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You may use the following information wherever necessary:

a) $R = 8.31\ J\ mol^{-1}\ K^{-1} = 0.0821\ atm\ dm^3\ mol^{-1}\ K^{-1} = 0.0821\ atm\ L\ mol^{-1}\ K^{-1}$

b) $k = Ae^{-Ea/RT}$

c) $\ln\frac{k_2}{k_1} = \frac{E_a}{R} \times \frac{(T_2 - T_1)}{T_1T_2}$

d) $\ln\frac{[A]_t}{[A]_0} = -kt$

e) $t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$

f) $K_p = K_c\,(0.0821T)^{\Delta n(gas)}$

g) $K_w = 1.0 \times 10^{-14}$ at 298 K

h) $K_a\ (CH_3COOH) = 1.8 \times 10^{-5}$

i) $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

j) $pH = pK_a + \log\frac{[base]}{[acid]}$

k) $E = E^o - \frac{0.059}{n}\log Q$

Section A: Multiple Choice

Select the best answer for each question and shade the letter corresponding to the answer on the answer sheet provided. [35 marks

Questions 1-3

The reaction $2NO_2^-(aq) + 4\ H^+ + 2\ I^-(aq) \rightarrow I_2 + 2\ NO\ (g) + 2\ H_2O\ (l)$ is first order in nitrite ion and iodide ion and second order in hydrogen ion.

1. The rate law for the reaction is

   A Rate = $k\ [NO_2^-]^2[H^+][I^-]^2$

   B Rate = $k\ [NO_2^-]^2[H^+][I^-]$

   C Rate = $k\ [NO_2^-][H^+]^2[I^-]$

   D Rate = $k\ [NO_2^-][H^+][I^-]^2$

   E Rate = $k\ [NO_2^-]^2[H^+]^4[I^-]^2$

2. If the rate of the reaction is expressed in M s^{-1}, the correct unit for the rate constant, *k*, is

   A $M^{-2}\ s^{-1}$

   B $M^2\ s^{-1}$

   C $M\ s^{-1}$

   D $M^{-2}\ s^{-2}$

   E $M^{-3}\ s^{-1}$

3. By what factor would the rate of the reaction change if the concentrations of all the reactants are doubled?

   A 1/2

   B 2

   C 4

   D 8

   E 16

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4. Ammonia can be oxidized according to the equation:
$4\ NH_3\ (g) + 5\ O_2\ (g) \rightarrow 4\ NO\ (g) + 6\ H_2O\ (g)$

If in a particular reaction the Δ[NO] is 0.006 mol dm^{-3}, then $\Delta[O_2]$, in mol dm^{-3}, is

A $-5/4 \times 0.006$

B $5/4 \times 0.006$

C $-4/5 \times 0.006$

D $4/5 \times 0.006$

E $4 \times 5 \times 0.006$

5. Which statement best explains the observation that reaction rates increase when temperature is increased?

A At a higher temperature the energy of activation is reduced.

B At a higher temperature the energy of activation is increased.

C At a higher temperature the concentration of the reactants is higher.

D At a higher temperature a larger fraction of reactant molecules have sufficient energy to form the transition state.

E At a higher temperature there is no need to form the transition state.

6. Which statement about catalysts is **NOT** true?

A A catalyst has no effect on the enthalpy change for the reaction which it catalyses.

B A catalyst does not participate in the reaction which it catalyses.

C Catalysts are specific in their action.

D A catalyst changes the rate of the forward and reverse reactions for a reversible reaction by the same factor.

E A catalyst does not affect equilibrium position for a reversible reaction.

7. The following mechanism has been proposed for a reaction:

Step 1: $H_2O_2\ (aq) + I^-\ (aq) \rightarrow H_2O\ (l) + IO^-\ (aq)$ slow

Step 2: $IO^-(aq) + H_2O_2\ (aq) \rightarrow H_2O\ (l) + O_2\ (g) + I^-\ (aq)$ fast

Which statement is **NOT** consistent with this proposed mechanism?

A The overall reaction is: $2\ H_2O_2\ (aq) \rightarrow 2\ H_2O\ (l) + O_2\ (g)$

B IO^- is a reactive intermediate.

C I^- is a catalyst.

D The reaction is first order with respect to the catalyst.

