Name: _____ Student number: _____

Chemistry 1AA3 **Final Exam** **April 12, 2008**

McMaster University **VERSION 1**

Instructors: P. Berti, P. Lock, J. Valliant

Duration: 3 hours

This exam contains 30 numbered pages printed on both sides. There are **37** multiple-choice questions appearing on pages numbered 3 to 26. Page 29 includes some useful data. There is a periodic table on page 30. Pages 27 and 28 may be used for rough work. You may tear off the last pages to view the periodic table and to do your rough work.

You must enter your name and student number on the question sheets, as well as on the answer sheet. Your invigilator will be checking your student card for identification.

You are responsible for ensuring that your copy of the question paper is complete. Bring any discrepancy to the attention of your invigilator.

Questions 1 to 29 are each worth 2 marks; questions 30 – 37 are each worth 3 marks. The total marks available are 82. There is **no** additional penalty for incorrect answers.

BE SURE TO ENTER THE CORRECT VERSION NUMBER OF YOUR EXAM (shown near the top of page 1), IN THE SPACE PROVIDED ON THE ANSWER SHEET.

ANSWER ALL QUESTIONS ON THE ANSWER SHEET, IN PENCIL.
Instructions for entering multiple-choice answers are given on page 2.

SELECT ONE AND ONLY ONE ANSWER FOR EACH QUESTION from the answers **(A)** through **(E). No work written on the question sheets will be marked**. The question sheets may be collected and reviewed in cases of suspected academic dishonesty **or to confirm version number**.

Academic dishonesty may include, among other actions, communication of any kind (verbal, visual, *etc*.) between students, sharing of materials between students, copying or looking at other students' work. If you have a problem, please ask the invigilator to deal with it for you. Do not make contact with other students directly. Try to keep your eyes on your own paper – looking around the room may be interpreted as an attempt to copy.

Only Casio FX 991 electronic calculators may be used; but they must NOT be transferred between students. Use of periodic tables or any aids, other than those provided, is not allowed.

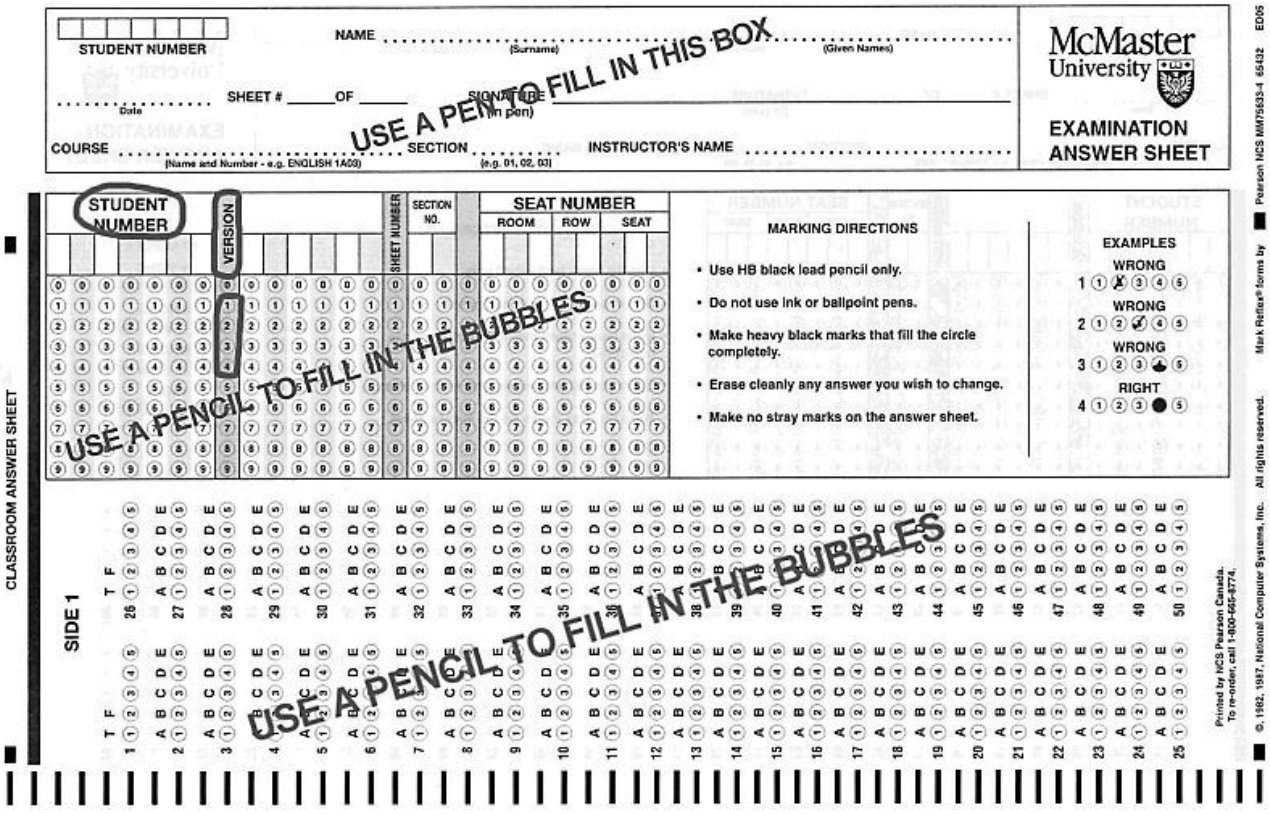
Name: _____ Student number: _____

OMR EXAMINATION – STUDENT INSTRUCTIONS

NOTE: IT IS YOUR RESPONSIBILITY TO ENSURE THAT THE ANSWER SHEET IS PROPERLY COMPLETED. YOUR EXAMINATION RESULT DEPENDS UPON PROPER ATTENTION TO THESE INSTRUCTIONS.

The scanner, which reads the sheets, senses the bubble shaded areas by their non-reflection of light. **A heavy mark must be made, completely filling the circular bubble, with an HB pencil.** Marks made with a pen will **NOT** be sensed. Erasures must be thorough or the scanner will still sense a mark. Do **NOT** use correction fluid on the sheets. Do **NOT** put any unnecessary marks or writing on the sheet.

