SECTION I: Multiple Choice Questions *Select the SINGLE best alternative in each of the following cases and indicate your answer by marking the corresponding letter on the answer sheet provided.*

Questions 1 to 4 concern an experiment to determine the initial rate of reaction between the oxidising agent ammonium peroxodisulfate ($(NH_4)_2S_2O_8$) and potassium iodide.
A series of experimental runs was carried out. In each of these a certain volume of a very dilute solution of sodium thiosulfate and 3 drops of starch indicator solution were placed in a test tube together with a measured volume of potassium iodide solution and sufficient water to make the total volume in this first tube up to 10 cm^3. In a second test tube a certain volume of the ammonium peroxodisulfate solution was mixed with sufficient water to make the total volume in this tube 10 cm^3, and the mixture poured quickly into the first test tube. The mixture was stirred vigorously and a stop-watch started. The following reactions took place:

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$
$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

The time taken for the solution to darken was noted.
The calculated initial concentrations of the ammonium peroxodisulfate and potassium iodide in the reaction mixture, together with the times taken for the mixture to darken, are given below.

Initial concs./mol dm^{-3}

Ammonium Peroxodisulfate	Potassium Iodide	Darkening Time /s
0.10	0.20	35
0.05	0.20	70
0.03	0.20	117
0.10	0.10	70
0.10	0.067	105

1) Which one of the following rate laws is consistent with the above observations?
   - A Rate $\propto [S_2O_8^{2-}]$
   - B Rate $\propto [I^-]$
   - C Rate $\propto [S_2O_8^{2-}][I^-]$
   - D Rate $\propto 1/([S_2O_8^{2-}][I^-])$
   - E Rate $\propto [S_2O_8^{2-}]^2[I^-]^2$

2) Which one of the following is the reason for adding the sodium thiosulfate?
   - A To react with a certain definite quantity of iodine.
   - B To provide sodium ions.
   - C To catalyse the reaction.
   - D To react with a certain definite quantity of ammonium peroxodisulfate.
   - E To oxidize the iodide ions to free iodine.

3) The darkening of the solution was due to which one of the following?
   - A The precipitation of sulfur.
   - B The formation of an iodine/thiosulfate complex.
   - C The oxidation of sodium thiosulfate.
   - D The formation of free iodine and its reaction with the starch.
   - E The reduction of iodine to iodide by the thiosulfate ion.

4) In a further experimental run the initial concentrations of ammonium peroxodisulfate and potassium iodide were 0.20M and 0.40M respectively. Which one of the following times is closest to the expected darkening time?
   - A 35 seconds.
   - B 140 seconds.
   - C 70 seconds.
   - D 18 seconds.
   - E 9 seconds.

****

5) The reaction between propanone ($CH_3COCH_3(aq)$) and iodine in acidified aqueous solution is described by the following equation:

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_2ICOCH_3(aq) + H^+(aq) + I^-(aq)$$

The reaction is first order with respect to both propanone and hydrogen ion, but zero order with respect to iodine. Which of the following conclusions may be drawn from these observations?
   - A The reaction must occur in more than one elementary step.
   - B Iodine is involved in the rate-determining step.
   - C Increasing the concentration of hydrogen ion decreases the rate of reaction.
   - D Propanone is not involved in the rate-determining step.
   - E Increasing the concentration of iodine increases the rate of the reaction.

6) The rates of chemical reactions depend strongly on temperature. Which one of the following statements best explains this observation?

A At high temperatures the activation energy of the reaction is lower.
B At high temperatures almost all molecules are present as activated complexes.
C At high temperatures the concentrations of reactants is higher.
D At high temperatures the partial pressures of the reactants are higher.
E At high temperatures a much larger proportion of molecules have sufficient energy to react.

7) The decomposition of dinitrogen pentoxide in tetrachloromethane solution may be represented by the equation:

$$2N_2O_5 \rightarrow 4NO_2 + O_2(g)$$

The nitrogen dioxide is soluble in tetrachloromethane whilst the oxygen is not. Measurement of which one of the following physical properties could **NOT** be used for determining the rate of this reaction?

A Electrical conductivity of the solution.
B Volume of oxygen evolved.
C Absorbance of light by the solution.
D Mass of the reacting mixture.
E Pressure of oxygen evolved.

8) The experimentally determined rate equation for the reaction represented by the equation:

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(aq)$$

is: rate = $k[BrO_3^-][Br^-][H^+]^2$

If the concentration of each of the reactants is doubled, which one of the following statements regarding the rate of reaction is true?