E The reaction is second order with respect to H_2O_2.

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8. 0.24 mol of NO_2 and 0.20 mol of Cl_2 were introduced into a 1 dm^3 vessel at constant temperature. When the system reached equilibrium, 0.16 mol of NOCl was present.

The reaction is: $2\,NO_2(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$.

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

	$[NO_2]$/moldm^{-3}	**$[Cl_2]$/moldm^{-3}**	**[NOCl]/moldm^{-3}**
A	0.08	0.12	0.16
B	0.08	0.04	0.16
C	0.08	0.08	0.16
D	0.16	0.08	0.16
E	0.12	0.12	0.16

9. The equilibrium constant for the reaction $P(aq) \rightleftharpoons Q(aq)$ is 3.2×10^{-5}.

Which of the following statements is **TRUE**?

A The equilibrium concentration of P is less than that of Q.

B The equilibrium concentration of P is greater than that of Q.

C Adding a suitable catalyst will increase the equilibrium concentration of Q.

D Adding a catalyst will increase the value of the equilibrium constant.

E Adding more P to an equilibrium mixture of P and Q will increase the value of the equilibrium constant.

10. For which equilibrium system, at constant temperature, will decreasing the volume **not** cause the equilibrium position to shift?

A $2\,CO(g) + O_2(g) \rightleftharpoons 2\,CO_2(g)$

B $C(s) + O_2(g) \rightleftharpoons CO_2(g)$

C $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

D $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$

E $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

11. Consider the process: $Fe_2O_3(s) + 3\,H_2(g) \rightleftharpoons 3H_2O(g) + 2\,Fe(s) \quad \Delta H = +98.7$ kJ

Which statement is **NOT** true for this system?

A $K_p = K_c$ at a stated temperature.

B Addition of some H_2 to an equilibrium mixture will cause equilibrium to shift to the right.

C Increasing the mass of Fe_2O_3 will cause equilibrium to shift to the right.

D The value of K_p can be increased by increasing the temperature.

E Decreasing the volume of the container does not upset equilibrium.

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12. 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 **forward** reaction occur to establish equilibrium?

	$p_i PCl_5$/atm	$p_i PCl_3$/atm	$p_i Cl_2$/atm
A	1	2	1
B	2	2	2
C	1	1	2
D	2	2	3
E	3	2	2

13. According to the Bronsted-Lowry definition, a **base** is a species which

A donates a hydrogen atom.

B donates a hydrogen ion.

C accepts a hydrogen atom.

D accepts a hydrogen ion.

E accepts a hydroxide ion.

14. Which does **NOT** constitute an acid/base conjugate pair?

A H_2CO_3/ HCO_3^-

B NH_3/ NH_2^-

C NH_4^+/ NH_3

D H_3O^+/ OH^-

E HNO_2/ NO_2^-

15. Which is a weak acid?

A HI

B $HClO_4$

C HBr

D HF

E HCl

16. 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 HCl, HBr, HF

D HF, H_2O, NH_3

E HPO_4^{2-}, H_3PO_4, $H_2PO_4^-$,

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17. The acidity constant for an acid, HA, is 2.5×10^{-5}. The pK_b of its conjugate base is closest to

A 4.6

B 9.4

C 4.0×10^{-10}

D 1.0×10^{-14}

E 14

18. Assuming all of the following solutions have the same molar concentration, which one would be expected to have the **lowest** pH?

A $FeCl_3$

B $FeCl_2$

C $CaCl_2$

D KCl

E $BaCl_2$

Questions 19-23 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

19. would there be a decreases in pH as the titrant is added?

20. would the pH be greater than 7 at the equivalence point?

21. would the pH be lower than 7 at the equivalence point?

22. would phenolphthalein (pH range 8.3 – 10.0) be unsuitable as an indicator?

23. would bromocresol green (pH range 3.8 – 5.4) be unsuitable as an indicator?

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

A NH_4NO_3

B LiH

C H_2O_2

D $NaHSO_4$

E HF

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25. In which compound does oxygen carry an oxidation number of -1?