1. On SIDE 1 (**red side**) of the form, in the top box, print your student number, name, course name, and the date in the spaces provided, *in pen*. Then you **MUST** write your signature, in the space marked SIGNATURE.
2. In the second box, mark your student number and **test or exam version number (1, 2, 3 …)** by filling in the corresponding bubbles underneath, *in pencil*.
3. Answers: mark only **ONE** choice from the alternatives (A,B,C,D,E) provided for each question. The question number is to the left of the bubbles. Make sure that the number of the question on the scan sheet is the same as the number on the test paper. Begin answering Question # 1 using the first set of bubbles, marked "1".

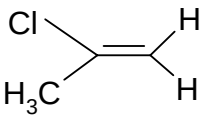


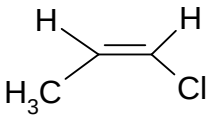
Name: _____ Student number: _____

You are writing VERSION 1 of this exam. Make sure you have correctly entered your version number ("1") in the correct column on your scan sheet (see p. 2 for details).

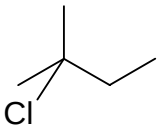
Questions 1 through 29 are worth two (2) marks each.

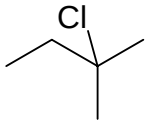
1. Which of the following relationships between pairs of molecules is/are **CORRECT**?

(i) 

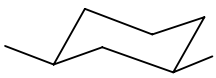
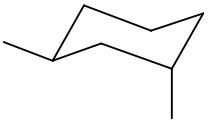
and 

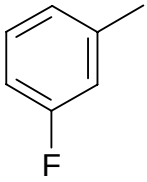
geometric isomers

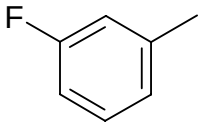
(ii) 

and 

same molecule

(iii) 
and 
geometric isomers

(iv) 

and 

structural isomers

(A) i, iv

(B) i, iii

(C) ii, iii

(D) ii

(E) ii, iv

2. What statement about pyrimidine is **not true**?

(A) It is aromatic.

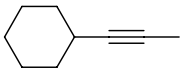
(B) Both nitrogen atoms are sp^2 hybridized.

(C) Pyrimidine could act as a nucleophile.

(D) The orbitals containing the lone pairs on the heteroatoms are perpendicular to the π-system.

(E) Treatment of pyrimidine with HCl would render the ion not aromatic.

3. Treatment of the alkyne below with sodium metal in liquid ammonia gives the same functional group as a Lindlar's reduction but the opposite isomer. Which of the following statements is **not true**?



(A) The substituents in the product are oriented *trans* to each other.

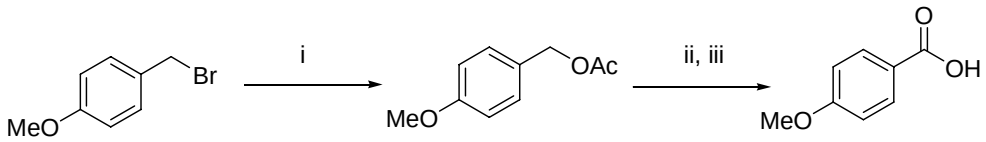
(B) Reduction by Lindlar's catalyst and reduction by sodium in liquid ammonia yield products with different configurations.

(C) The product of the reaction involving sodium is a Z-alkene.

(D) A reduction can involve the addition of hydrogen to a molecule.

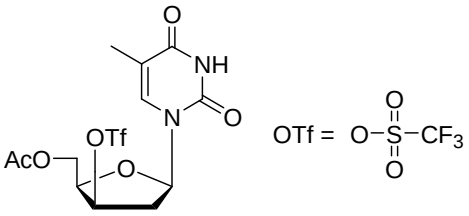
(E) Addition of HCl to the reduction product would yield a mixture of chlorocyclohexylpropane and 2-chlorocyclohexylpropane.

4. Which is the **correct combination of reagents** to accomplish the following synthesis? Note that not all products are shown.

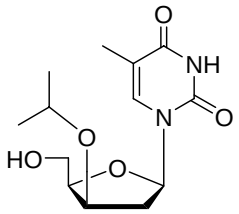


(A)	i) NaOAc	ii) HCl(aq)	iii) $K_2Cr_2O_7$, H_3O^+
(B)	i) NaOAc	ii) HCl(aq)	iii) PCC, CH_2Cl_2
(C)	i) NaOAc	ii) Br_2, light	iii) NaOH
(D)	i) CH_3CONH_2, heat	ii) $LiAlH_4$, Et_2O	iii) H_3O^+
(E)	i) Mg	ii) CO_2(s)	iii) HCl(aq)

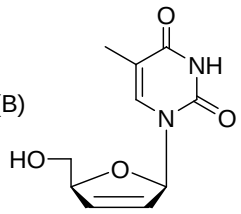
5. When the nucleic acid derivative shown below is treated with isopropanol, which reacts via an S_N1 process, followed by HCl(aq), the **organic product(s)** will be:



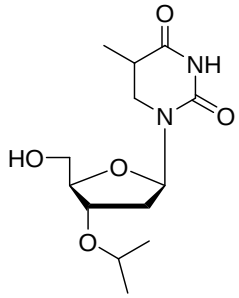
(A)



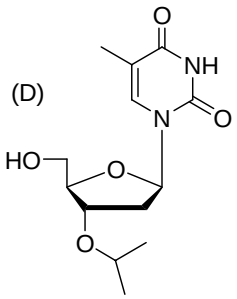
(B)



(C)



(D)



(E) Both A and D are correct.

6. What is the **correct rate law** for a reaction that yields the following initial rates?

Expt. #	[A] (M)	[B] (M)	[C] (M)	v_0 (M/s)
1	1	1	1	0.054
2	2	1	1	0.108
3	1	1	2	0.216
4	2	2	2	0.432

(A) $v_0 = k[A][B][C]$

(B) $v_0 = k[A][B][C]^2$

(C) $v_0 = k[A][B]^{-1}[C]^2$

(D) $v_0 = k[A][C]^2$

(E) $v_0 = k[A][C]$

7. ^{11}C is a radioactive isotope of carbon. Its radioactive decay was followed by plotting $ln([^{11}C])$ versus t, which gave a slope of -0.034 min^{-1}. If the radioactivity in a ^{11}C sample was initially 2.2×10^6 dpm (disintegrations per minute), **how long would it take to decay to 2.2×10^5 dpm**?

(A) 68 min

(B) 6.8 min

(C) 61 min

(D) 0.015 min

(E) 29 min

8. **By what factor does the rate of a reaction increase** if its activation energy is 50. kJ/mol and the temperature is increased from 300 K to 320 K?

