

Name:
Student number:

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Chemistry 1AA3
McMaster University
Instructors: M. Austen, P. Lock

Midterm Test
Version A – Solutions & part marks

March 14th, 2003
Duration: 120 minutes

This test contains 18 numbered pages. There are **26** multiple-choice questions appearing on pages numbered 3 to 15, and a periodic table on page 18. Page 17 is for rough work. You may tear off the last page to view the periodic table and the first page to view the data below.

Question 1 identifies the version of the test that you are writing. Be sure to answer this question correctly.

Questions 2 to 21 are each worth 2 marks, questions 22 – 26 are each worth 3 marks; the total marks available are 55. There is **no** additional penalty for incorrect answers.

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

ANSWER ALL QUESTIONS ON THE ANSWER SHEET PROVIDED.

No work written on the question sheets will be marked.

Instructions for entering multiple-choice answers are given on page 2.

Select one answer in each question from the answers **(A)** through **(E)**.

Your answers to all questions must be entered onto THE ANSWER SHEET IN PENCIL.

Enter one and only one answer for each question.

Only Casio FX 991 electronic calculators may be used; but they must NOT be transferred between students. Use of periodic tables, other than the table on page 18, is not allowed.

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

$$R = 8.314 \text{ J/(K}\cdot\text{mol)} = 0.08206 \text{ L}\cdot\text{atm/(K}\cdot\text{mol)}$$

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

$$1 \text{ atm} = 760 \text{ mm Hg} = 101.325 \text{ kPa}$$

$$0^\circ\text{C} = 273.15 \text{ K}$$

$$K_w = 1.0 \times 10^{-14}$$

$$k = Ae^{-E_a/RT}$$

$$\ln[A] - \ln[A]_0 = \ln([A]/[A]_0) = -kt$$

Continued on next page.

Name:
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You are writing **VERSION A**. Please choose answer **A** for question 1.

(A) YES (B) no (C) no (D) no (E) no

Questions 2 through 21 are worth two (2) marks each.

Answers have been highlighted in blue. Part marks are noted in green.

1. For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, under some conditions, the instantaneous rate of appearance of ammonia (NH_3) is 1.00×10^{-5} mol of NH_3 / L·s. At the same instant, what is the **rate of disappearance of hydrogen gas (H_2)**?

- (A) 5.00×10^{-6} mol of H_2 / L·s
(B) 6.67×10^{-6} mol of H_2 / L·s
(C) 1.00×10^{-5} mol of H_2 / L·s
(D) 1.50×10^{-5} mol of H_2 / L·s **2**
(E) 3.00×10^{-5} mol of H_2 / L·s

$$\begin{aligned}\frac{1}{2} \frac{d[NH_3]}{dt} &= -\frac{1}{3} \frac{d[H_2]}{dt} \\ -\frac{d[H_2]}{dt} &= \frac{3}{2} \frac{d[NH_3]}{dt} \\ -\frac{d[H_2]}{dt} &= \frac{3}{2} \left(1.00 \times 10^{-5} \frac{\text{mol}}{\text{L} \cdot \text{s}} \right)\end{aligned}$$

2. Which of the following rate laws have an **overall order of two**?

- (i) Rate = $k[I]^2 [Ar]^{-1}$ $2 - 1 = 1$
(ii) Rate = $k[H_2]^{3/2} [Br_2]^{1/2}$ $3/2 + 1/2 = 4/2 = 2$
(iii) Rate = $k[S_2O_8^{2-}] [I^-]$ $1 + 1 = 2$
(iv) Rate = $k[NO_2]^2$ $2 = 2$

Overall order = sum of exponents in the rate law

- (A) (i) and (iv)
(B) (i), (ii) and (iii)
(C) (ii) and (iii) **1**
(D) (ii), (iii) and (iv) **2**
(E) (iv) only **0.5**

Continued on next page.

