THE COLLEGE OF THE BAHAMAS

DEPARTMENT OF CHEMISTRY

CHEM225 COLLEGE CHEMISTRY II 04-2001 **FINAL EXAMINATION**
TIME: 3 HOURS

This examination consists of 13 pages with 30 multiple choice and 6 structured questions. Answer the multiple choice questions by circling the most appropriate answer. Answer the structured questions in the spaces provided. The paper is marked out of 100.

SECTION A: MULTIPLE CHOICE (30 MARKS)

1. The half-life of a first order reaction is 160 years. Starting with a concentration of 0.68 M, what will be the concentration after 480 years?

   A. 0.34 M
   B. 0.68 M
   C. 0.085 M
   D. 0.17 M
   E. 0.0425 M

2. For the reaction $J_{(aq)} + K_{(aq)} \rightarrow L_{(aq)} + M_{(aq)}$, the rate law is $R = k[J]^{6/5}[K]^{3/10}$ The unit of k is

   A. $M^{-15/10}\ s^{-1}$
   B. $M^{-10/5}\ s^{-1}$
   C. $M^{5/10}\ s^{-1}$
   D. $M^{-1/2}\ s^{-1}$
   E. $M^{-1}\ s^{-1}$

3. A first order reaction has a half-life of 7 days. How long will it take for the concentration to decrease to 12.5 % of its original value?

   A. 21 days
   B. 1.75 days
   C. 14 days
   D. 0.875 days
   E. 28 days

4. If doubling the concentration of a reactant increases the rate of reaction nine times, what is the order of the reaction with respect to that reactant?

   A. 9
   B. 3
   C. 7
   D. 4.5
   E. 3.17

5. For a reaction with the rate law $R = k[F]^2[G]^2$, what will happen to the rate if the concentrations of both F and G are doubled?

   A. It increases 4-fold
   B. It increases 16-fold
   C. It increases 8-fold
   D. We cannot say unless the value of k is known
   E. It increases 32-fold

6. Which statement is **FALSE**?

A. Intermediate compound formation applies to homogeneous catalysis.
B. In heterogeneous catalysis, the catalyst exists in a different phase from the reactants.
C. Surface action theory does not apply to solid catalysts.
D. Catalysts affect reaction rates by providing an alternative route with a lower E_a.
E. Transition elements are often used as catalysts.

7. Which statement is **TRUE**?

A. Most reactions occur by a single mechanism.
B. Trimolecular reactions are more common than bimolecular reactions.
C. The order of a reaction must be determined by experiment.
D. If the exponents in the rate law are not the same as the coefficients in the reaction equation, the overall reaction must consist of a single step.
E. It is possible for an intermediate to be present in a rate law.

8. The reaction $U_{(aq)} + V_{(aq)} \rightarrow X_{(s)} + Y_{(aq)}$ is first order with respect to U and second order with respect to V. If $[U]_o = 0.17$ M, $[V]_o = 0.15$ M and $k = 7.42 \times 10^{-6}$ $M^{-2}s^{-1}$, the initial rate is:

A. 3.83×10^{-3} M s^{-1}
B. 2.84×10^{-8} M s^{-1}
C. 1.89×10^{-7} M s^{-1}
D. 3.22×10^{-8} M s^{-1}
E. 4.83×10^{-9} M s^{-1}

9. Which statement is **FALSE**?

A. A reversible system is in dynamic equilibrium when the rate of the forward reaction is equal to the rate of the backward reaction.
B. A homogeneous equilibrium system has all components in the same phase.
C. When a reversible system is in equilibrium, the concentration of each substance in the system remains constant.
D. The concentration of each component in a K_c expression is its initial concentration.
E. The value of K_c for a given reaction is constant at a constant temperature.

10. Which statement is **TRUE**?

A. In non-aqueous systems, where water is a reactant or product, its concentration does not appear in the K_c expression.
B. In aqueous systems where water is the solvent and is present in a large excess, its concentration appears in the K_c expression.
C. Solids always appear in K_c expressions.
D. For gaseous systems, K_c equals K_p.
E. Pure liquids do not appear in K_c expressions.