(A) 3.5
(B) 5.0
(C) 0.5
(D) 7.1
(E) 1.25

9. Pepsin ($k_{cat} = 23\ s^{-1}$) is the enzyme in your stomach that digests proteins by hydrolyzing amide bonds. Trypsin ($k_{cat} = 124\ s^{-1}$) does the same job in your intestines. The uncatalyzed rate constant for amide bond hydrolysis is $5.5 \times 10^{-11}\ s^{-1}$. **How much lower** is the **activation energy** for the **trypsin-catalyzed reaction** at body temperature, 37 °C?

(A) 4.3 J/mol
(B) 1.3 kJ/mol
(C) 2.3 kJ/mol
(D) 4.3 kJ/mol
(E) 7.3 kJ/mol

10. The reaction $2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$ has an activation energy of 100. kJ/mol and a rate constant of 8.0×10^{-6} $mol^{-1}Ls^{-1}$ at 350K. **What is the value of the rate constant at 400 K**?

(A) 5.9×10^{-4} $mol^{-1}Ls^{-1}$

(B) 9.5×10^{-4} $mol^{-1}Ls^{-1}$

(C) 1.18×10^{-3} $mol^{-1}Ls^{-1}$

(D) 2.95×10^{-3} $mol^{-1}Ls^{-1}$

(E) 9.5×10^{-4} $mol^{1}L^{-1}s^{1}$

11. Which of the following statements about the steady state approximation is **not true**?

(A) d[E•S]/dt = 0

(B) k_{-1} can be much greater than k_2

(C) k_2 is rate-limiting

(D) rate of [E•S] formation = k_2[E•S]

(E) k_{-1} can be less than k_2

12. You wish to make a buffer solution with pH = 10.8. In the lab you have solutions of HCl(aq) and NaOH(aq) available. Choose **one other** solution you will **use to make your buffer**.

(A) $CH_3COONa(aq)$, $K_b = 5.6 \times 10^{-10}$

(B) $NaOCl(aq)$, $K_b = 3.4 \times 10^{-7}$

(C) $HOCl(aq)$, $K_a = 2.9 \times 10^{-8}$

(D) $HCOOH(aq)$, $K_a = 1.8 \times 10^{-4}$

(E) $CH_3NH_2(aq)$, $K_b = 4.4 \times 10^{-4}$

13. Regarding the titration of a weak base (A^-) with a strong acid, choose the **TRUE** statements:

    (i) The pH at the equivalence point depends on the concentrations used.

    (ii) The solution will have neutral pH at the equivalence point.

    (iii) The pH at the half-equivalence point equals the pK_a of HA.

    (iv) The best indicator for this titration will have a pK_a similar to the pH of the half-equivalence point.

(A) all are true

(B) i, iv

(C) ii, iii

(D) i, iii

(E) iii, iv

14. Alazarin yellow R is an acid-base indicator with a pK_a of 11.0. The acidic form is yellow and the basic form is violet. A few drops of this indicator are added to the titration of methylamine (pK_b = 3.36) with HCl. Find the **FALSE** statement(s) about this titration experiment.

(i) The alazarin yellow R indicator is an appropriate choice for locating the equivalence point of this titration.

(ii) The indicator starts to change from violet to yellow at about pH = 12 and completes the change at about pH = 10.

(iii) The indicator will be yellow over the entire buffer region of the titration curve.

(A) i

(B) ii

(C) iii

(D) i, iii

(E) ii, iii

15. Carbon dioxide dissolves in water and reacts to give H_2CO_3, which then ionizes to produce HCO_3^- in the equilibria shown below. These equilibria are critical for maintaining an optimal blood pH = 7.4. Assuming this is the only system controlling blood pH, what is the **ratio of [HCO_3^-] to [H_2CO_3]** in the blood of a patient with severe acidosis (blood pH = 7.0)?

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+ \quad K_a = 4.3 \times 10^{-7}$$

(A) 0.096

(B) 2.6

(C) 4.3

(D) 6.4

(E) 10.7

16. What is the **approximate pH of the endpoint** of the titration of 100.0 mL of 0.050M HNO_3 by 0.050 M KOH if phenolphthalein is used as an indicator? Phenolphthalein is colourless in acid solution and pink in basic solution. The pK_a for phenolphthalein is 9.5.

(A) 13
(B) 10
(C) 8.3
(D) 7.0
(E) 4.74

17. **What will the effect be on the pH** of a 1.0 M HCN solution upon addition of the following reagents in each of the following flasks? (Assume no volume change upon addition). (K_a(HCN) = 6.2×10^{-10})

Flask 1: Addition of KCN(s) to 1.0 L of 1.0 M HCN (aq)
Flask 2: Addition of KCl(s) to 1.0 L of 1.0 M HCN (aq)
Flask 3: Addition of HCl(g) to 1.0 L of 1.0 M HCN (aq)

	Flask 1	Flask 2	Flask 3
(A)	no change	increase	increase
(B)	increase	decrease	decrease
(C)	increase	no change	decrease
(D)	decrease	no change	increase
(E)	increase	no change	increase

18. What is the **pH of the solution that results** after 50.0 mL of 0.010 M CH_3CH_2COOK have been titrated with 25.0 mL 0.010 M HBr? ($K_a(CH_3CH_2COOH) = 1.3 \times 10^{-5}$).

(A) 2.88
(B) 3.79
(C) 4.89
(D) 8.67
(E) 9.11

19. Which of the following mixtures is/are **buffers**?

(i) 10 mL of 0.1 M HNO_3 + 5 mL of 0.1 M $NaNO_2$

(ii) 5 mL of 0.1 M HNO_3 + 10 mL of 0.1 M NH_3

(iii) 10 mL of 0.1 M HNO_3 + 5 mL of 0.1 M $NaNO_3$

(iv) 5 mL of 0.1 M HNO_2 + 5 mL of 0.1 M NaOH

(v) 10 mL of 0.1 M HNO_3 + 5 mL of 0.1 M HNO_2

(A) i
(B) ii, iii
(C) iii, v
(D) iv
(E) ii

20. Arrange the following 3 solutions **in order of increasing pH** (from lowest to highest pH): (K_a (C_6H_5COOH) = 6.3×10^{-5})

(i) 0.1 M C_6H_5COOH + 0.1 M C_6H_5COONa

(ii) 0.1 M C_6H_5COONa

(iii) 0.1 M C_6H_5COOH

(A) iii < ii < i
(B) iii < i < ii
(C) ii < iii < i
(D) ii < i < iii
(E) i < ii < iii

21. Titration of 15.0 ml of an unknown weak base with a strong acid (0.103 M) required 18.2 mL to reach the equivalence point. The pH at the equivalence point was 2.74 and the K_a of the conjugate acid is 5.9×10^{-5}. What was the **original concentration of the weak base**?

