THE COLLEGE OF THE BAHAMAS

EXAMINATION

SEMESTER 04-2005

FACULTY OF PURE AND APPLIED SCIENCES

SCHOOL OF SCIENCES AND TECHNOLOGY

X NASSAU
FREEPORT
EXUMA
ELEUTHERA

DATE AND TIME OF EXAMINATION: Monday, December 5, 2005 at 2 pm
DURATION: 3 HOURS

COURSE NUMBER: CHEM 225

COURSE TITLE: COLLEGE CHEMISTRY II

STUDENT NAME:

STUDENT NUMBER:

LECTURER'S NAME

INSTRUCTIONS TO CANDIDATES: This paper has 11 pages and 45 questions. Please follow instructions given.

SECTION I: Multiple Choice Questions

Select the SINGLE best alternative in each of the following cases and indicate your answer on the answer sheet provided. Answer* ALL *questions in this section.

1) Which of the following is the rate determining step of a reaction?
   A The first step.
   B The slowest step.
   C The last step.
   D The fastest step.
   E The step with the highest molecularity.

2) For the reaction
   $H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$
   the rate law is
   $$R = k[H_2O_2]^2[H^+]$$
   Which of the following statements is true?
   A The rate depends on the concentration of H_2O_2, H^+ and I^-.
   B I^- is a catalyst.
   C Doubling the concentration of H_2O_2 causes the reaction rate to double.
   D Doubling the concentration of H^+ causes the reaction rate to double.
   E I^- is not necessary for the reaction to proceed.

3) Consider the reaction
   $NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$
   The activation energy for this reaction is 10kJ, whilst the activation energy for the reverse reaction is 210kJ. What is the enthalpy change for the forward reaction, in kJ?
   A -200
   B -210
   C -220
   D -2000
   E -20

4) For the reaction
   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   the average rate with respect to the production of ammonia is expressed as
   $$\frac{\Delta[NH_3]}{\Delta t}$$
   An expression whose value is the same is:
   A $\frac{-\Delta[N_2]}{\Delta t}$
   B $\frac{\Delta[N_2]}{\Delta t}$
   C $\frac{-2\Delta[N_2]}{\Delta t}$
   D $\frac{\Delta[H_2]}{2\,\Delta t}$
   E $\frac{\Delta[H_2]}{3\,\Delta t}$

5) The *rate constant* (k) for a chemical process can be altered by
   A a change in temperature.
   B a change in the concentration of the reactants.
   C a change in pressure.
   D the addition of more reactants.
   E the removal of products.

6) For a chemical system in a state of equilibrium which of the following statements is **false**?
   A The equilibrium constant remains the same provided the temperature is constant.
   B Reactants and products must all be in the same physical state.
   C The rate of the forward reaction is equal to that of the back reaction.
   D The equilibrium concentrations of the substances present vary with temperature.
   E The reaction quotient (Q) is equal to the equilibrium constant (K).

7) For which systemwill K_c be equal to K_p?
   A $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
   B $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
   C $2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$
   D $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$
   E $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$

8) When iron and steam are placed in a closed container at 700°C, the following equilibrium is set up:
   $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$
   ΔH = -ve
   The amount of hydrogen present at equilibrium can be increased by
   A adding more Fe_3O_4.
   B decreasing the temperature to 600°C.
   C adding an inert gas at constant volume.
   D increasing the temperature to 800°C.
   E increasing the mass of iron.

9) The hydronium ion concentration of a solution consisting of a weak acid (HA) in aqueous solution together with its sodium salt (Na^+A^-) is given by
   A $[H_3O^+] = K_a[A^-]$
   B $[H_3O^+] = K_a[HA]$
   C $[H_3O^+] = K_a[A^-] + [HA]$
   D $[H_3O^+] = K_a[HA]/[A^-]$
   E $[H_3O^+] = K_a[A^-]/[HA]$

10) Two aqueous solutions, one of a monoprotic strong acid and the other of a monoprotic weak one, have the same concentration. Equal volumes of each are titrated with sodium hydroxide solution of a certain molarity. Which of the following statements is true?