11. If $Q < K$, which of the following is **FALSE**?

A. The reverse process occurs to establish equilibrium.
B. The system is not at equilibrium.
C. It is possible to determine the direction of reaction.
D. The forward reaction occurs to establish equilibrium.
E. The system will reach equilibrium when Q becomes equal to K.

12. For the reaction $2AB\ (g) \rightleftharpoons 2A\ (g) + 2B\ (g)$, $K_c = 2.0 \times 10^{-3}$. K_c for the reaction $2A\ (g) + 2B\ (g) \rightleftharpoons 2AB\ (g)$ is

A. 0.5
B. 500
C. 2.0×10^{3}
D. 5
E. 2.0×10^{-3}

13. After mixing 40 cm^3 of 0.10 M HNO_3 with 35 cm^3 of 0.20 M NaOH, there is

A. an excess of 0.0933 M OH^-
B. an excess of 0.040 M OH^-
C. an excess of 0.30 M OH^-
D. an excess of 0.10 M OH^-
E. equimolar quantities of H^+ and OH^-

14. If the pOH of a solution is 2.5 at 298K, which one of the following is **FALSE**?

A. $[OH^-] = 3.16 \times 10^{-3}$ M
B. $[H_3O^+] = 3.17 \times 10^{-12}$ M
C. pH = 11.5
D. pH + pOH = 14
E. The solution is acidic.

15. Which one of the following statements is **TRUE**?

A. A buffer solution can maintain a fairly constant pH when large amounts of acid or base are added to it.
B. A buffer solution is prepared by mixing a strong acid with a salt of the same acid.
C. A buffer solution with higher concentrations of acid and base would be more effective than one in which the concentrations are lower.
D. The Henderson Hasselbach equation states that
$pH = pK_a + \log([acid]/[base])$
E. Water is a good buffer.

16. In a solution that has $[H_3O^+] = 5.20 \times 10^{-9}$ M, the $[OH^-]$ equals:

A. 5.20×10^{-9} M
B. 5.0×10^{-5} M
C. 5.0×10^{-6} M
D. 8.80×10^{-6} M
E. 1.92×10^{-6} M

17. Which statement is **TRUE**?

A. $pOH = -\log_{10}[OH^-]$
B. $\log K_w = \log_{10}[H_3O^+] - \log_{10}[OH^-]$
C. $K_w = [H_3O^+]\,[OH^-]^2$
D. $pH = \log_{10}[H_3O^+]$
E. 14 - pH = - pOH

18. The equation for the ionisation of CH_3COOH is

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

K_a equals

A. $[H_3O^+]\,[CH_3COO^-]$

B. $\dfrac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]\,[H_2O]}$

C. $\dfrac{[CH_3COOH]}{[H_3O^+]\,[CH_3COO^-]}$

D. $\dfrac{[CH_3COOH]\,[H_2O]}{[H_3O^+]\,[CH_3COO^-]}$

E. $\dfrac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]}$

19. In any aqueous solution at 298 K, the sum of the pH and the pOH is always:

A. 7.0
B. 1.0×10^{-7}
C. 7.0×10^{-14}
D. 14.0
E. 1.0×10^{-14}

20. The K_a for ethanoic acid is 1.70×10^{-5}. The pK_a is therefore

A. 1.7×10^{5}
B. 1.7
C. - 4.77
D. 4.77
E. -2.3×10^{-6}

21. Formic acid, benzoic acid, chloroacetic acid and hypochlorous acid have the following K_a values respectively: 1.80×10^{-4}, 6.50×10^{-5}, 1.40×10^{-3}, 4.0×10^{-8}. Acidity **INCREASES** in the following order:

A. formic < benzoic < chloroacetic < hypochlorous
B. hypochlorous < benzoic < formic < chloroacetic
C. hypochlorous < chloroacetic < benzoic < formic
D. chloroacetic < formic < benzoic < hypochlorous
E. chloroacetic < formic < hypochlorous < benzoic

