Chemistry 225 Final Examination Semester 04-2003 Time allowed: 3 hours Page 1 of 9

Student Name:................................ Student Number .... Section ....

You may use the following information wherever necessary:

$R = 8.31\ J\ mol^{-1}\ K^{-1}\ =\ 0.0821\ atm\ dm^3\ mol^{-1}\ K^{-1}\ =\ 0.0821\ atm\ L\ mol^{-1}\ K^{-1}$
$K_p = K_c\ (0.0821T)^{\Delta n(gas)}$
$K_w = 1.0 \times 10^{-14}$ at 298 K
$K_a(CH_3COOH) = 1.8 \times 10^{-5}$

Remember to include units in your answers wherever appropriate.

SECTION A: Multiple Choice . Answer **all** questions. [1 mark each = 40 marks]

Each question is followed by five suggested answers. Select the best answer for each question and shade the letter corresponding to this answer on the answer sheet provided. You are advised to use a pencil for this section.

1. Bromide ions can be oxidized according to the equation:
$5\ Br^-\ (aq) + BrO_3^-\ (aq) + 6\ H^+(aq) \rightarrow 3\ Br_2\ (aq) + 3\ H_2O\ (l)$
If in a particular reaction the rate of consumption of bromide ions is -0.004 mol dm^{-3}, then the rate of production of bromine, in mol dm^{-3}, is

A -(5/3) x 0.004
B (5/3) x 0.004
C -(3/5) x 0.004
D (3/5) x 0.004
E 3 x 5 x 0.004

2. The reaction: $CO\ (g) + NO_2\ (g) \rightarrow CO_2\ (g) + NO\ (g)$ is second order in nitrogen dioxide and zero order in carbon monoxide.
Which of the following will have **no effect** on the rate of the reaction?

A Increasing the concentration of carbon monoxide.
B Increasing the concentration of nitrogen dioxide.
C Using a suitable catalyst.
D Increasing the temperature.
E Increasing the partial pressure of both reactants.

3. The following elementary steps have been proposed for a reaction:
$NO + \frac{1}{2}\ O_2 \rightarrow NO_2$
$NO_2 + H_2O + SO_2 \rightarrow H_2SO_4 + NO$
The catalyst in this process is

A NO
B O_2
C NO_2
D SO_2
E H_2SO_4

4. 0.16 mol of SO_2 and 0.12 mol of O_2 were introduced into a 1 dm^3 vessel at constant temperature. When the system reached equilibrium, 0.06 mol of SO_3 was present.
The reaction is: $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$.

Which set of values shows the concentration of each gas at equilibrium?

	$[SO_2]$/mol dm^{-3}	**$[O_2]$/mol dm^{-3}**	**$[SO_3]$/mol dm^{-3}**
A	0.16	0.12	0.06
B	0.10	0.09	0.06
C	0.16	0.09	0.06
D	0.16	0.12	0.10
E	0.10	0.06	0.10

5. At a given temperature, T, some PCl_5, at an initial concentration of 1.0 M, was placed in a container and allowed to dissociate into PCl_3 and Cl_2. It was found that the PCl_5 was 40 % dissociated at equilibrium. K_c for the process: $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$ at temperature, T, is closest to

A 0.27
B 0.40
C 0.60
D 3.7
E 4.0

6. At 1000K, K_c for the process: $C(s) + O_2(g) \rightleftharpoons CO_2(g)$ is 4.8×10^{20}.
Which **CANNOT** be deduced from this information?

A $K_c = \dfrac{[CO_2]}{[O_2]}$

B The quotient, $\dfrac{[CO_2]}{[O_2]}$, in any equilibrium mixture of carbon, oxygen and carbon dioxide at 1000 K is 4.8×10^{20}.

C When carbon and oxygen react at 1000 K, the limiting reagent is almost completely used up.

D At equilibrium, the rate of the forward process far exceeds the rate of the reverse process.

E At 1000K, K_p for the process is 4.8×10^{20}.

7. In an equilibrium system, a catalyst increases

A the activation energy of the forward process whilst decreasing that of the reverse process.
B the rate of forward process whilst decreasing that of the reverse process.
C the activation energy of both the forward and reverse processes.
D the enthalpy change for the reverse process.
E the rates of both the forward and reverse processes.

8. Which of the following **CANNOT** upset the equilibrium position of the system:
$NH_4Cl(s) \rightleftharpoons NH_3(g) + Cl_2(g)$?