A The rate is doubled.
B The rate is tripled.
C The rate is increased four-fold.
D The rate is increased eight-fold.
E The rate is increased sixteen-fold

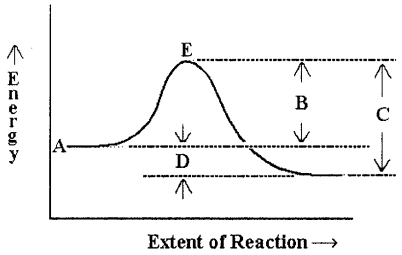
9) At a certain temperature the partial pressures of carbon monoxide, chlorine and carbon oxide dichloride ($COCl_2$) in the equilibrium mixture defined by the equation:

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

were 2, 4 and 48 atm respectively. What is the numerical value of K_p?

A 0.167
B 6
C 24
D 54
E 86

Questions 10 to 13 involve the following diagram:



10) Which letter on the diagram represents the activation energy for the forward reaction?

11) Which letter on the diagram represents ΔH for the reaction?

12) Which letter on the diagram represents the activation energy for the back reaction?

13) Which letter on the diagram represents the activated complex?

****

14) Consider the following system at equilibrium:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \quad \Delta H +ve$$

Which one of the following operations would displace the equilibrium position to the right?

A Adding more $CaCO_3(s)$ to the system at constant pressure.
B Adding more CaO(s) to the system at constant pressure.
C Adding more $CO_2(g)$ to the system at constant pressure.
D Heating the system.
E Adding an inert gas at constant volume.

15) Which one of the following changes the value of the ***equilibrium constant*** for a reaction?

A Reducing the total pressure.
B Increasing the total volume.
C Increasing the concentration of reactants.
D Reducing the temperature of the system.
E Removing one of the products.

16) Given that the K_a values of the following five acids decrease in the order: HI > HCl > C_6H_5COOH > CH_3COOH > HPO_4^{2-}, which one of the following salts would be expected to give the highest pH value when in 0·1M solution?
A NaCl
B NaI
C C_6H_5COONa
D CH_3COONa
E Na_2HPO_4

17) In which one of the following reactions (which take place in aqueous solution) is water acting as an acid?
A $H_2O + HCl \rightarrow H_3O^+ + Cl^-$
B $H_2O + CH_3COOH \rightarrow H_3O^+ + CH_3COO^-$
C $H_2O + C_2H_5NH_2 \rightarrow C_2H_5NH_3^+ + OH^-$
D $H_2O + HSO_4^- \rightarrow H_3O^+ + SO_4^{2-}$
E $4H_2O + Cu^{2+} \rightarrow [Cu(H_2O)_4]^{2+}$

18) The K_b value for a certain base X^- is 10^{-6} at 25°C. The K_a value for HX at the same temperature is therefore:
A 10^{-8}
B 10^{-6}
C 10^{6}
D 10^{8}
E 6

19) Solutions of magnesium sulfate in water are weakly acidic because:
A Water molecules bound to the magnesium ion lose protons more readily than free water molecules.
B Sulfuric acid is not a very strong acid.
C The second proton of sulfuric acid is lost with some difficulty.
D Magnesium ions react readily with protons.
E Such solutions are usually impure.

20) Which one of the following statements regarding the ionic product of water (K_w) is **NOT** true?
A K_w is the equilibrium constant for the reaction:
$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
B K_w is decreased by the addition of an acid to an aqueous solution.
C K_w is altered by a change in temperature.
D K_w is constant for any dilute aqueous solution at constant temperature.
E K_w is approximately 10^{-14} at 25°C.

21) A certain weak monoprotic acid has a pK_a value of 4.8. What is the pH of a buffer solution which is 0.2M in the weak acid and 0.2M in the sodium salt of the acid?
A 2.8
B 3.8
C 4.8
D 5.8
E 6.8

22) Dilute sodium hydroxide solution gradually becomes more dilute on standing. Which one of the following statements is the best explanation for this?
A Sodium hydroxide is deliquescent.
B Sodium hydroxide reacts with carbon dioxide from the air.
C The solution tends to evaporate.
D Sodium hydroxide reacts with oxygen from the air.
E Sodium hydroxide decomposes on standing.

23) When $20cm^3$ of 0.1M ammonia solution are added to $20cm^3$ of 0.1M dilute hydrochloric acid, the resulting solution is:
A Strongly basic.
B Weakly basic.
C Neutral.
D Weakly acidic.
E Strongly acidic.

24) Which one of the following statements regarding a 10^{-8}M solution of hydrochloric acid in water is correct?
A The solution is very slightly acidic.
B The solution has a pH of 8.
C Such a solution cannot be prepared.
D The solution is a buffer solution.
E The solution is extremely acidic.