22. Substances that can react as an acid or as a base are called

A. amphophilic
B. conjugate acid-base pairs
C. amphoteric
D. ionic products
E. neutral

23. The oxidation number of aluminium in $Al(OH)_4^-$ is

A. +3
B. –3
C. +4
D. +2
E. –4

24. The solubility product of a salt AB is 6.40×10^{-10}. Assuming that neither ion undergoes appreciable hydrolysis, the solubility of AB is

A. 6.4×10^{-10}
B. 2.53×10^{-10}
C. 2.53×10^{-5}
D. 6.4×10^{-5}
E. 3.2×10^{-10}

Questions 25-27 inclusive refer to the following list:

A ClO_4^-
B ClO_3^-
C $FeCl_4^-$
D $FeCl_3$
E ClO_2^-

25. Which species has chlorine in a +5 oxidation state?

26. Which species is known as 'chlorate (III)'?

27. Which species has the trivial name 'chlorate'?

28. Acid strength **INCREASES** in which order?

A. HF < HCl < HBr < HI
B. HF < HBr < HI < HCl
C. HI < HBr < HCl < HF
D. HBr < HF < HI < HCl
E. HI < HF < HBr < HCl

29. The slope of a plot of $\log_{10} \Delta t$ versus 1/T equals

A. E_a
B. E_a/R
C. $E_a/R \times 1/T$
D. $E_a/2.303R$
E. R/T

30. For a weak acid in the presence of its conjugate base, which of the following is **TRUE**?

A. $pH = -\log_{10}[H_3O^+]$
B. $pH = pK_w + \log_{10}[OH^-]$
C. $pH = pK_a$
D. $pH = pK_a + \log_{10}([base]/[acid]$
E. $pH = pK_a - ½\log_{10}[H_3O^+]$

SECTION B: STRUCTURED QUESTIONS (70 MARKS)

1. ACID/BASE EQUILIBRIA

The Henderson-Hasselbach equation states

$$pH = pK_a + \log_{10} ([base]/[acid])$$

a) Starting with a weak monoprotic acid, HA, derive the Henderson-Hasselbach equation. (4 marks)

b) When is the pH of a buffer solution = pK_a of the weak acid in the buffer? (1 mark)

c) A buffer solution is formed by mixing 45 cm^3 of 0.25 M HA and 40 cm^3 of 0.25 M NaA. The K_a of HA is 8.60×10^{-5}. What is the pH of this buffer? (3 marks)

d) Compare the pH change when 2 cm^3 of 1.0 M KOH are added to 2 dm^3 of

i) H_2O (assume the pH of water is 7.0) (2 marks)

ii) a buffer solution which is 0.45 M in HA and 0.45 M in NaA.
(K_a of HA = 8.60×10^{-5}) (3 marks)

2. REDOX CHEMISTRY

Balance the following equations for redox reactions in

(i) **acidic solution**: $PbS_{(s)} + NO_3^-{}_{(aq)} \rightarrow PbSO_{4\,(s)} + NO_{(g)}$ (4 marks)

(ii) **basic solution**: $Al_{(s)} + OH^-{}_{(aq)} \rightarrow Al(OH)_4^-{}_{(aq)} + H_{2\,(g)}$ (4 marks)

3. GENERAL EQUILIBRIA

(a) Nitrogen gas and hydrogen gas react to produce ammonia gas according to the equation:

$$N_{2\,(g)} + 3\,H_{2\,(g)} \rightarrow 2\,NH_{3\,(g)} + \text{heat}$$

Consider a mixture of all three gases in a sealed 1.0 dm^3 vessel at equilibrium. According to Le Chatelier's principle, in which direction will equilibrium shift in each of the following cases? In each case, give the reason for your decision.