A Increasing the mass of ammonium chloride.
B Increasing the temperature.
C Decreasing the temperature.
D Increasing the volume of the containing vessel.
E Adding some chlorine gas without changing the volume of the containing vessel.

9. Consider the process: $P_4(g) + 6\,H_2(g) \rightleftharpoons 4\,PH_3(g) \quad \Delta H = +110.5$ kJ
at equilibrium. The value of K_c can be increased by

A Using a suitable catalyst.
B Adding some H_2 to the equilibrium mixture.
C Increasing the concentration of PH_3.
D Increasing the temperature.
E Decreasing the volume of the container.

10. Ammonium hydrogen sulphide dissociates into ammonia and hydrogen sulphide:
$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$
When ammonium hydrogen sulphide is introduced into a closed vessel at 282.5 K, the total pressure at equilibrium is 0.230 atm. K_p for the system at 282.5 K is closest to

A 0.230
B 0.115
C $(0.230)^2$
D $(0.115)^2$
E 2 x 0.230

11. For the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, $K_p = 1.7$ at 298K. Five systems were set up with the initial partial pressure of each gas as shown in the table. In which system would the **reverse** reaction occur to establish equilibrium?

	Initial partial pressure /atm		
	PCl_5	PCl_3	Cl_2
A	1	1	1
B	2	2	2
C	1	0.5	1.5
D	2	2	1
E	3	1	2

12. According to the Bronsted-Lowry definition, an **acid** is a substance which donates a

A hydrogen atom.
B hydrogen ion.
C hydrogen molecule.
D hydride ion.
E hydroxide ion.

13. Which does **not** constitute an acid/base conjugate pair?

A H_2SO_4/ HSO_4^-
B $H_2PO_4^-/HPO_4^{2-}$
C NH_4^+/ NH_3
D HNO_2/ NO_2^-
E H_3O^+/ OH^-

14. Which is **NOT** a strong acid?
A HI
B HCl
C $HClO_4$
D HCOOH
E HNO_3

15. Which set shows the substances in order of **increasing** acid strength?

A HClO, $HClO_2$, $HClO_3$
B H_2SO_4, H_2SO_3, HSO_4^-
C HBr, HCl,, HF
D HF, H_2O, NH_3
E H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}

16. The basicity constant for a base is 3.5×10^{-6}. The pK_a of its conjugate acid is

A 5.5
B 8.5
C 2.9×10^{-9}
D 1.0×10^{-14}
E 14

17. Which salt would be expected to produce a solution with the **lowest** pH? Assume all solutions have the same molar concentration.

A KCl
B $MgCl_2$
C $FeCl_3$
D $FeCl_2$
E $BaCl_2$

18. Which salt would produce a solution with the **highest** pH? Assume all solutions are the same molar concentration.
A NaCl
B NaClO
C NH_4Cl
D $FeCl_2$
E $FeCl_3$

Questions 19 to 23 refer to the following solutions.

A 1×10^{-4} M HCl
B 1×10^{-4} M KOCl
C 1×10^{-4} M $Fe(NO_3)_3$
D 1×10^{-4} M KNO_3
E 1×10^{-4} M KOH

Select, from A to E,

19. the solution which would have the lowest pH.
20. the solution which would have the highest pH.
21. the solution which would have a pH closest to 7.
22. the solution which would have a pH between 4 and 7.
23. the solution which would have a pH between 7 and 10.

<u>Questions 24 – 28</u> refer to the following titrations:

A The titration of 20.0 cm^3 of 0.1M HCl with 0.1 M NaOH
B The titration of 20.0 cm^3 of 0.1M HCl with 0.1 M NH_3
C The titration of 20.0 cm^3 of 0.1M CH_3COOH with 0.1 M NaOH
D The titration of 20.0 cm^3 of 0.1M KOH with 0.1 M HCl
E The titration of 20.0 cm^3 of 0.1M HNO_3 with 0.1 M KOH

For which titration

24. would there be a decreases in pH as the titrant is added?
25. would the pH be greater than 7 at the equivalence point?
26. would the pH be lower than 7 at the equivalence point?
27. would phenolphthalein (pH range 8.3 – 10.0) be most unsuitable as an indicator?
28. would bromocresol green (pH range 3.8 – 5.4) be unsuitable as an indicator?