25) Which one of the following substances is the strongest acid?
A HF
B HCl
C HBr
D HI
E H_2O

26) Which one of the following ions is the strongest acid?
A $Na^+(aq)$
B $K^+(aq)$
C $Mg^{2+}(aq)$
D $Al^{3+}(aq)$
E $Ag^+(aq)$

27) Which one of the following species is amphiprotic?
A HCO_3^-
B H_2CO_3

C CO_3^{2-}
D O_2
E Fe^{2+}

28) The e.m.f. of the cell:
$Pt,H_2(g) \mid HCl(aq) \parallel CuSO_4(aq) \mid Cu$
is **INDEPENDENT** of which one of the following?
A temperature
B concentration of hydrochloric acid
C concentration of copper(II) sulfate solution
D size of the platinum electrode
E pressure of hydrogen

29) Standard electrode potentials for the gain of one electron by the ions $Cu^+(aq)$ and $Cu^{2+}(aq)$ are as follows:
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$ $E^\ominus = +0.52v$
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$ $E^\ominus = +0.17v$
The standard electrode potential in volts for the disproportionation:
$2Cu^+(aq) \rightleftharpoons Cu^{2+}(aq) + Cu(s)$ is:
A -0.69
B -0.35
C +0.52
D +0.69
E +0.35

Questions 30 to 35 concern the following experimental situation.
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 0·01M KSCN(aq). The titre values were used to calculate the concentrations of the various species present at equilibrium and the equilibrium constant calculated.

30) 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.

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

32) 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.

33) 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 interfering with the equilibrium reactions.
D remove excess silver ions from the solution.
E collect it for weighing.

34) Using **ONLY** the titre value in *(4)*, together with the concentration of the potassium thiocyanate solution and the aliquot volume, 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.

35) 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.

Questions 36 to 39 concern the effect on the equilibrium constant, and the yield of product(s), caused by changes made to an equilibrium system.

	EFFECT ON K	EFFECT ON YIELD OF PRODUCTS
A.	increases	increases
B.	decreases	decreases
C.	no change	decreases
D.	no change	increases
E.	no change	no change

Select from A to E the pair of effects produced when the stated change is made to the equilibrium system shown.

36) The pressure is increased by decreasing the volume in the equilibrium system:

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$\Delta H = -196 \text{ kJ mol}^{-1}$

37) A catalyst is added to the equilibrium system:

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$\Delta H = -196 \text{ kJ mol}^{-1}$

38) The temperature is increased for the equilibrium system:

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

$\Delta H = -92{\cdot}4 \text{ kJ mol}^{-1}$

39) Hydrogen is added to the equilibrium system:

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$\Delta H = +51{\cdot}8 \text{ kJ mol}^{-1}$

****

40) The oxidation of ammonia produces nitrogen and water by the reaction:

$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$

If the rate of formation of N_2 is $2{\cdot}0 \text{ Ms}^{-1}$, then the rate at which

A H_2O is formed is $3{\cdot}0 \text{ Ms}^{-1}$

B NH_3 reacts is $8{\cdot}0 \text{ Ms}^{-1}$

C NH_3 reacts is $1{\cdot}0 \text{ Ms}^{-1}$

D O_2 reacts is $0{\cdot}67 \text{ Ms}^{-1}$

E O_2 reacts is $3{\cdot}0 \text{ Ms}^{-1}$

SECTION II: Attempt all questions in this section. Write your answers in the spaces provided on the question paper.

1) The following is a list of some standard electrode potentials at 298K. The arrangement is alphabetical.

HALF-CELL	$E^{\ominus}$/Volt
$Cd^{2+}(aq) \mid Cd(s)$	-0.40
$Cu^{2+}(aq) \mid Cu(s)$	+0.34
$Fe^{3+}(aq) \mid Fe^{2+}(aq)$	+0.77
$I_2(s) \mid I^-(aq)$	+0.54
$Ni^{2+}(aq) \mid Ni(s)$	-0.25
$Ti^{3+}(aq) \mid Ti^{2+}(aq)$	-0.37

You may also require the Nernst equation:

$$E = E^{\ominus} - [RT/(nF)]\ln Q$$

The term RT/F has the value 0.0257 in SI units.