A The titre value for the strong acid is the larger.
B The titre value for the weak acid is the larger.
C The two acids will give equal titre values.
D The relative sizes of the titre values cannot be predicted from the above information.
E The strong acid cannot have the same concentration as the weak acid.

11) Which indicator is most suitable for detecting the end-point of the titration of ethanoic acid with sodium hydroxide?

	INDICATOR	pH RANGE
A	thymol blue	1·2 to 1·8
B	methyl orange	3·1 to 4·4
C	methyl red	4·2 to 6·2
D	bromothymol blue	6·0 to 7·6
E	phenolphthalein	8·3 to 10·0

12) In which one of the following solvents would benzoic acid be expected to be strongest?

A liquid ammonia
B ethanoic acid
C nitric acid
D benzene (C_6H_6)
E water

13) Arsenic acid, H_3AsO_4 is a triprotic acid. The dissociation constant, K_{a1} for the first step of dissociation

$H_3AsO_4(aq)+H_2O(l) \rightleftharpoons H_2AsO_4^-(aq)+H_3O^+(aq)$

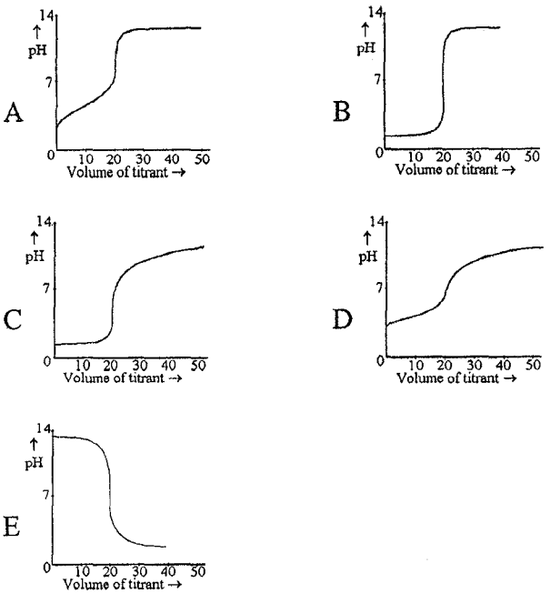
is $6{\cdot}5\times10^{-3}$. The dissociation constant, K_{a2}, for the second step is most likely to be

A $6{\cdot}5\times10^{-3}$
B $1{\cdot}1\times10^{-2}$
C $6{\cdot}5\times10^{-2}$
D $3{\cdot}6\times10^{-1}$
E 8.3×10^{-8}

14) Which one of the following pairs of species is an acid-base conjugate pair?

A H_3O^+ and OH^-
B $CH_3NH_4^+$ and CH_3NH_2
C $H_2PO_4^-$ and HPO_4^{2-}
D H_3PO_4 and PO_4^{3-}
E CO_2 and H_2CO_3

Questions 15-19. The diagrams A to E represent titration curves for the reaction between various acids and bases.



Given that each curve may be used once, more than once or not at all, choose from A to E the curve which best represents

15) the titration of 20 cm^3 of 0·1M HCl with 0·1M NaOH.
16) the titration of 20 cm^3 of 0·1M CH_3COOH with 0·1M NaOH.
17) the titration of 20 cm^3 of 0·1M CH_3COOH with 0·1M NH_3.
18) the titration of 20 cm^3 of 0·1M NaOH with 0·1M HCl.
19) the titration of 20 cm^3 of 0·1M HCl with 0·1M NH_3.

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20) The pK_a values for three acids P, Q, and R are 5·2, 4·8 and 3·4 respectively. It follows that

A R is the weakest acid.
B P has the largest K_a value.
C The basicity constant of the conjugate base of Q is $1{\cdot}58\times10^{-5}$.
D Q is stronger than P.
E The conjugate base of P is strong.

21) When the contents of an electrochemical cell are at equilibrium:

A The e.m.f. of the cell is zero.
B The e.m.f. of the cell is negative.
C The e.m.f. of the cell is positive.
D The e.m.f. of the cell cannot be measured.
E The e.m.f. of the cell is at a maximum.

Questions 22 to 24 involve the following data for the electrode potentials of three metals in water and liquid ammonia.