(A) 0.125 M
(B) 0.219 M
(C) 1.16 M
(D) 6.54×10^{-3} M
(E) 0.713 M

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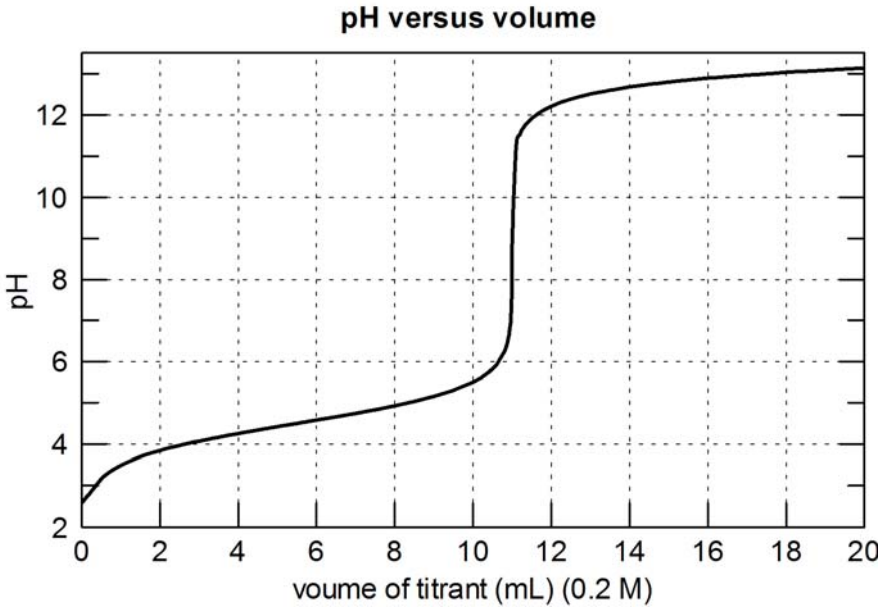
22. Given the following graph, what is the **approximate K_a of the weak acid** being titrated?



(A) 3.2×10^{-5}

(B) 4.5

(C) 8.5

(D) 3.1×10^{-9}

(E) 7.9×10^{-3}

23. $NaHCO_3(aq)$ was added to solutions of each of the following organic compounds.

For which solution would you expect a reaction producing $CO_2(g)$ to occur?

(A) C_6H_5CHO

(B) C_6H_5COOH

(C) C_6H_5COOMe

(D) $C_6H_5CH_2OH$

(E) $C_6H_5CONH_2$

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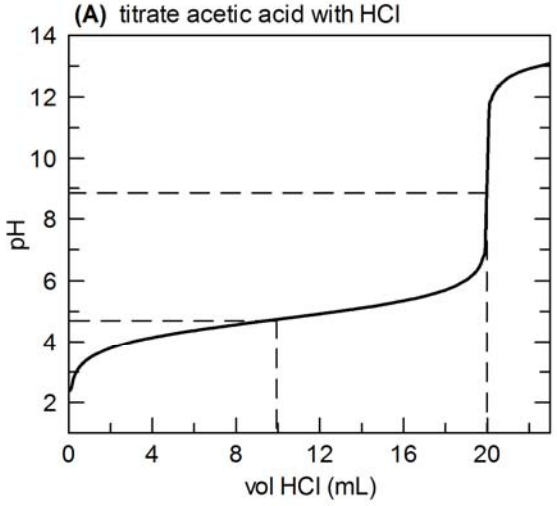
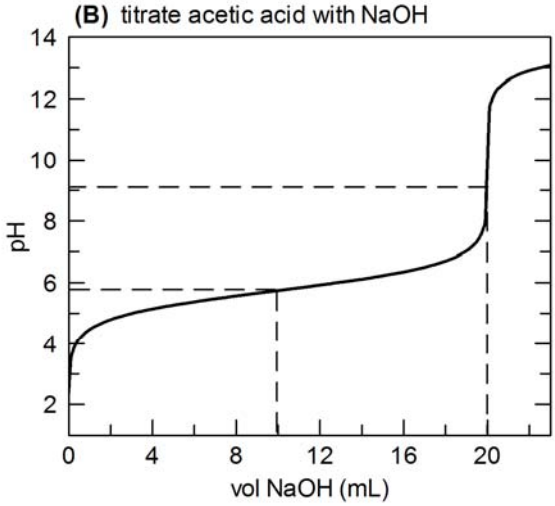
24. Which of the following titration graphs is **completely accurate**?