3. The concentration of a reactant, A , is monitored over time and the following data is obtained. What is the **average rate** of the reaction **a)** in the first 2 seconds, **b)** in the last 5 seconds, **c)** over the entire experiment?

time / s	$[A] / M$
0.0	0.1000
1.0	0.0917
2.0	0.0847
3.0	0.0787
4.0	0.0735
5.0	0.0690
6.0	0.0649
7.0	0.0613
8.0	0.0581
9.0	0.0552
10.0	0.0526

$$Rate = -\frac{\Delta[A]}{\Delta t}$$

$$a) -\frac{0.0847 - 0.1000}{2.0 - 0.0} = \frac{0.0153M}{2.0s} = 0.0076_5$$

$$b) -\frac{0.0526 - 0.0690}{10.0 - 5.0} = \frac{0.0164M}{5.0s} = 0.0032_8$$

$$c) -\frac{0.0526 - 0.1000}{10.0 - 0.0} = \frac{0.0474M}{10.0s} = 0.0047_4$$

- (A) a) $0.0070 M \cdot s^{-1}$ b) $0.0025 M \cdot s^{-1}$ c) $0.0026 M \cdot s^{-1}$
(B) a) $0.0077 M \cdot s^{-1}$ b) $0.0033 M \cdot s^{-1}$ c) $0.0047 M \cdot s^{-1}$ **2**
(C) a) $0.0077 M \cdot s^{-1}$ b) $0.0025 M \cdot s^{-1}$ c) $0.0026 M \cdot s^{-1}$
(D) a) $0.015 M \cdot s^{-1}$ b) $0.016 M \cdot s^{-1}$ c) $0.047 M \cdot s^{-1}$
(E) a) $0.015 M \cdot s^{-1}$ b) $0.016 M \cdot s^{-1}$ c) $0.026 M \cdot s^{-1}$

4. For the reaction $A(aq) + 2B(aq) \rightarrow 2C(aq)$, the rate law is second order in A and first order in B . Under some conditions, the instantaneous rate of disappearance of A is $4.00 \times 10^{-5} \text{ mol} / \text{L} \cdot \text{s}$. Given $[A] = 0.10 \text{ M}$ and $[B] = 0.20 \text{ M}$, what is the **rate constant** for this reaction?

- (A) $8.0 \times 10^{-8} M^2 \cdot s^{-1}$
(B) $0.0010 M^{-1} \cdot s^{-1}$
(C) $0.0020 M^{-1} \cdot s^{-1}$
(D) $0.010 M^{-2} \cdot s^{-1}$ **0.5**
(E) $0.020 M^{-2} \cdot s^{-1}$ **2**

$$Rate = k[A]^2[B]^1$$

$$4.00 \times 10^{-5} M/s = k(0.10M)^2(0.20M)$$

$$k = \frac{4.00 \times 10^{-5} M/s}{0.00020M^3} = 0.020 M^{-2} s^{-1}$$

Version B of test – units error!

- (A) $0.020 M^2 \cdot s^{-1}$ **2**
(B) $0.010 M^{-1} \cdot s^{-1}$
(C) $0.0020 M^{-1} \cdot s^{-1}$
(D) $0.0010 M^{-2} \cdot s^{-1}$ **2**
(E) $8.0 \times 10^{-8} M^{-2} \cdot s^{-1}$ **2**

This is our mistake and we have tried to amend it as fairly as possible.

Continued on next page.

5. The reaction $2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$ was studied by the initial rates method. The results are shown in the table below. What is the **rate law** for this reaction?

$[H_2] / M$	$[NO] / M$	rate / (M/s)
0.1	0.1	3.80×10^{-7}
0.1	0.2	1.52×10^{-6}
0.2	0.2	3.04×10^{-6}

- (A) Rate = k $[H_2]$ $[NO]$
 (B) Rate = k $[H_2]$ $[NO]^2$ **2**
 (C) Rate = k $[H_2]$ $[NO]^3$
 (D) Rate = k $[H_2]^2$ $[NO]^2$
 (E) Rate = k $[H_2]^3$ $[NO]^2$

$$Rate = k[H_2]^m[NO]^n$$

$$\frac{1.52 \times 10^{-6} M/s}{3.80 \times 10^{-7} M/s} = \frac{k[0.1M]^m[0.2M]^n}{k[0.1M]^m[0.1M]^n}$$

$$4 = 2^n \Rightarrow n = 2$$

$$\frac{3.04 \times 10^{-6} M/s}{1.52 \times 10^{-6} M/s} = \frac{k[0.2M]^m[0.2M]^n}{k[0.1M]^m[0.2M]^n}$$

$$2 = 2^m \Rightarrow m = 1$$

$$Rate = k[H_2]^1[NO]^2$$

6. Phosphine, PH_3 , decomposes according to first-order kinetics. If an initial concentration of 0.0300 mol/L of phosphine decomposes with a rate constant of $0.0135 s^{-1}$, what is the phosphine **concentration after 2.00 minutes**?