Electrode	$E^{\ominus}$ (H_2O)/V	$E^{\ominus}$ (NH_3)/V
K^+/K	-2·93	-1·98
Ca^{2+}/Ca	-2·87	-1·74
Na^+/Na	-2·71	-1·85

22) In ammonia the strongest reducing agent is
- A sodium
- B calcium ions
- C calcium
- D potassium ions
- E potassium

23) Each of the metals is a
- A weaker reducing agent in ammonia than in water.
- B weaker reducing agent in water than in ammonia.
- C weaker oxidising agent in ammonia than in water.
- D weaker oxidising agent in water than in ammonia.
- E No such generalisation can be made.

24) The standard e.m.f. of the cell
$Na(s) \mid Na^+(aq) \parallel Ca^{2+}(NH_3) \mid Ca(s)$
should be
- A +0·97V
- B -0·97V
- C +0·11V
- D -0·11V
- E +0·16V

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Questions 25 to 30 concern the following experimental situation which you have encountered in your practical course.

Six equilibrium mixtures *(1)* were made up with various volumes of 0·10M iron(III) nitrate solution, dilute nitric acid and 0·10M silver nitrate solution. The solutions were stirred for 15 minutes until a precipitate *(2)* formed, and then filtered into separate test tubes. 5cm^3 aliquots were each mixed with about 1cm^3 of 1M iron(III) nitrate *(3)* and titrated *(4)* with 0·010M KSCN(aq). The titre values were used to calculate the concentrations of the various species present at equilibrium and hence the equilibrium constant.

25) The equilibrium studied, referred to in *(1)*, involves an equilibrium between
- A nitrate ions, hydronium ions and nitric acid molecules.
- B iron(III) ions, thiocyanate ions and thiocyanato-iron(III) complex.
- C iron(III) ions, iron(II) ions, silver ions and silver.
- D iron(III) ions and iron(II) ions.
- E silver ions, iron(II) ions, nitrate ions and silver.

26) Precipitate *(2)* was
- A silver nitrate
- B silver chloride
- C silver thiocyanate
- D silver
- E iron(III) thiocyanate

27) The iron(III) nitrate *(3)* was added in order to
- A oxidise any silver still present to silver ions.
- B react with excess thiocyanate ions to form a coloured complex.
- C catalyse the reaction between titrant and titrand in *(4)*.
- D prevent the forward reaction in the equilibrium from occurring.
- E prevent the precipitation of silver thiocyanate.

28) The precipitate *(2)* was filtered off in order to
- A prevent the equilibrium concentration of silver ions being changed during the titration *(4)*.
- B make the solution clear so that the end-point in *(4)* could be seen more clearly.
- C prevent solid matter blocking the burette.
- D remove excess silver ions from the solution.
- E collect it for weighing.

29) Using **ONLY** the titre value in *(4)*, together with the concentration of the potassium thiocyanate solution, the aliquot volume and the stoichiometry of the reaction involved in the titration, one may calculate
- A the equilibrium concentration of silver ion.
- B the equilibrium concentration of iron(III) ion.
- C the equilibrium concentration of nitrate ion
- D the initial concentration of silver ion.
- E the initial concentration of iron(III) ion.

30) Nitric acid was added in order to
- A neutralise any base which might have been added accidentally.
- B prevent formation of hydroxo-complexes of iron(III).

C oxidise iron(II) to iron(III).
D redissolve any metals which might be precipitated.
E keep the total concentration of nitrate ions constant throughout.