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29. The solubility of silver phosphate(Ag_3PO_4) is x moldm^{-3}. The solubility product of this compound is

A x
B $4x^2$
C $4x^3$
D $27x^4$
E $3x^2$

<u>Questions 30 and 31</u> require the following information:

The solubility product of AgCl is 1.8×10^{-10}.

30. The solubility of AgCl in water is closest to

A 1.3×10^{-5} mol dm^{-3}
B $9.0\ 10^{-11}$ mol dm^{-3}
C 3.6×10^{-10} mol dm^{-3}
D 7.2×10^{-10} mol dm^{-3}
E 1.8×10^{-9} mol dm^{-3}

31. The solubility of AgCl in 0.10 M KCl is closest to

A 1.8×10^{-11} mol dm^{-3}
B 1.8×10^{-10} mol dm^{-3}
C 1.8×10^{-9} mol dm^{-3}
D 3.6×10^{-10} mol dm^{-3}
E 3.6×10^{-9} mol dm^{-3}

B

<u>Questions 32 –33</u> concern the following compounds:

A NH_4NO_3
B NaH
C H_2O_2
D $NaHSO_4$
E HOBr

32. In which compound does hydrogen carry an oxidation number of –1?

33. In which compound does oxygen carry an oxidation number of –1?

<u>Questions 34-35</u> concern the following reactions:

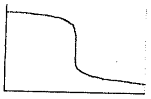
A $MgCO_3 \rightarrow MgO + CO_2$
B $2\ C_2H_6 + 7\ O_2 \rightarrow 4\ CO_2 + 6\ H_2O$
C $5\ HClO_2 \rightarrow 4\ ClO_2 + HCl + 2\ H_2O$
D $S_2O_8^{2-} + 2\ I^- \rightarrow 2\ SO_4^{2-} + I_2$
E $XeF_2 + 2\ Cl^- \rightarrow Xe + 2\ F^- + Cl_2$

34. Which is **<u>not</u>** a redox reaction?

35. Which is a disproportionation reaction?

Questions 36 - 40 concern the following graphs:

A



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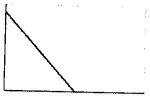

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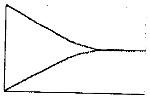
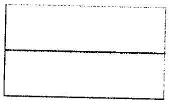
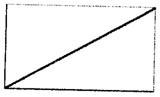


D



E



Select, from A to E, the graph which best represents:

36. Concentration of X versus time for a reaction which is zero order in X.
37. Rate of reaction versus concentration of X for a reaction which is zero order in X.
38. Rate of reaction versus concentration of X for a reaction which is first order in X.
39. Rate of reaction versus time for a reversible process which attains equilibrium after some time.
40. The titration curve for the titration of a base with an acid.

SECTION B: Answer **all** questions in the spaces provided in the question paper.

You may use the following information wherever necessary:

$R = 8.31\ J\ mol^{-1}\ K^{-1} = 0.0821\ atm\ dm^3\ mol^{-1}\ K^{-1} = 0.0821\ atm\ L\ mol^{-1}\ K^{-1}$
$K_p = K_c\ (0.0821T)^{\Delta n(gas)}$
$K_w = 1.0 \times 10^{-14}$ at 298 K
$K_a(CH_3COOH) = 1.8 \times 10^{-5}$

Remember to include units in your answers wherever appropriate.

1. The following rate data were collected in three experiments carried out at the same temperature for the reaction:
$2ClO_2(aq) + 2OH^-(aq) \rightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$

Experiment	Initial $[ClO_2]$/M	Initial $[OH^-]$/M	Initial rate of ClO_3^- formation/Ms^{-1}
1	1.5×10^{-2}	1.5×10^{-2}	3.88×10^{-4}
2	3.0×10^{-2}	1.5×10^{-2}	1.55×10^{-3}
3	1.5×10^{-2}	3.0×10^{-2}	7.76×10^{-4}

a) Write a rate law for the reaction. [2 marks]

b) Find the value of the rate constant, *k*, stating its units [1 mark]

c) Why was it necessary to carry out the three experiments at the same temperature? [1 marks]

d) Find the rate of the reaction the instant $20cm^3$ of $0.10\ M\ ClO_2$ is mixed with $30cm^3$ of $0.40\ M\ OH^-$
[3 marks]

2. At 298 K, the equilibrium constant, K_p, is 0.20 for the reaction : $CO\ (g) + Cl_2\ (g) \rightleftharpoons COCl_2(g)$.

