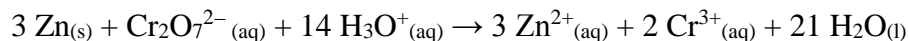
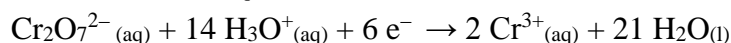
- (b) [10 marks] A Galvanic cell is constructed using a $\text{Zn}_{(\text{s})}$ anode and a cathode reaction involving the reduction of $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ (see the reduction potential table on the last page).

(i) Write the balanced overall reaction.

The reaction at the anode is: $\text{Zn}_{(\text{s})} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{ e}^-$

and at the cathode: $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{ H}_3\text{O}^+(\text{aq}) + 6 \text{ e}^- \rightarrow 2 \text{ Cr}^{3+}(\text{aq}) + 21 \text{ H}_2\text{O}(\text{l})$

To balance, we must multiply the anode reaction by 3 and add to the reduction reaction:



(ii) Calculate the standard cell potential (in V).

$$E^\circ = -(-0.762) + 1.232 = 1.994 \text{ V}$$

(iii) Calculate the cell potential at 30°C at pH 2.00, when $[\text{Cr}_2\text{O}_7^{2-}(\text{aq})] = 0.01 \text{ M}$, and $[\text{Zn}^{2+}(\text{aq})] = [\text{Cr}^{3+}(\text{aq})] = 0.10 \text{ M}$

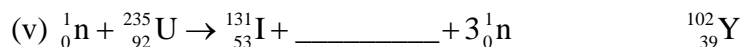
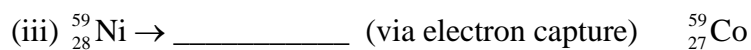
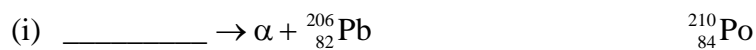
$$Q = \frac{[\text{Zn}^{2+}(\text{aq})]^3 [\text{Cr}^{3+}(\text{aq})]^2}{[\text{Cr}_2\text{O}_7^{2-}(\text{aq})] [\text{H}_3\text{O}^+(\text{aq})]^{14}} = \left(\frac{0.10^3 0.10^2}{0.01(10^{-2})^{14}} \right) = 1.0 \times 10^{25}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln(Q)$$

$$= 1.994 \text{ J C}^{-1} - \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1} (30 + 273.15) \text{ K}}{6(96,487 \text{ C mol}^{-1})} \ln(1.0 \times 10^{25})$$

$$= 1.994 - 0.251 = 1.743 \text{ V}$$

B2. (a) [5 marks] Complete the following nuclear reactions by filling in the blanks.



(b) [10 marks] Calculate the total energy produced (in kJ, not kJ mol⁻¹) when 100 kg ²³⁵U undergoes fission according to the reaction ${}^1_0\text{n} + {}^{235}_{92}\text{U} \rightarrow {}^{91}_{36}\text{Kr} + {}^{142}_{56}\text{Ba} + 3{}^1_0\text{n}$, given the following masses in amu: ¹n 1.0087; ²³⁵U 235.0439; ⁹¹Kr 90.9234; ¹⁴²Ba 141.9164

$$\Delta m = 90.9234 + 141.9164 + 3(1.0087) - 1.0087 - 235.0439$$

$$= -0.1867 \text{ amu (per nucleus)}$$

$$\times \frac{1.66 \times 10^{-27} \text{ kg}}{\text{amu}} \times 6.02 \times 10^{23} \text{ mol}^{-1} = -1.87 \times 10^{-4} \text{ kg mol}^{-1}$$

$$\frac{100 \text{ kg}}{0.235 \text{ kg mol}^{-1}} = 425 \text{ mol } {}^{235}\text{U}$$

$$425 \text{ mol } {}^{235}\text{U} (-1.87 \times 10^{-4} \text{ kg mol}^{-1}) = 0.0796 \text{ kg}$$

$$\Delta E = \Delta mc^2$$

$$= 0.0796 \text{ kg} (3.00 \times 10^8 \text{ m s}^{-1})^2$$

$$= 7.16 \times 10^{15} \text{ J}$$

$$= 7.16 \times 10^{12} \text{ kJ}$$

(c) [5 marks] The half-life of ²⁶⁶Mt is 3.4 ms. Calculate the mass (in ng) of ²⁶⁶Mt left after 20.0 ms from an initial mass of 12.0 ng.