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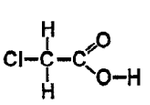
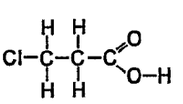
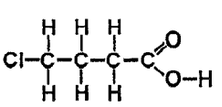
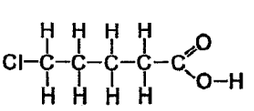
31) Deuterium, hydrogen-2, (D) is an isotope of hydrogen and therefore has very similar chemical properties to hydrogen-1 (H). Heavy water (D_2O) is made commercially by electrolysis of ordinary water (mostly H_2O) which naturally contains a small proportion of D_2O. As electrolysis continues the proportion of D_2O in the remaining water gradually increases. On the basis of this data the standard electrode potentials for the two reactions:
$D_2O + 2e^- \rightarrow D_2(g) + O^{2-}$ ...($E_1^\ominus$) and
$H_2O + 2e^- \rightarrow H_2(g) + O^{2-}$ ...($E_2^\ominus$)
may be described as follows:
A ($E_1^\ominus$) and ($E_2^\ominus$) are exactly the same.
B ($E_1^\ominus$) is slightly greater than ($E_2^\ominus$).
C ($E_1^\ominus$) is slightly less than ($E_2^\ominus$).
D ($E_1^\ominus$) is much greater than ($E_2^\ominus$).
E ($E_1^\ominus$) is much less than ($E_2^\ominus$).

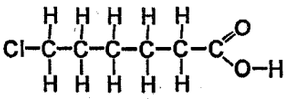
Questions 32 to 37 concern various acids. Pick the strongest acid in each case.

32) A HClO B $HClO_2$ C $HClO_3$
D $HClO_4$ E HBrO

33) A  B 

C 

D 

E 

34) A **HF** B **HCl** C **HBr**
D **HI** E **H_2S**

35) A **SiH_4** B **PH_3** C **H_2S**
D **HCl** E **CH_4**

36) An acid with:
A $pK_a = 2$ B $pK_a = 4$
C $pK_a = 6$ D $pK_a = -6$
E $pK_a = -4$

37) A H_2SO_4 B H_2SeO_4
C H_2TeO_4 D H_2SO_3
E H_3PO_4

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38) Which one of the following equations represents a redox reaction?
A $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
B $PCl_5(aq) + H_2O(l) \rightarrow POCl_3(l) + 2H^+(aq) + 2Cl^-(aq)$
C $Cu^{2+}(aq) + 4Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq)$
D $[Fe(CN)_6(aq) + \frac{1}{2}Cl_2(g) \rightarrow [Fe(CN)_6]^{3-}(aq) + Cl^-(aq)$
E $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

39) Which half-reaction correctly represents reduction?
A $Cr_2(g) \rightarrow 2Cr(g)$
B $Cr^{3+} + \rightarrow Cr(s) + 3e^-$
C $Cr(s) \rightarrow Cr^{3+} + 3e^-$
D $Cr(s) + 3e^- \rightarrow Cr^{3+}$
E $Cr^{3+} + 3e^- \rightarrow Cr(s)$

40) Which quantities are conserved in all oxidation-reduction reactions?
A charge only
B mass only
C oxidation number
D neither oxidation number nor charge, nor mass
E both charge and mass

SECTION II: Structured Questions. ***Answer* ALL *of the following questions in the spaces provided on the question paper. Underline numerical answers and express them to the correct number of figures. Brief details of working must be included even when they are not asked for specifically. Clarity of expression is of the highest importance.***

1) For the reaction

$$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$

the following experimental rate data were collected in three experiments carried out at the same temperature.

INITIAL [NO] / M	INITIAL [H_2] / M	INITIAL RATE OF N_2O FORMATION / M $min.^{-1}$
0·60	0·37	0·18
1·20	0·37	0·72
1·20	1·11	2·16

a) Write a rate law for the reaction. (2)

b) Why was it necessary to carry out the three experiments at the same temperature? (1)

c) A research worker proposed the following mechanism:

$$2NO(g) \rightleftharpoons N_2O_2(g) \quad \text{...fast equilibrium, 1}$$
$$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g) \quad \text{... slow, 2}$$

i) Show how this mechanism leads to the observed rate law. (4)

ii) Why is it *not* possible to conclude from the above information that the mechanism is correct? What further piece of information would help to confirm the mechanism? (2)

2) a) Define pH. (1)

---

b) Write an expression to define the *ionic product* of water. State its value at 25°C. (2)

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c) Calculate the pH of each the following solutions at 25°C.