a) Find the equilibrium partial pressure of each gas when 0.20 mol each of CO and Cl_2 are admitted into a 2000 cm^3 vessel at 298 K and the system reaches equilibrium. [5 marks]

b) Find the total pressure of the system at equilibrium. [1 mark]

c) What effect, if any, will the addition of 0.01mol of an inert gas have on the equilibrium position if the **volume** is kept constant? **Show your reasoning**. [2 marks]

d) What effect, if any, will the addition of 0.01mol of an inert gas have on the equilibrium position if the **total pressure** is kept constant? **Show your reasoning.** [2 marks]

3. Use the given K_p values for the processes X and Y to find K_p for the process Z. [2 marks]

Process X: $2\ BrF\ (g) \rightleftharpoons Br_2\ (g) + F_2\ (g)$	$K_p = K_x = 4.57 \times 10^{-5}$
Process Y: $Br_2\ (g) + 3\ F_2\ (g) \rightleftharpoons 2\ BrF_3\ (g)$	$K_p = K_y = 5.29$
Process Z: $BrF_3\ (g) \rightleftharpoons BrF\ (g) + F_2\ (g)$	$K_p = K_z$

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4. Find the pH of the following solutions:

a) 0.20 M HCl [1 mark]

b) 0.20 M NaOH [1 mark]

c) a mixture of 20.0 cm^3 of 0.20 M HCl + 30.0 cm^3 of 0.20 M NaOH. [2 marks]

5. Find the pH of the following solutions:

a) 0.20 M CH_3COOH [3 marks]

b) 0.20 M CH_3COONa [3 marks]

b) a mixture of 20.0 cm^3 of 0.20 M CH_3COOH + 30.0 cm^3 of 0.20 M NaOH. [3 marks]

c) a mixture of 30.0 cm^3 of 0.20 M CH_3COOH + 20.0 cm^3 of 0.20 M NaOH. [3 marks]

6. Use the following table of standard reduction potentials wherever necessary.

	E^0/V
MnO_4^- (aq) + 8 H^+ (aq) + 5 e^- → Mn^{2+} (aq) + 4 H_2O (l)	+1.51
Cl_2 (g)+ 2 e^- → $2Cl^-$ (aq)	+1.36
$Cr_2O_7^{2-}$ (aq) + 14 H^+ (aq) + 6 e^- → 2 Cr^{3+} (aq) + 7 H_2O (l)	+1.33
Ag^+ (aq) + e^- → Ag (s)	+0.80
Fe^{3+} (aq) + e^- → Fe^{2+} (aq)	+0.77
2 H^+ (aq) + 2e^- → H_2 (g)	0.00
Fe^{3+} (aq) + 3e^- → Fe (s)	-0.036
Fe^{2+} (aq) + 2e^- → Fe (s)	-0.44
Mg^{2+} (aq) + 2e^- → Mg (s)	-2.38

a) The cell notation represents a **standard** galvanic cell:
Mg (s) | $MgCl_2$ (aq) || $FeCl_3$ (aq), $FeCl_2$ (aq)|Pt (s)

i) Write a balanced **ionic** equation for the cell reaction.[1 mark]

ii) What is the cell potential? [1 mark]

iii) Draw a **fully labeled** diagram of the galvanic cell. Show the direction of flow of electrons, the polarity of the electrodes and the concentration of all solutions. [5 marks]

b) By reference to the standard electrode potentials given, explain why hydrochloric acid can be used to provide an acid medium with potassium dichromate but NOT with potassium manganate (VII) as oxidizing agents.
[2 marks]

c) Given the Nernst Equation: $E = E^0 - \frac{0.059}{n}\log Q$, at 298 K, find the value of the equilibrium constant for the reaction: 5 Fe^{2+} (aq) + MnO_4^- (aq) + 8 H^+ (aq) ⇌ Mn^{2+} (aq) + 4 H_2O (l) + 5 Fe^{3+} (aq) at 298 K.
[3 marks]

7. Derive a balanced **ionic** equation for each reaction by writing half equations and then combining them.

a) $PbS\ (s) + NO_3^-(aq) \rightarrow S\ (s) + Pb^{2+}\ (aq) + NO\ (g)$ (in **acid** medium) [3 marks]

b) $MnO_4^-\ (aq) + IO_3^-\ (aq) \rightarrow MnO_2\ (s) + IO_4^-\ (aq)$ (in **basic** medium) [3 marks]

END OF EXAMINATION