A $NaHSO_4$

B NH_4NO_3

C H_2O_2

D Fe_2O_3

E FeO

26. In which compound does oxygen carry an oxidation number of +2?

A F_2O

B NH_4NO_3

C $KHSO_4$

D CuO

E Cu_2O

27. Which is **NOT** a redox reaction?

A $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

B $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

C $2NBr_3 + H_2O \rightarrow N_2 + 4Br^- + 2HOBr$

D $ZnCO_3 \rightarrow ZnO + CO_2$

E $XeF_2 + 2Cl^- \rightarrow Xe + 2F^- + Cl_2$

28. Which is a disproportionation reaction?

A $SO_2 + H_2O \rightarrow H_2SO_3$

B $CH_4 + 2O_2 \rightarrow CO_2 + 2\ H_2O$

C $3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$

D $2\ KMnO_4 + 5\ SO_2 + 2\ H_2O \rightarrow 2\ MnSO_4 + K_2SO_4 + 2\ H_2SO_4$

E $S_2O_8^{2-} + 2\ I^- \rightarrow 2\ SO_4^{2-} + I_2$

29. Which quantities are conserved in a redox reaction?

A Mass only.

B Charge only.

C Oxidation number.

D Neither mass nor charge.

E Both mass and charge.

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30. The e.m.f. of the cell: Pt (s)| H_2 (g)|HCl (aq)|| $CuSO_4$ (aq)| Cu (s) does **NOT** depend on

A temperature.

B the size of the copper electrode.

C the concentration of HCl.

D the concentration of $CuSO_4$.

E the pressure of H_2.

31. When the contents of an electrochemical cell are at equilibrium, the e.m.f. of the cell

A is zero.

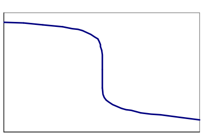
B is at a maximum.

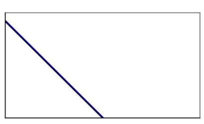
C is negative.

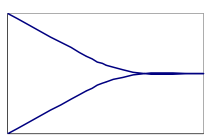
D is positive.

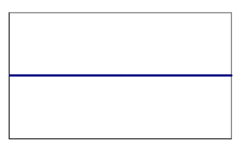
E cannot be measured.

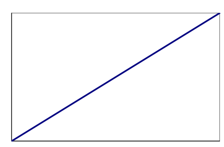
Questions 32 - 35 concern the following graphs:


A


B


C


D


E

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

32. Rate of reaction versus concentration of X for a reaction which is zero order in X.

33. Rate of reaction versus concentration of X for a reaction which is first order in X.

34. Rate of reaction versus time for a reversible process which attains equilibrium after some time.

35. The titration curve for the titration of a base with an acid.

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<u>SECTION B</u>: Answer **<u>ALL</u>** questions **<u>in the spaces provided on the question paper</u>**.

<u>Remember to include units in your answers wherever appropriate</u>.

1. The following data were obtained for the reaction:
$6\ I^-\ (aq) + BrO_3^-\ (aq) + 6\ H^+\ (aq) \rightarrow 3\ I_2\ (aq) + Br^-\ (aq) + 3\ H_2O\ (l)$

Experiment	Initial $[I^-]$/M	Initial $[BrO_3^-]$/M	Initial $[H^+]$/M	Initial Rate of I_2 formation/Ms^{-1}
1	0.0020	0.0080	0.020	8.89×10^{-5}
2	0.0040	0.0080	0.020	1.78×10^{-4}
3	0.0020	0.0160	0.020	1.78×10^{-4}
4	0.0020	0.0080	0.040	3.56×10^{-4}

a) Derive the rate law for the reaction. [3]

b) i) Use the data from experiment 1 to find the value of the rate constant, *k*, <u>stating its correct units</u>. [2]

ii) What would be the value of the **<u>rate constant</u>** if the concentration of all reactants were doubled? [1]

c) What effect, if any, would doubling the concentration of the reactants have on the energy of activation for the process? [1]

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d) What effect, if any, would increasing the temperature of the reaction mixture have on the energy of activation for the process? [1]

e) What effect, if any, would increasing the temperature of the reaction mixture have on the value of the rate constant for the process? [1]

f) What effect, if any, would using a catalyst have on the energy of activation for the process? [1]

2. The activation energy for the reaction: $2\ N_2O\ (g) \rightarrow 2\ N_2\ (g) + O_2\ (g)$ is 200 kJ mol^{-1}.

How many times faster would this reaction proceed at 230°C than at 200°C? [4]