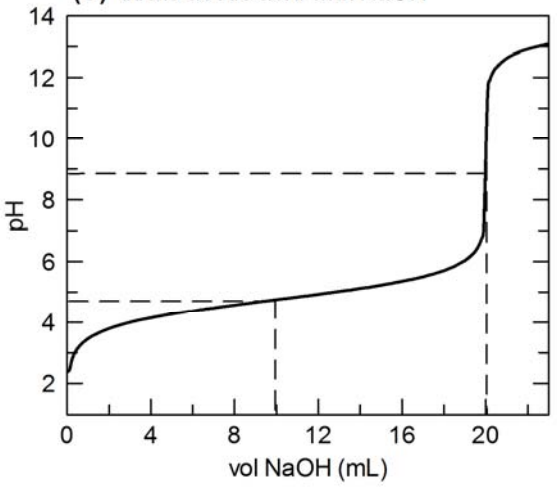
(A) titrate acetic acid with HCl



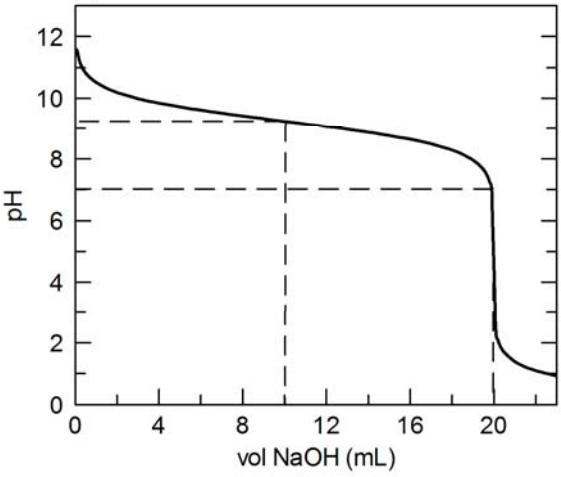
(B) titrate acetic acid with NaOH



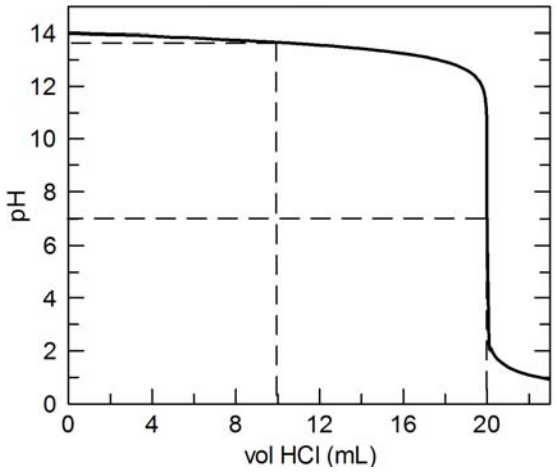
(C) titrate acetic acid with NaOH



(D) titrate ammonia with NaOH



(E) titrate ammonia with HCl



25. Find the **FALSE** statement regarding the phase diagram shown below.

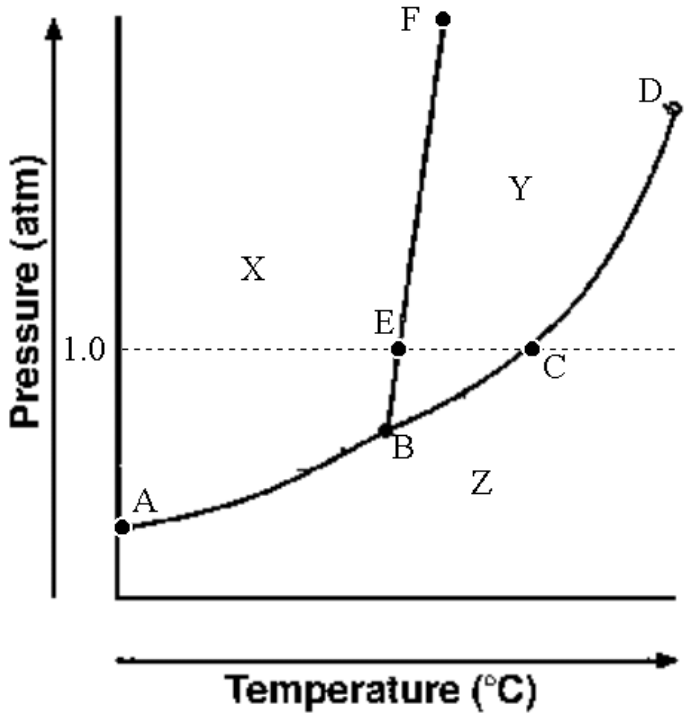
(A) Along curve A-B, the solid and gaseous phases are in equilibrium.

(B) Point B is a triple point; the only point at which the solid, liquid and gas phases are all in equilibrium.

(C) In region Y, the substance is a liquid.

(D) Point D is the critical point, beyond which no liquid-gas phase transitions are observed.

(E) Point E is the normal boiling point of the substance.



26. The liquids H_2O and CH_3CH_2OH are **miscible because of the**:

(A) strong intermolecular forces between H_2O molecules.

(B) strong intermolecular forces between CH_3CH_2OH molecules.

(C) hydrogen bonding between H_2O and CH_3CH_2OH molecules.

(D) weak dipole of the H_2O molecules.

(E) large difference in molar masses of H_2O and CH_3CH_2OH.

27. In pure samples of the following compounds, which ones exhibit **hydrogen bonding**?

(i) CH_2F_2

(ii) NH_2OH

(iii) HBr

(iv) CH_3OCH_3

(v) CH_3CH_2OH

(A) i, ii, iv

(B) i, iii

(C) iv, v

(D) ii, v

(E) iii, iv

28. Select the **TRUE** statements regarding physical properties and intermolecular forces:

(i) The boiling point of propanal is higher than that of propanol.

(ii) The vapour pressure of hexane is higher than that of hexanol.

(iii) Propanol has a higher boiling point than propane because of hydrogen bonding.

(iv) The dominant intermolecular force in methanol is the London dispersion force.

(v) Methyl benzoate can participate in hydrogen bonding with alcohols.

(A) i, iii, iv

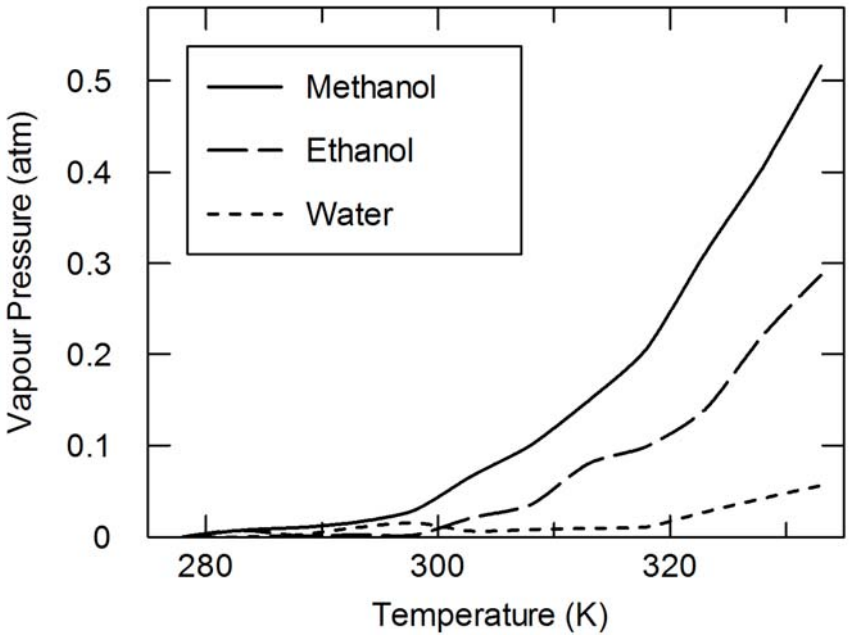
(B) ii, iii, v

(C) i, iv

(D) ii, iv

(E) ii, iii

29. **Which is the FALSE statement** regarding the following graph of vapour pressure *versus* temperature for water, methanol and ethanol?