- (A) 0.00594 M **2**
 (B) 0.0286 M
 (C) 0.0292 M **0.5**
 (D) 0.0308 M
 (E) 0.152 M

Note unit conversion from minutes to seconds!

$$\ln([A]/[A]_0) = -kt \Rightarrow [A]/[A]_0 = \exp(-kt)$$

$$[PH_3] = [PH_3]_0 \exp(-kt) = 0.0300M \exp(-0.0135s^{-1} \cdot 120s)$$

$$[PH_3] = 0.0300M \cdot 0.198 = 0.00594M$$

7. The first-order rate constant at $25^\circ C$ is $3.32 \times 10^{-10} s^{-1}$ for the substitution reaction $CH_3Cl(aq) + H_2O(l) \rightarrow CH_3OH(aq) + HCl(aq)$. What is the **half-life** of this reaction?

- (A) $2.30 \times 10^{-10} s$
 (B) $4.79 \times 10^{-10} s$
 (C) $2.09 \times 10^9 s$ **2**
 (D) $3.01 \times 10^9 s$
 (E) $4.35 \times 10^9 s$

$$\ln([A]/[A]_0) = -kt$$

$$\ln(1/2) = -kt_{1/2}$$

$$t_{1/2} = -\frac{\ln(0.5)}{k} = \frac{\ln 2}{k}$$

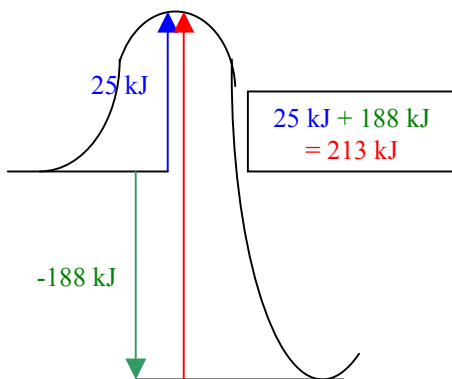
$$t_{1/2} = \frac{0.693}{3.32 \times 10^{-10} s^{-1}} = 2.09 \times 10^9 s$$

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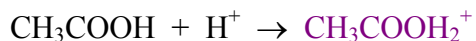
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8. The activation energy for the reaction $O + O_3 \rightarrow 2 O_2$ is 25 kJ, and the reaction is exothermic by 188 kJ. What is the **activation energy** for the decomposition of O_2 by the reverse reaction?

- (A) 25 kJ
(B) 50 kJ
(C) 163 kJ
(D) 188 kJ
(E) 213 kJ **2**



9. Consider the following steps in the mechanism for the formation of an ester from an alcohol and a carboxylic acid:



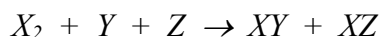
Which of the species shown (is a)/(are) reactive intermediate(s)?

Intermediates are formed in an early step and consumed in a later step

- (A) H^+ H^+ is a catalyst; consumed then reformed
(B) H^+ , H_2O H_2O is a product of the overall reaction
(C) H_2O , $\text{CH}_3\text{COOH}_2^+$, $\text{C}_3\text{H}_9\text{O}_3^+$
(D) H^+ , $\text{CH}_3\text{COOH}_2^+$, $\text{C}_3\text{H}_9\text{O}_3^+$ **0.5**
(E) $\text{CH}_3\text{COOH}_2^+$, $\text{C}_3\text{H}_9\text{O}_3^+$ **2**

Continued on next page.

10. For the reaction



It is found that the rate equation is $\text{rate} = k [X_2] [Y]$. Which statement best explains why the concentration of Z has no effect on the rate?

(A) The concentration of Z is very small and the other reactant concentrations are very large.

This would not remove it from the rate law, though a very high concentration could.

(B) Z reacts in a step after the rate-determining step. **2**

(C) Z is an intermediate.

Z is shown as a reactant in the overall reaction, it is not an intermediate.

(D) The activation energy for Z to react is very high.