a) What precisely is meant by the statement that the standard electrode potential for the half cell $Cu^{2+}(aq) \mid Cu(s)$ is +0.34v? (4)

b) Consider the cell:

$$Cd(s) \mid Cd^{2+}(aq, 1M) \parallel Ti^{3+}(aq, 1M), Ti^{2+}(aq, 1M) \mid Pt$$

i) Calculate the e.m.f. of the cell and state which electrode is positive. (2)

ii) Write down a balanced equation for the reaction occurring in the cell. (Make sure that you have the correct ***direction*** of reaction.) (2)

iii) Calculate the e.m.f. of the cell if the concentration of the Ti^{3+} (only) is reduced to 0.311M. (2)

iv) Comment on the result obtained in (iii) above by reference to chemical equilibrium. (1)

c) From the table at the beginning of this question pick out (2)

(i) the strongest reducing agent and _____

(ii) the strongest oxidizing agent. _____

2) This question is concerned with acids and bases. The ionic product of water may be taken as $1{\cdot}00\times10^{-14}M^2$

a) The following equations describe acid/base reactions. For each reaction identify (i) the reactant which is acting as an acid and (ii) its conjugate base. Write their formulae in the spaces provided. (3)

i) $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

ACID _____ CONJUGATE BASE _____

ii) $2H_2SO_4 + HNO_3 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

ACID _____ CONJUGATE BASE _____

iii) $CH_3COOH + HNO_3 \rightarrow CH_3COOH_2^+ + NO_3^-$

ACID _____ CONJUGATE BASE _____

b) Aqueous solutions of a particular monobasic acid, HA, have the following pH values.

	[HA]/mol dm^{-3}	pH	[H_3O^+]/mol dm^{-3}
SOLUTION A	0.1	2.80	1.585×10^{-3}
SOLUTION B	0.001	3.85	????

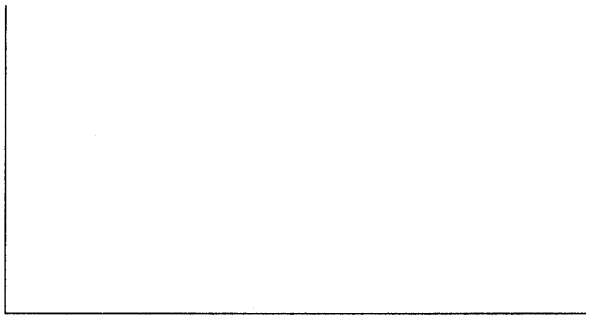
i) Complete the table by calculating the hydronium ion concentration of solution B. (1)

ii) Write down the chemical equation showing the ionisation of the acid HA in aqueous solution. (1)

iii) Write down the expression for the acidity constant, K_a of the acid HA. (1)

iv) Use values from the table to calculate the acidity constant for the acid HA. (2)

c) On the axes below sketch the curve showing the variation in pH which occurs when $20cm^3$ ethanoic acid solution (in a conical flask fitted with a pH meter) is titrated with sodium hydroxide solution of the same molar concentration. Label the axes and indicate the pH (qualitatively), and the volume of sodium hydroxide solution added, at the equivalence point. (4)



d) Calculate the pH of a 0.15M solution of sodium ethanoate. $pK_a(CH_3COOH) = 4.76$ (5)

3) 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 for the above reaction:

$2NO(g) \rightleftharpoons N_2O_2(g)$ ...fast equilibrium step 1

$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$ ... slow step 2

i) Derive the rate law suggested by this mechanism. (4)

ii) When a suggested mechanism leads to a correct rate law, it is still not certain that the mechanism is correct. Why is this? What further piece of information would help to confirm the mechanism suggested above?

(2)

4) a) Chemical equilibrium is described as a *dynamic equilibrium*. Why? (2)

b) State two ways in which the time taken to establish such an equilibrium may be altered. (2)

c) The following data indicate the effect of temperature and pressure on the equilibrium concentration of the product, X, of the forward reaction in a gaseous equilibrium.

TEMPERATURE /°C	PERCENTAGE OF X PRESENT IN THE EQUILIBRIUM MIXTURE AT		
	1atm	100atm	200atm
550	0.077	6.70	11.9
650	0.032	3.02	5.71
750	0.016	1.54	2.99
850	0.009	0.87	1.68

i) Use the above data to deduce whether the production of X is accompanied by an increase or a decrease in number of moles of gas and explain your answer. (2)

ii) Use the above data to determine whether the production of X is an exothermic or an endothermic process and explain your answer. (2)

iii) State qualitatively the theoretical optimum conditions of temperature and pressure suggested by the above data for the commercial production of X. (2)

iv) Explain why a catalyst might be added to the reaction mixture. (1)

THIS IS THE END OF THE PAPER. GO BACK AND CHECK YOUR WORK.