(A) Water is the least volatile of the three liquids.

(B) The molecule with the highest molecular weight has the lowest vapour pressure at 330 K.

(C) In general, vapour pressure is not linearly proportional to temperature.

(D) Hydrogen bonding has the biggest influence on vapour pressure for these three liquids.

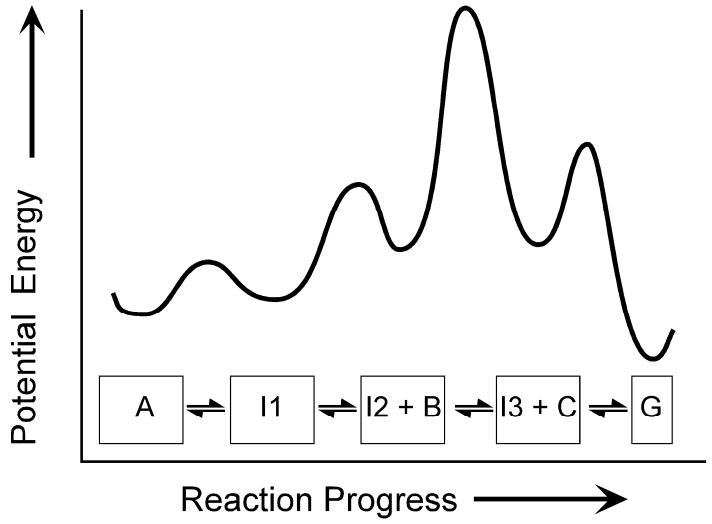
(E) If spilled on the bench top, methanol would evaporate the fastest.

Questions 30-37 are worth three (3) marks each.

30. The reaction profile shown below is for the overall reaction:

$A + B + C \rightarrow G$,

which includes intermediates I1, I2, and I3. What is the **overall rate equation** for this reaction?



(A) $v_0 = k[A]$

(B) $v_0 = k[A][B]$

(C) $v_0 = k[A][B][C]$

(D) $v_0 = k[A]^2[B][C]$

(E) $v_0 = k[A]^2[B][C]^0$

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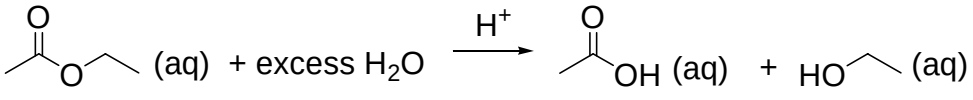
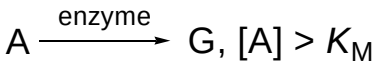
31. Which of the following reactions **are consistent** with a first order or pseudo-first order rate equation?

(*i*) tBu-Cl + MeOH → tBu-OMe + HCl

(*ii*) $H_3C\text{-}Cl + {}^{-}OH \rightarrow H_3C\text{-}OH + Cl^{-}$

(*iii*) 

(*iv*) 

(A) ii, iv

(B) i, ii

(C) i, iii, iv

(D) iii, iv

(E) i, iii

32. For the overall reaction:

$2\ NO + O_2 \rightarrow 2\ NO_2$,

the experimental kinetic data are consistent with two possible mechanisms having a fast equilibrium step followed by a slow step:

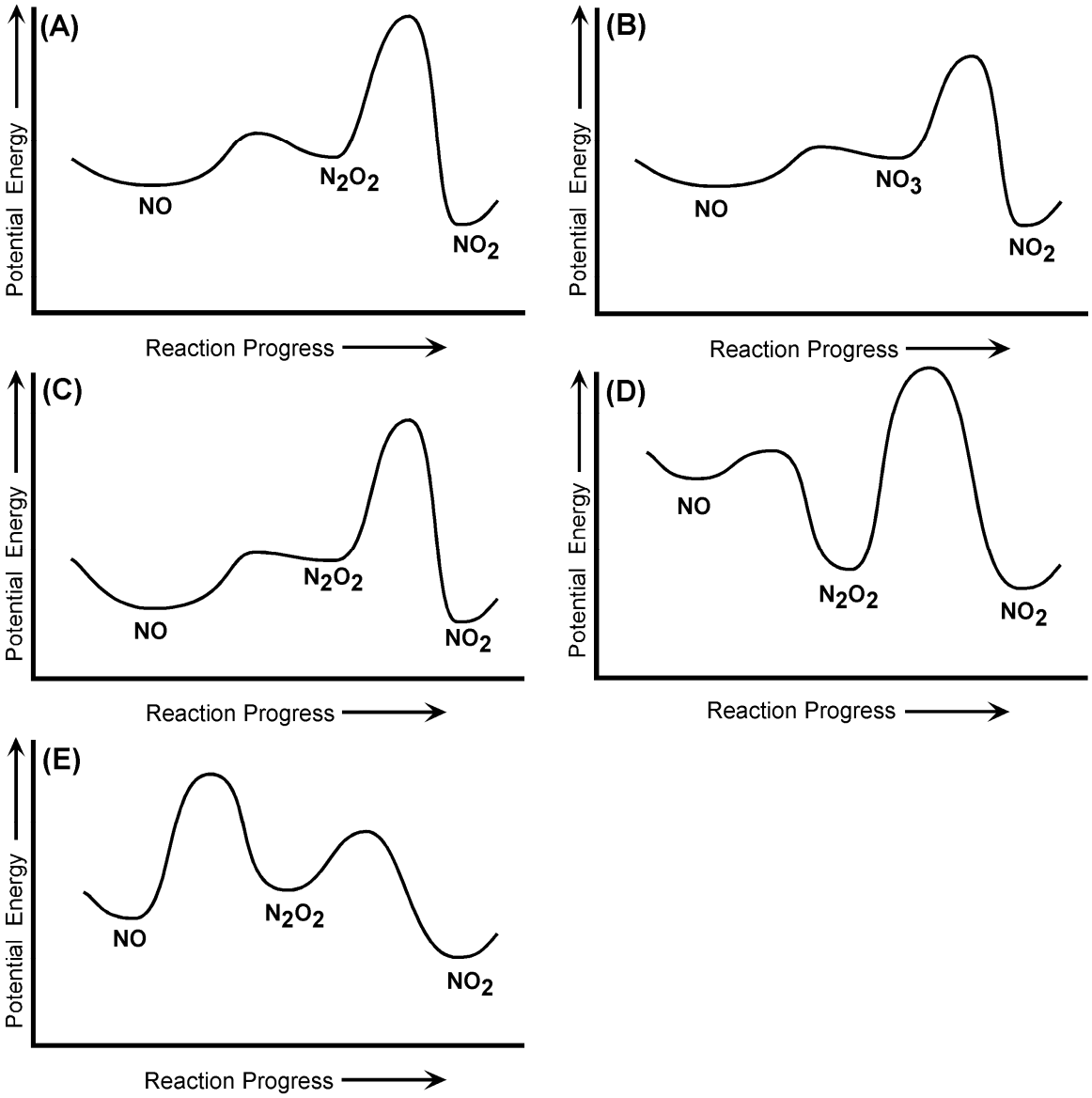
$$2\ NO \rightleftharpoons N_2O_2 + O_2 \longrightarrow 2\ NO_2$$