$$k = \frac{0.693}{t_{1/2}} = \frac{.693}{.0034 \text{ s}} = 203.8 \text{ s}^{-1}$$

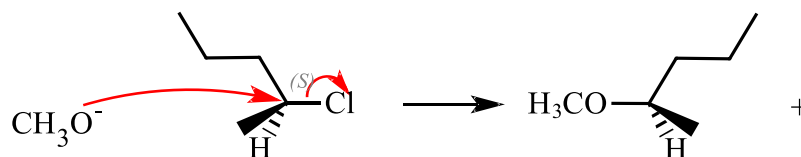
$$N = N_0 e^{-kt}$$

$$\text{or, } m = m_0 e^{-kt} = 12.0 \text{ ng} (e^{-203.8 \text{ s}^{-1} (0.020 \text{ s}^{-1})}) = 0.204 \text{ ng}$$

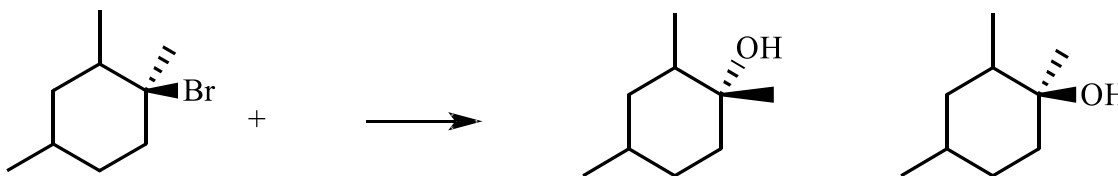
Part C. Answer any four of the six questions C1 – C6. If you answer more than four, the best four will be used to calculate your mark (20 marks each).

C1. (a) Show the S_N2 mechanism for the reaction of the CH_3O^- ion with *S*-2-chloropentane. Show the flow of electrons with arrows, draw the leaving group, and draw the product with the proper stereochemistry.

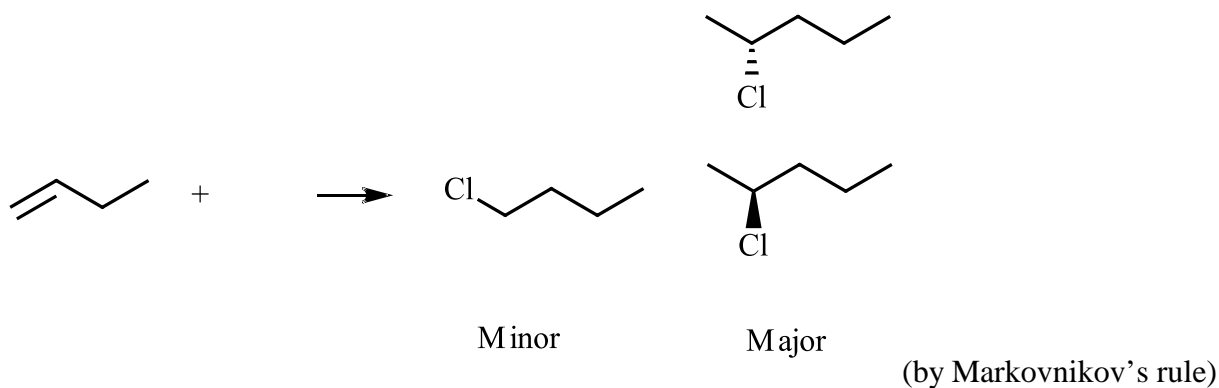
I meant *S*-2-chloropentane, not *S*-2-chloropropane. *S*-2-chloropropane is not chiral so the question is meaningless and will not be graded. The other three will be reweighted as shown below.



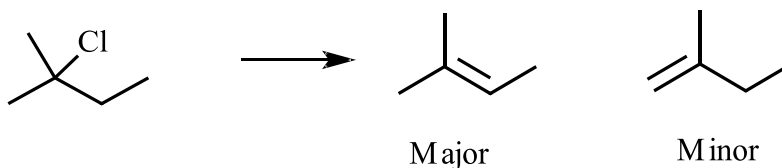
(b) [6 marks] Draw the two possible products of the following substitution reaction:



(c) [7 marks] Draw the two possible products (with stereochemistries) for the addition reaction of HCl with 1-butene and indicate which is major and which is minor.