This would be the rate-determining step, making Z very likely to be in the rate law.

(E) The fraction of molecules of Z that have very high energies is zero.

This depends on the temperature, in the same way for all reactants, $f_E = \exp(-E/RT)$.

11. The following statements discuss the kinetics of reactions. Which one of the following statements is **TRUE**?

(A) The activation energy of a reaction is thought to undergo **large changes** as temperature is changed.

E_a is essentially independent of temperature, Arrhenius plot has constant slope.

(B) **All** collisions which attain the activation energy will be successful in causing a chemical reaction. **0.5**

*Only collisions with sufficient energy and appropriate **orientation** can lead to reaction. Some collisions may reach the transition state yet revert back to reactants anyway.*

(C) For an exothermic reaction, the products contain **more** potential energy than the reactants.

In an exothermic reaction energy is released, so the PE of the products is lower.

(D) As the temperature is increased, the number of collisions that reach the transition state increases. **2**

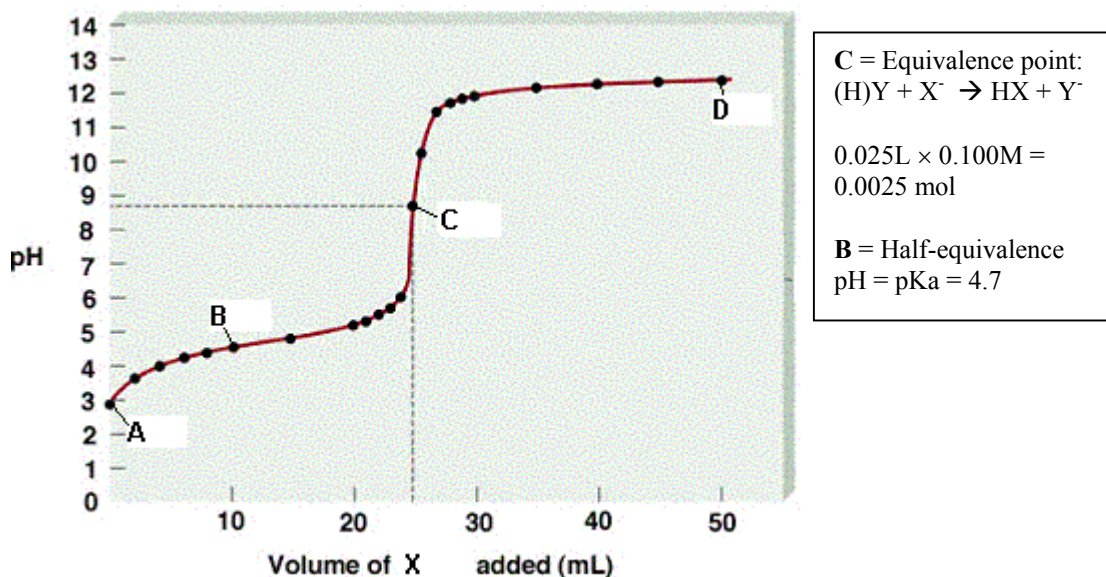
True, see kinetic theory and collision theory, $\text{fraction} = P \exp(-E_a/RT)$

(E) Increasing the temperature is the **only** way to increase the reaction rate and improve yield.

A catalyst will increase the rate but not the yield. Increasing temperature may actually lower the yield. A better approach is to continuously remove product and add reactant to the mixture so that equilibrium is never reached (see the Haber process for NH_3).

Continued on next page.

Questions 13 and 14 relate to the figure below:



12. Regarding the figure above, select the **TRUE** statements from the list below.

- (i) The curve represents a strong acid – strong base titration.
- (ii) The curve represents a weak acid – strong base titration.
- (iii) The curve represents a weak base – strong acid titration.
- (iv) **X** (the solution added) is an acid.
- (v) **X** (the solution added) is a base.

*The mixture starts out acidic $pH < 7$, and pH is increasing, so X is a base.
The curve near the beginning of the titration suggests that the original acid is weak, as does the slightly basic pH of the equivalence point*

- (A) (i) and (v)
- (B) (ii) and (iv)
- (C) (ii) and (v) (Note – some versions will have a different answer because the
- (D) (iii) and (iv) order of the statements above was changed).
- (E) (iii) and (v)

13. Both the acid and the base in the titration plotted above are monoprotic. The concentration of the added solution, **X**, is 0.100 M. You start with a solution of **Y** at point **A**. Find the **FALSE** statement.