OR

$$NO + O_2 \rightleftharpoons NO_3 + O_2 \longrightarrow 2\ NO_2$$

.

Which of the following reaction profiles is **not consistent** with the experimental data for the overall reaction?



33. Zyprexa Adhera is a slow-release anti-schizophrenia drug. It is injected once per month and quickly reaches a constant concentration in the blood. Its release into the blood is zero-order, with $k = 5$ μM/day. It is destroyed by the body in process that follows first order kinetics, with $k = 2$ day^{-1}. What is the **Zyprexa Adhera concentration in the blood**?

(A) 1 μM
(B) 2 μM
(C) 2.5 μM
(D) 5 μM
(E) 10 μM

34. What **mass of KOH (in grams)** must be added to 1.00 L of 0.105 M solution of acetic acid to give pH = 5.80? Assume no volume change upon addition of KOH. ($K_a(CH_3COOH) = 1.8 \times 10^{-5}$).

(A) 3.76 g
(B) 5.42 g
(C) 1.20 g
(D) 5.61 g
(E) 0.0965 g

35. HEPES is a weak acid, with pK_a = 7.55. You want to make 1.0 L of a HEPES buffer, pH 7.0, using only HEPES (238.3 g/mol) and the salt of its conjugate base, Na•HEPES (260.3 g/mol). The total concentration of HEPES + Na•HEPES should be 0.1 M. **How many grams of HEPES would you use**?

(A) 1.2 g
(B) 5.2 g
(C) 8.7 g
(D) 18.6 g
(E) 20.3 g

36. In the lab, you dissolve CH_3CH_2MgBr (0.034 mol) in diethyl ether (0.5 L). You add solid CO_2 (44 g), followed by excess HCl(aq) for work-up (assume the yield is 100%). You separate the organic product and dissolve it in sufficient water to create 1 L of solution. You then add 75.00 mL of 0.0500 M NaOH(aq) to this solution. What is the **pH of the solution that results?**
$K_a(H_2CO_3) = 4.5 \times 10^{-7}$; $K_a(HCO_3^-) = 4.8 \times 10^{-11}$; $K_a(CH_3CH_2COOH) = 1.3 \times 10^{-5}$

(A) 3.8
(B) 4.0
(C) 4.9
(D) 6.1
(E) 8.6

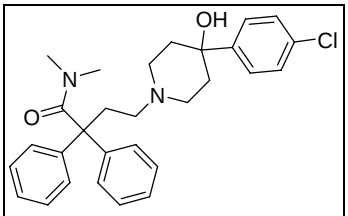
Name: _____ Student number: _____

37. Loperamide (shown below) is a biologically active compound for the treatment of diarrhea. To create a library of Loperamide analogues that may have enhanced activity and reduced side effects, three separate reactions of Loperamide itself were attempted.

(i) Reaction 1: treatment with aqueous HCl at 25°C

(ii) Reaction 2: treatment with PCC in CH_2Cl_2.

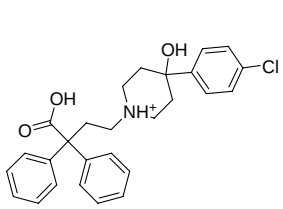
(iii) Reaction 3: treatment with conc. H_2SO_4 at 100°C.



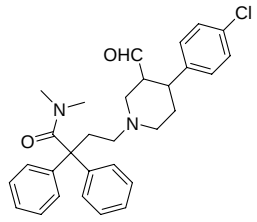
Loperamide

The **expected products of these three separate reactions** are:

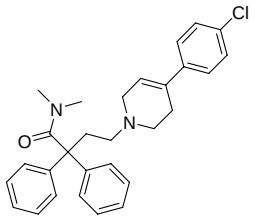
(A)



Reaction 1

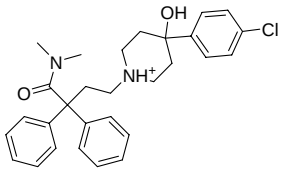


Reaction 2

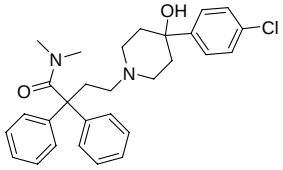


Reaction 3

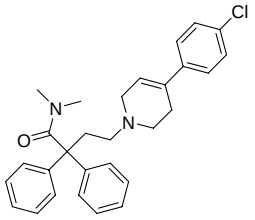
(B)



Reaction 1

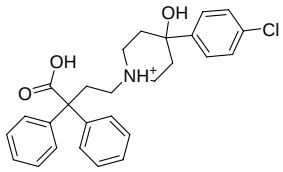


Reaction 2

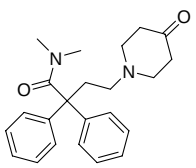


Reaction 3

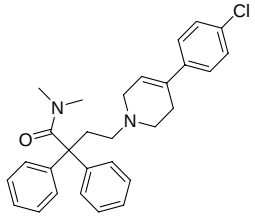
(C)



Reaction 1

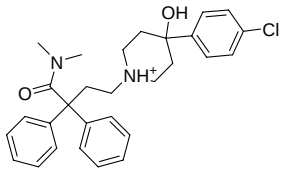


Reaction 2

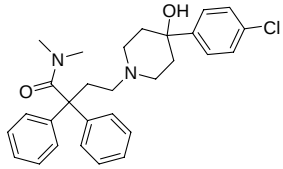


Reaction 3

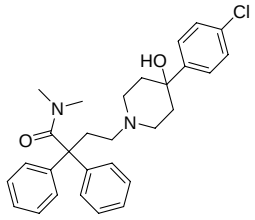
(D)



Reaction 1



Reaction 2



Reaction 3

(E) No reaction in all cases.