i) $2{\cdot}00\times10^{-3}$M hydrochloric acid (1)

ii) $2{\cdot}00\times10^{-3}$M potassium hydroxide (2)

iii) a mixture which is prepared by adding 30·0 cm^3 of 0·10M HCl to 20·0 cm^3 of 0·10M KOH. (2)

iv) $0{\cdot}55\,M\ CH_3COOH(aq),\ K_a = 1{\cdot}76\times10^{-5}$ (4)

d) For each salt given, state whether you expect its solution to have a pH greater than 7, less than 7, or approximately 7. (HCN is a weak acid and NH_3 is a weak base.) Wherever a hydrolysis reaction occurs, write an equation for the hydrolysis reaction. If there is none, write "NONE". (8)

SALT	pH	HYDROLYSIS REACTION
KNO_3		
KCN		
NH_4Cl		
$Al(NO_3)_3$		

3) The solubility product of $Ca(OH)_2$ is $5{\cdot}5\times10^{-6}$ at 25°C.

a) Find the molar solubility of $Ca(OH)_2$ in water at 25°C. (3)

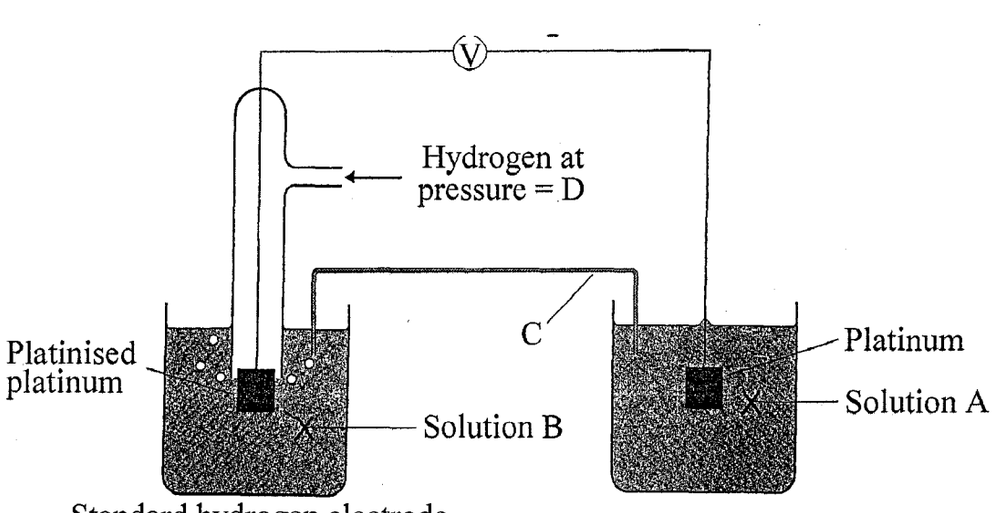
b) A solution is 0.10M in Ca^{2+} and 0.10M in OH^-. Does precipitation take place? Explain your answer. (2)

4) The following is a list of standard redox potentials.

	E^θ/V
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	1·51
$Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$	1·36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1·33
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0·77
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00

This question is about electrode potentials.

a) The incompletely labelled diagram shows an experimental arrangement by which the standard electrode potential of the Fe^{3+}/Fe^{2+} couple may be determined.



What is represented by each of the labels A to C? (Give concentrations where appropriate.) (6)

A: _____

B: _____

C: _____

D: What is the value of D? _____

b) Mark on the diagram

i) the positive pole of the cell. (1)

ii) the direction of electron flow in the external circuit. (1)

c) Write a cell diagram to represent the cell. (2)

_____

d) Calculate the e.m.f. of the cell? (1)

_____

e) Write an equation to represent the reaction taking place in the cell. (1)

_____

f) Under what conditions would the cell potential be reduced to zero? (1)

_____

g) By reference to the standard electrode potentials given above, explain why hydrochloric acid can be used to provide an acid medium with potassium dichromate but **NOT** with potassium manganate(VII) as oxidizing agents. (4)

_____

_____

_____

_____

_____

5) Give careful and complete descriptions of SIX of the following terms: (12)

a) Brønsted-Lowry acid.

_____

_____

b) Anode.

_____

_____

c) Equivalence point.

d) End-point.

e) Polyprotic acid.

f) Hydrolysis.

g) Hydration shell.

h) Buffer solution.

i) Acid/base indicator.

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