(A) 0.0025 moles of **Y** were present at the beginning of this titration (*point A*).
Equals moles of X added at the equivalence point = 0.025L x 0.100M = 0.0025mol.

(B) The pK_a or pK_b of **Y** is between 4.0 and 5.0.
At half-equivalence point (B), $pH = pK_a = 4.7$ (Y is acetic acid)

(C) The solution present at point **C** is a solution of the conjugate of **Y**.
 $HA + OH \rightarrow H_2O + A^-$ has gone to 'completion'. Can treat as solution of weak base.

(D) The solution present at point **C** is a buffer.
Point B is a buffer, at point C there is not a significant amount of weak acid.

(E) An appropriate indicator for this titration could have a pK_a anywhere in the range from 7 to 10.

We want to have a colour change in the steep region of the curve. The colour change for an indicator usually occurs in a pH range of $\{pK_a(\text{Ind}) \pm 1\}$.

14. Which of the following mixtures will result in the formation of a **buffer solution**, when dissolved in 2.00 L of water?

- (i) 0.35 mol NaOH and 0.35 mol HF
- (ii) 0.35 mol LiF and 0.35 mol HF
- (iii) 0.70 mol LiF and 0.35 mol HCl
- (iv) 0.70 mol LiF and 0.70 mol HCl

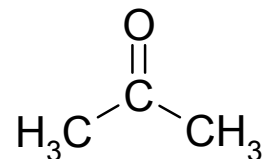
- (A) (i) and (iii)
- (B) (i) and (iv)
- (C) (ii) only **1**
- (D) (ii) and (iii) **2**
- (E) (i), (ii) and (iv)

Require a mixture of a weak acid (HF) and its conjugate base (F^-). Can be directly added, as in choice (ii) or as a result of reaction, as in choice (iii) where half of the LiF reacts with the added strong acid, leaving 0.35 mol of LiF and forming 0.035 mol of HF. In choice (i) all of the HF reacts with NaOH, leaving only NaF and H_2O , as at an equivalence point. Similarly, in choice (iv) all of the LiF reacts with the HCl, leaving only HF and the neutral salt LiCl.

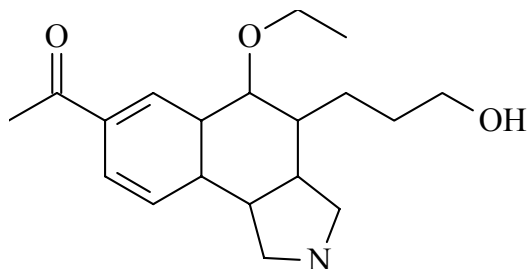
15. Which **one** of the following represents the formula for a **ketone**?

- (A) CH_3CHO aldehyde
- (B) CH_3OCH_3 ether
- (C) CH_3COOH carboxylic acid
- (D) CH_3CH_2OH alcohol
- (E) CH_3COCH_3 ketone **2**

A ketone has a $C=O$ double bond and the C is attached to two other C atoms, so we need at least three C atoms, which is only present in choice (E).



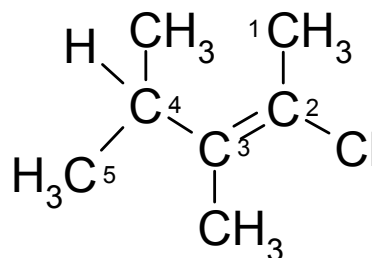
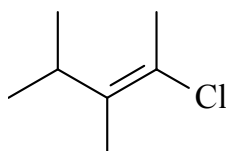
16. There are many functional groups present in the following molecule. These **functional groups** include:



Not present:

- | | | |
|-----|---|--|
| (A) | an alkene, a secondary amine, and an ester. | RC(=O)-OR |
| (B) | an ether, a primary alcohol and a ketone. 2 | <i>Also present: alkene, 2° amine</i> |
| (C) | an aldehyde, an ether and a secondary amine. | RC(=O)-H |
| (D) | a secondary amide, an alkene, and a primary alcohol. 0.5 | RC(=O)-NHR |
| (E) | a secondary alcohol, a ketone, and a tertiary amine. | R ₂ HC-OH, R ₃ N |