(d) [7 marks] If HCl is eliminated from the molecule shown below, draw the two products and indicate which is major and which is minor.



(The major product is the more highly substituted alkene)

C2. For the reaction $2 \text{NO}_{(g)} + \text{Cl}_{2(g)} \rightarrow 2 \text{NOCl}_{(g)}$, the following rate data were collected at 25.0°C:

Experiment	$[\text{NO}_{(g)}], \text{M}$	$[\text{Cl}_{2(g)}], \text{M}$	Rate, M s^{-1}
1	.13	.20	0.010
2	.26	.20	0.040
3	.13	.10	0.005

(a) [4 marks] Determine the rate law for this reaction. Comparing experiments 1 and 2, we see that if the concentration of $\text{NO}_{(g)}$ is doubled, the rate quadruples, thus the reaction is second order in $[\text{NO}_{(g)}]$. Comparing experiments 1 and 3, we see that if the concentration of $\text{Cl}_{2(g)}$ is doubled, the rate doubles, thus the reaction is first order in $[\text{Cl}_{2(g)}]$. The rate law is therefore $\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$.

(b) [4 marks] Calculate the value and units of the rate constant.

$$\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$$

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{NO}]^2[\text{Cl}_2]} \\ &= \frac{0.010 \text{ M s}^{-1}}{(0.13 \text{ M})^2(0.20 \text{ M})} \\ &= 2.96 \text{ M}^{-2}\text{s}^{-1} \text{ (or } 2.96 \text{ L}^2\text{mol}^{-2}\text{s}^{-1}\text{)} \end{aligned}$$

(Note that we could have used any of the three experiments to arrive at this same result.)

(c) [4 marks] Calculate the rate of reaction if $[\text{NO}_{(g)}] = 0.35 \text{ M}$ and $[\text{Cl}_{2(g)}] = 0.05 \text{ M}$.

$$\text{rate} = k[\text{NO}]^2[\text{Cl}_2] = 2.96 \text{ M}^{-2}\text{s}^{-1}(0.35 \text{ M})^2(0.05 \text{ M}) = 0.0181 \text{ M s}^{-1}$$

(d) [8 marks] Experiment #1 was repeated using the same concentrations, but at 35.0°C. Calculate the reaction rate under these conditions. The reaction has an activation energy of 11.5 kJ mol^{-1} .

$$k_{25^\circ\text{C}} = \text{Ae}^{\left(\frac{-E_a}{R(298\text{K})}\right)}$$

$$k_{35^\circ\text{C}} = \text{Ae}^{\left(\frac{-E_a}{R(308\text{K})}\right)}$$

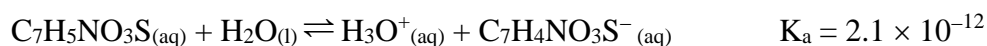
$$\frac{k_{35^\circ\text{C}}}{k_{25^\circ\text{C}}} = \frac{\text{Ae}^{\left(\frac{-E_a}{R(308\text{K})}\right)}}{\text{Ae}^{\left(\frac{-E_a}{R(298\text{K})}\right)}} = \frac{e^{\left(\frac{-E_a}{R(308\text{K})}\right)}}{e^{\left(\frac{-E_a}{R(298\text{K})}\right)}} = \frac{e^{\left(\frac{-11500 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1}\text{mol}^{-1}(308\text{K})}\right)}}{e^{\left(\frac{-11500 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1}\text{mol}^{-1}(298\text{K})}\right)}} = \frac{0.0112}{0.00964} = 1.16$$

In other words, the rate constant is 1.16 times greater at 35°C.

Thus $k = 1.16(0.010 \text{ M s}^{-1}) = 0.0116 \text{ M s}^{-1}$ at 35°C.