Name: _____ Student number: _____

Some general data are provided on this page. Other data appear with the questions.

A periodic table is provided on the next page.

STP = 273.15 K, 1 atm

R = 8.3145 J/K·mol = 0.08206 L·atm/K·mol

1 atm = 760 mm Hg = 101.325 kPa

1 J = 1 kg m^2 s^{-2} = 1 kPa·L = 1 Pa·m^3

1 cm^3 = 1 mL

F = 96485 C/mol

$N_A = 6.022 \times 10^{23}$ mol^{-1}

0°C = 273.15 K

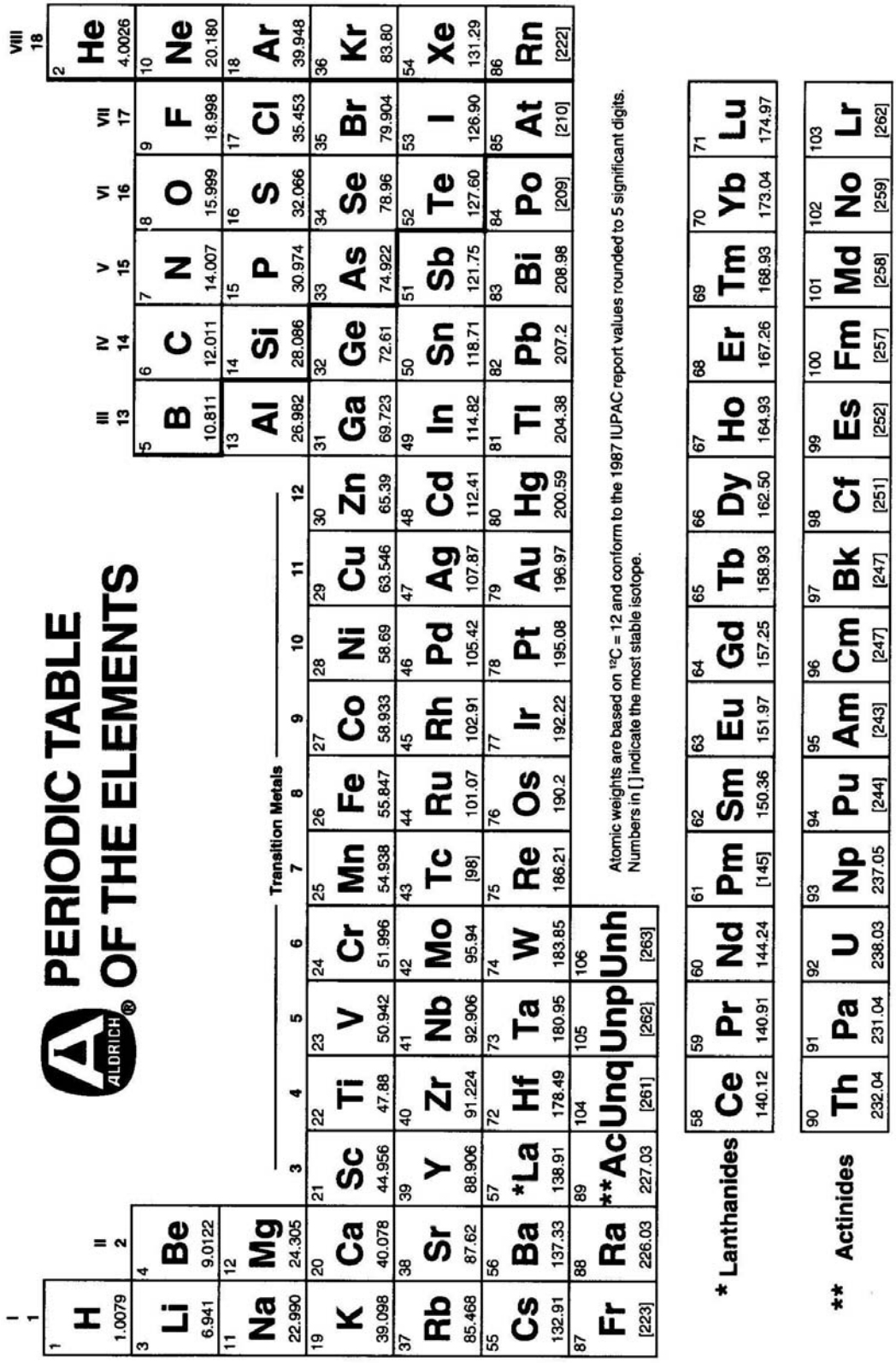
1 m = 10^9 nm = 10^{10} Å

1 g = 10^3 mg

μM = 10^{-6} M

$\text{average rate} = -\frac{1}{a}\frac{\Delta[\text{A}]}{\Delta t} = \ldots = \frac{1}{g}\frac{\Delta[\text{G}]}{\Delta t}\ldots$	$v = \lim_{t \to 0} \frac{1}{g}\frac{\Delta[\text{G}]}{\Delta t} = \frac{1}{g}\frac{d[\text{G}]}{dt}$
$v_0 = k[\text{A}]^m[\text{B}]^n$	$ln\frac{[\text{A}]_t}{[\text{A}]_0} = -kt$
$[\text{A}]_t = [\text{A}]_0 \bullet e^{-kt}$	$t_{1/2} = \frac{ln\,2}{k} = \frac{0.69}{k}$
$[\text{A}]_t = [\text{A}]_0 - kt$	$v_0 = k[\text{A}]^2$ or $k[\text{A}][\text{B}]$
$\frac{d[\text{E}\bullet\text{S}]}{dt} = 0$	$v_0 = \frac{k_2[\text{E}]_0[\text{S}]}{K_M + [\text{S}]}$
$k = Ae^{-E_a/RT}$	$ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

Name: _____ Student number: _____



END OF EXAM