17. What is the name of the following compound?



- | | | |
|-----|---------------------------------------|----------|
| (A) | (E)-1-chloro-1,2,3-trimethyl-1-butene | |
| (B) | (Z)-1-chloro-1,2,3-trimethyl-1-butene | |
| (C) | (Z)-2-chloro-3,4-dimethyl-2-heptene | |
| (D) | (Z)-2-chloro-3,4-dimethyl-2-pentene | 1 |
| (E) | (E)-2-chloro-3,4-dimethyl-2-pentene | 2 |

Longest chain of carbon atoms is 5 C → pent-. The most important functional group is a double bond. Number from the closest end → pent-2-ene or 2-pentene.

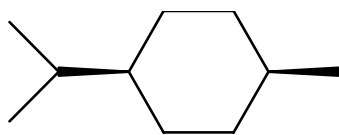
The substituents present are a Cl (chloro) on C2 and two CH₃ groups (dimethyl) on C3 and C4. Put these in alphabetical order → 2-chloro-3,4-dimethyl-2-pentene.

Looking at the double bond we label the geometry *E* or *Z* by assigning priority to the directly attached atoms, based on highest atomic number; Cl > C and CH(CH₃)₂ > CH₃.

Cl and CH(CH₃)₂ are on opposite sides of the C=C bond, so the geometry is *E*.

Continued on next page.

18. What is the name of the following compound?



- (A) *trans*-1-isopropyl-4-methylcyclohexane
(B) *trans*-1-methyl-4-isopropylcyclohexane
(C) *cis*-1-isopropyl-4-methylcyclohexane 2
(D) *cis*-1-methyl-4-isopropylcyclohexane 1
(E) 1-methyl-4-isopropylcyclohexane

The ring is the most important feature of this structure: cyclohexane. There are two substituents, a CH₃ (methyl) and a CH₃CHCH₃ group attached at the second carbon (isopropyl). There is no precedence here, so we give the **first alphabetically** the lower carbon number (1-isopropyl-), and then number around the ring, here either way gives 4-methyl. List these alphabetically → 1-isopropyl-4-methylcyclohexane. The substituents are the same side of the ring plane, so we label the geometry as *cis*.

19. Which of the following statements are **TRUE** regarding the properties of alkanes?

- (i) Alkanes are nonpolar molecules.

True. C-C bonds are non-polar, C-H bonds are essentially non-polar and the bond dipoles cancel out.

- (ii) Alkanes burn in air to give H₂O and CO₂.

True. This combustion reaction is an essential source of heat and energy.

- (iii) Alkanes are highly miscible (mix well) with water.

False, the non-polar molecules do not mix well with water. See lab 9.

- (iv) The strongest intermolecular force between alkane molecules is the dipole-dipole interaction.

False, there are no permanent dipoles, so the strongest forces are dispersion forces (induced dipole- induced dipole).

- (A) (i) and (ii) 2
(B) (i), (ii) and (iii)
(C) (i), (ii) and (iv) 0.5
(D) (ii) and (iv)
(E) (iii) and (iv)

20. Which of the following pairs are **geometrical isomers**?

- (i) $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
- (ii) $\begin{array}{c} \text{Cl} \\ | \\ \text{CH}_3-\text{CH}-\text{CH}-\text{CH}_3 \\ | \\ \text{Cl} \end{array}$ and $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$
- (iii) $\begin{array}{c} \text{CH}_3\text{CH}_2 \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \text{Cl} \end{array}$ and $\begin{array}{c} \text{CH}_3 \quad \text{Cl} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{CH}_2\text{Cl} \end{array}$
- (iv) $\begin{array}{c} \text{H}_2\text{ClC} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{CH}_2\text{Cl} \end{array}$ and $\begin{array}{c} \text{H}_2\text{ClC} \quad \text{CH}_2\text{Cl} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$

- (A) (i) and (ii)
(B) (i), (ii) and (iii)
(C) (ii) and (iii)
(D) (iii) and (iv) **0.5**
(E) (iv) only **2**

Structural isomers have atoms connected differently, atoms bonded to different atoms. Geometrical isomers have the same connectivity, but different arrangements in space. The names of geometric isomers differ only by E/Z or cis/trans. Structural isomers may vary in the locator numbers or more drastically. All isomers have the same molecular formulas.