3. The first order rate constant for the decomposition of a certain hormone in water at 25°C is 0.0342 day^{-1}.

a) If a 0.0200 M solution of the hormone is stored for 40 days, what will be its concentration at the end of that period? [3]

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b) What is the half life of the hormone? [2]

c) How many days will it take for a sample of the hormone to be 65% decomposed? [2]

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

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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5. The equilibrium constant, K_p, for the dissociation of dinitrogen tetroxide to nitrogen dioxide is 11 at 398K. The reaction is: $N_2O_4\ (g) \rightleftharpoons 2\ NO_2(g)$.

a) Find the equilibrium partial pressure of each gas when N_2O_4, at an initial pressure of 1.20 atm, dissociates at 398 K. [6]

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

c) Find the percent dissociation of dinitrogen tetroxide. [1]

6. Find the pH of

a) 0.020 M NaOH [1]

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b) 0.020 M CH_3COOH [5]

c) a mixture of 20.0 cm^3 of 0.020 M CH_3COOH + 20.0 cm^3 of 0.020 M NaOH [7]

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d) a mixture of 30.0 cm^3 of 0.020 M CH_3COOH + 20.0 cm^3 of 0.020 M NaOH [5]

e) a mixture of 20.0 cm^3 of 0.020 M CH_3COOH + 30.0 cm^3 of 0.020 M NaOH [4]

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

PbS (s) + NO_3^-(aq) $\rightarrow$ S (s) + Pb^{2+} (aq) + NO (g) (in **acid** medium) [4]

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8. Use the following table of standard redox potentials wherever necessary.

	E°/V
MnO_4^- (aq) + 8 H^+ (aq) + 5 e^- $\rightarrow$ Mn^{2+} (aq) + 4 H_2O (l)	+1.51
Cl_2 (g) + 2e^- $\rightarrow$ 2Cl^- (aq)	+1.36
Ag^+ (aq) + e^- $\rightarrow$ Ag (s)	+0.80
Fe^{3+} (aq) + e^- $\rightarrow$ Fe^{2+} (aq)	+0.77
NiO_2 (s) + 2 H_2O (l) + 2e^- $\rightarrow$ $Ni(OH)_2$ (s) + 2 OH^- (aq)	+0.49
Cu^{2+} (aq) + 2e^- $\rightarrow$ Cu (s)	+0.34
2H^+ (aq) + 2e^- $\rightarrow$ H_2 (g)	0.00
Ni^{2+} (aq) + 2e^- $\rightarrow$ Ni (s)	-0.25
Fe^{3+} (aq) + 3e^- $\rightarrow$ Fe (s)	-0.036
Cd^{2+} (aq) + 2e^- $\rightarrow$ Cd (s)	-0.40
Fe^{2+} (aq) + 2e^- $\rightarrow$ Fe (s)	-0.44
$Cd(OH)_2$(s) + 2e^- $\rightarrow$ Cd (s) + 2 OH^- (aq)	-0.81
Mg^{2+} (aq) + 2e^- $\rightarrow$ Mg (s)	-2.38

a) Rechargeable nickel-cadmium cells are used in calculators and other battery powered devices. The cell reaction is:

NiO_2 (s) + Cd (s) + 2 H_2O (l) $\rightarrow$ $Ni(OH)_2$ (s) + $Cd(OH)_2$ (s).

What is the cell potential of a standard nickel-cadmium cell? [1]

b) 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]

ii) 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]

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c) i) Find the standard cell potential for a cell in which the reaction:

$Ag^{+}(aq) + Fe^{2+}(aq) \rightleftharpoons Ag(s) + Fe^{3+}(aq)$ takes place. [1]

ii) Find K_c for the process: $Ag^{+}(aq) + Fe^{2+}(aq) \rightleftharpoons Ag(s) + Fe^{3+}(aq)$ [4]

d) Find the e.m.f of the cell: Cu (s) | Cu^{2+} (0.001 M) || Cu^{2+} (0.250 M) | Cu (s) [4]

e) Explain why hydrochloric acid cannot be used to provide an acid medium with potassium manganate (VII) as an oxidizing agent. [2]

END OF EXAMINATION