- C3. [20 marks] The sugar substitute saccharin ($C_7H_5NO_3S$) is a very weak acid ($K_a = 2.1 \times 10^{-12}$ – think carefully about the magnitude of this number). Calculate the pH in a solution that contains 3.48 g of saccharin per litre. You may not neglect the autohydrolysis of water in this problem.

$$\frac{3.48 \text{ g}}{(7 \times 12.01 + 5 \times 1.00 + 14.00 + 3 \times 16.00 + 32.06) \text{ g mol}^{-1}} = 0.0190 \text{ mol saccharin}$$



Total positive charge is that of $H_3O^+_{(aq)}$ alone.

Total negative charge is from $OH^-_{(aq)}$ as well as $C_7H_4NO_3S^-_{(aq)}$

Thus,

$$\begin{aligned} [H_3O^+_{(aq)}] &= [OH^-_{(aq)}] + [C_7H_4NO_3S^-_{(aq)}] \\ &= \frac{1.0 \times 10^{-14}}{[H_3O^+_{(aq)}]} + [C_7H_4NO_3S^-_{(aq)}] \end{aligned}$$

$$\text{or, } [C_7H_4NO_3S^-_{(aq)}] = [H_3O^+_{(aq)}] - \frac{1.0 \times 10^{-14}}{[H_3O^+_{(aq)}]}$$

$$\frac{[H_3O^+_{(aq)}][C_7H_4NO_3S^-_{(aq)}]}{[C_7H_5NO_3S_{(aq)}]} = K_a \quad \text{but } K_a \text{ is so small that } [C_7H_5NO_3S_{(aq)}] \approx 0.0190 \text{ mol L}^{-1}$$

Thus,

$$\frac{[H_3O^+_{(aq)}][C_7H_4NO_3S^-_{(aq)}]}{0.0190} = K_a$$

$$\frac{[H_3O^+_{(aq)}] \left[[H_3O^+_{(aq)}] - \frac{1.0 \times 10^{-14}}{[H_3O^+_{(aq)}]} \right]}{0.0190} = K_a$$

$$[H_3O^+_{(aq)}]^2 - 1.0 \times 10^{-14} = 0.0190 K_a$$

$$[H_3O^+_{(aq)}]^2 - 1.0 \times 10^{-14} = 0.0190 (2.1 \times 10^{-12})$$

$$[H_3O^+_{(aq)}]^2 - 1.0 \times 10^{-14} = 3.99 \times 10^{-14}$$

$$[H_3O^+_{(aq)}] = (3.99 \times 10^{-14} + 1.00 \times 10^{-14})^{1/2} = 2.23 \times 10^{-7}$$

$$\text{pH} = -\log_{10} [H_3O^+_{(aq)}] = -\log_{10} (2.23 \times 10^{-7}) = 6.65$$

C4. Consider the reaction: $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$, for which the equilibrium constant is 0.920 at 800°C.

(a) [10 marks] If 0.050 bar of $\text{H}_2(\text{g})$ and 0.040 bar of $\text{CO}_2(\text{g})$ are placed in a container at 800°C, find the partial pressures of each gas when equilibrium is reached.

	$\text{H}_2(\text{g})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$	$\text{CO}(\text{g})$
Initial pressure, bar	0.050	0.040	0	0
Change, bar	-x	-x	+x	+x
Equilibrium pressure, bar	0.050-x	0.040-x	x	x

$$K = \frac{P_{\text{H}_2\text{O}}P_{\text{CO}}}{P_{\text{H}_2}P_{\text{CO}_2}} = \frac{x(x)}{(0.050-x)(0.040-x)} = 0.920$$

$$x^2 = 0.920(0.002 - 0.090x + x^2)$$

$$x^2 = 0.00184 - 0.0828x + 0.920x^2$$

$$0.080x^2 + 0.0828x - 0.00184 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.0828 \pm \sqrt{(0.0828)^2 - 4(0.080)(-0.00184)}}{2(0.080)}$$

$$= \frac{-0.0828 \pm 0.08628}{0.160} = -1.057 \text{ or } 0.02176$$

Choosing the positive root (since x is a partial pressure),

$$p_{\text{H}_2} = 0.050 - 0.022 = 0.028 \text{ bar} \quad p_{\text{CO}_2} = 0.040 - 0.022 = 0.018 \text{ bar}$$

$$p_{\text{H}_2\text{O}} = x = 0.022 \text{ bar} \quad p_{\text{CO}} = x = 0.022 \text{ bar}$$