(i) Nitrogen is added to the mixture. (1 mark)

(ii) The volume of the container is reduced to 0.5 dm^3. (1 mark)

(iii) Ammonia is added to the mixture. (1 mark)

(iv) The mixture is heated. (1 mark)

(v) Ammonia is removed from the mixture. (1 mark)

(vi) A specific catalyst is added. (1 mark)

(vii) Nitrogen and ammonia are both added to the mixture. (2 marks)

(b) What does Le Chatelier's principle state about the effect of an addition of ammonia on a mixture of nitrogen and hydrogen **BEFORE** it attains equilibrium? (1 mark)

(c) Consider the decomposition of hydrogen iodide.

$$2\ HI_{(g)} \rightleftharpoons H_{2\ (g)} + I_{2\ (g)}$$

0.256 g of HI was heated at 764 K in a sealed 0.1 dm^3 vessel. When an equilibrium was established, the vessel was cooled to room temperature and the iodine present determined by titration. At this equilibrium, it was found that 0.00028 moles of iodine were present.

Calculate

(i) the number of moles of HI in 0.256 g HI. [RAM H = 1, I = 127] (1 mark)

(ii) the number of moles of hydrogen formed. (1 mark)

(iii) the number of moles of HI unreacted. (2 marks)

(iv) Calculate K_c for the reaction at 764 K. (2 marks)

4. ELECTROCHEMISTRY

(i) Draw a labelled diagram of the apparatus which could be used to measure the emf of the cell

$$Zn_{(s)} \mid Zn^{2+}_{(aq,\ 1\ M)} \mid\mid Ni^{2+}_{(aq,\ 1\ M)} \mid Ni_{(s)}$$ (6 marks)

	E° (V)
$Na^{+} + e^{-} \rightarrow Na$	-2.71
$Zn^{2+} + 2\ e^{-} \rightarrow Zn$	-0.76
$Fe^{2+} + 2\ e^{-} \rightarrow Fe$	-0.44
$Ni^{2+} + 2\ e^{-} \rightarrow Ni$	-0.25
$Cu^{2+} + 2\ e^{-} \rightarrow Cu$	+0.34
$Ag^{+} + e^{-} \rightarrow Ag$	+0.80

(ii) What reaction occurs at the anode? (1 mark)

(iii) What reaction occurs at the cathode? (1 mark)

(iv) Using the table of standard electrode potentials above, calculate E°_{cell}. (1 mark)

5. REACTION KINETICS

Dr. McBride carried out an experiment in order to determine the activation energy of a particular gas reaction

$$A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$$

He carried out the reaction at five different temperatures between 10 °C and 50 °C in order to give a measure of the rate of reaction at each of these temperatures. Here are the results he obtained:

Expt.	Temp. (°C)	Temp. (K)	1/T (K^{-1})	Δt (s)	$1/\Delta t$ (s^{-1})	ln Δt
1	10			420		
2	20			380		
3	25			225		
4	35			120		
5	50			89		

a) Complete the table of results. (5 marks)

b) Plot ln Δt (y-axis) versus 1/T (x-axis) *(on the graph paper provided).* (5 marks)

c) The slope of a plot of ln Δt versus 1/T is equal to E_a/R. If the gas constant R = 8.31 J mol^{-1} K^{-1}, calculate E_a in the space below. (3 marks)

E_a = _____

d) Temperature is one factor which affects the rate of chemical reactions. In gases, there is a wide distribution of the velocities of molecules in a gas. Illustrate this effect of temperature on the velocities of molecules in a gas by sketching a Maxwell-Boltzmann diagram. (3 marks)

6. SOLUBILITY EQUILIBRIA

(a) The solubility of CaF_2 in water at 298 K is found to be 2.14×10^{-4} M. What is the value of K_s at this temperature? (2 marks)

(b) Equal volumes of a 2.0×10^{-3} M $Pb(NO_3)_2$ solution and a 2.0×10^{-3} M NaI solution are mixed. Will a precipitate of PbI_2 form? [K_s $PbI_2 = 7.90 \times 10^{-9}$] (3 marks)

(c) (i) What is the solubility of $PbCl_2$ in 1.0 M HCl? [K_s $PbCl_2 = 1.70 \times 10^{-5}$] (3 marks)

(ii) It is found that the solubility of $PbCl_2$ <u>in water</u> is 0.016 M. Comparing this value with your answer from question (i), what effect is being described? (1 mark)

END OF EXAMINATION