(b) [5 marks] Calculate ΔG° for this reaction at 800°C (kJ mol^{-1})

$$\Delta G^\circ = -RT \ln(K)$$

$$= -8.314 \text{ J K}^{-1} \text{ mol}^{-1} (800 + 273)\text{K} (\ln(0.920))$$

$$= 743.8 \text{ J mol}^{-1}$$

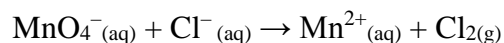
$$= 0.744 \text{ kJ mol}^{-1}$$

(c) [5 marks] The reaction has $\Delta H^\circ = 41.2 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = 42.1 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculate the temperature (in K) above which the reaction becomes non-spontaneous.

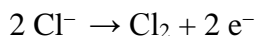
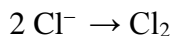
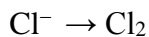
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\text{When the reaction just becomes spontaneous, } \Delta G^\circ = 0, \text{ thus } T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{41.2 \times 10^3 \text{ J mol}^{-1}}{42.1 \text{ J K}^{-1} \text{ mol}^{-1}} = 979\text{K}$$

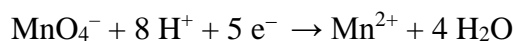
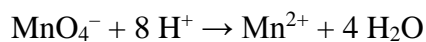
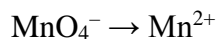
C5. [20 marks] Balance the following redox reaction in a basic solution:



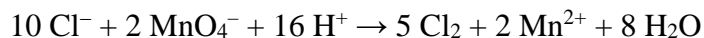
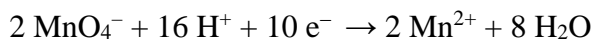
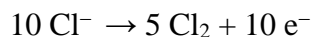
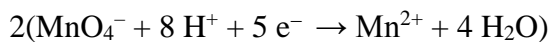
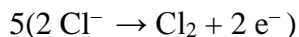
Oxidation:



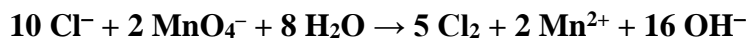
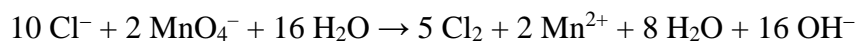
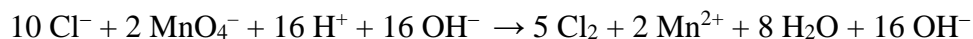
Reduction:



Addition:



Convert to basic solution by adding 16 OH⁻ to each side:



- C6. (a) [10 marks] Propane has a vapour pressure of 0.533 bar at -55.6°C and $\Delta H_{\text{vap}} = 15.7 \text{ kJ mol}^{-1}$. Calculate its boiling point ($^{\circ}\text{C}$).

The boiling point is the temperature at which the vapour pressure is equal to 1.00 atm, or 1.01325 bar.

Thus,

$$T_1 = -55.6^{\circ}\text{C} = (-55.6 + 273.15) \text{ K} = 217.55 \text{ K}$$

$$p_1 = 0.533 \text{ bar}$$

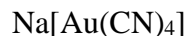
$$p_2 = 1.01325 \text{ bar}$$

$$\ln(p_2) - \ln(p_1) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

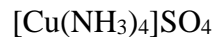
Rearranging,

$$\begin{aligned} T_2 &= \left[\frac{1}{T_1} - \frac{R}{\Delta H_{\text{vap}}} (\ln(p_2) - \ln(p_1)) \right]^{-1} \\ &= \left[\frac{1}{217.55 \text{ K}} - \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{15700 \text{ J mol}^{-1}} (\ln(1.01325) - \ln(0.533)) \right]^{-1} \\ &= 234.9 \text{ K} \\ &= -38.2^{\circ}\text{C} \end{aligned}$$

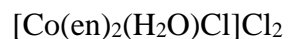
- (b) [10 marks] Name the following transition metal complexes.



Sodium tetracyanoaurate(III)



Tetraamminecopper(II) sulphate



Aquachlorobis(ethylenediamine)cobalt(III) chloride



Ammonium trioxalatoferrate(III)



Hexacarbonylmolybdenum