[i] an ether and an alcohol – structural isomers

[ii] 2,3-dichlorobutane and 1,4-dichlorobutane – structural isomers

[iii] 1,2-dichlorobut-1-ene and 1,2-dichlorobut-2-ene – structural isomers

[iv] (E)-1,4-dichlorobut-2-ene and (Z)-1,4-dichlorobut-2-ene – **geometric isomers**

Questions 22 through 26 are worth three (3) marks each.

21. The carbon-14 isotope decays with a half-life of 5730 years. The concentration of carbon-14 in living tissue is about 1.0 parts per trillion (1.0×10^{-12}). A hominid skull at an archeological excavation is found to have a carbon-14 concentration of 0.062 parts per trillion (6.2×10^{-14}). What is the approximate **age** of the skull?

- (A) 360 years
(B) 1400 years
(C) 16,000 years
(D) 23,000 years **3**
(E) 92,000 years

$$\frac{[^{14}\text{C}]}{[^{14}\text{C}]_0} = \frac{6.2 \times 10^{-14}}{1.0 \times 10^{-12}} = 0.062 = \frac{1}{16.13} \approx \left(\frac{1}{2}\right)^4$$

Reducing the concentration by a factor of 16 requires 4 half lives = $4(5730) = 22920$ years.

$$\ln(0.062) = -kt = -2.78_{06} = -\left(\frac{\ln 2}{t_{1/2}}\right)t$$

$$t = 2.78 \left(\frac{5730 \text{ yrs}}{\ln 2} \right) = 22986 \text{ yrs}$$

22. The rate constant for a chemical reaction is 0.031 s^{-1} at 25°C , and the activation energy for the reaction is 36.5 kJ mol^{-1} . When the temperature is increased to a certain point, the rate constant increases to 0.093 s^{-1} . In order to obtain the observed rate increase, to what final **temperature (in $^\circ\text{C}$)** must the reaction be heated?

- (A) 25°C
(B) 49°C **3**
(C) 69°C
(D) 297°C
(E) 322°C **2**

$$\begin{aligned} k_1 &= A \cdot \exp(-E_a / RT_1) \\ k_2 &= A \cdot \exp(-E_a / RT_2) \\ \frac{k_1}{k_2} &= \exp\{(-E_a / RT_1) - (-E_a / RT_2)\} \\ \ln\left(\frac{k_1}{k_2}\right) &= -\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \end{aligned}$$

$$\ln\left(\frac{0.031 \text{ s}^{-1}}{0.093 \text{ s}^{-1}}\right) = -\frac{36.5 \times 10^3 \text{ J/mol}}{8.3145 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{298 \text{ K}} - \frac{1}{T_2} \right)$$

$$-1.09_{86} = -438_{9.9} \text{ K} \left(\frac{1}{298 \text{ K}} - \frac{1}{T_2} \right)$$

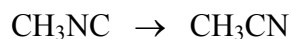
$$\frac{1.09_{86}}{438_{9.9} \text{ K}} = \frac{2.50_{26} \times 10^{-4}}{\text{K}} = \frac{3.35_{57} \times 10^{-3}}{\text{K}} - \frac{1}{T_2}$$

$$\frac{1}{T_2} = \frac{3.35_{57} \times 10^{-3}}{\text{K}} - \frac{2.50_{26} \times 10^{-4}}{\text{K}} = \frac{3.10_{54} \times 10^{-3}}{\text{K}}$$

$$\begin{aligned} T_2 &= 322 \text{ K} \\ T_2 &= 49^\circ\text{C} \\ &\text{Watch units!} \end{aligned}$$

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23. The isomerization of methyl isocyanide to acetonitrile:



follows first order kinetics. The half-lives for the reaction were found to be 161 min at 199 °C, and 12.5 min at 230 °C. Calculate the **activation energy** for this reaction.

- (A) 6.17×10^{-3} kJ
(B) 31.4 kJ **1**
(C) 78.2 kJ
(D) 124 kJ
(E) 163 kJ **3**

$$\begin{aligned} k_1 &= A \cdot \exp(-E_a / RT_1) \\ k_2 &= A \cdot \exp(-E_a / RT_2) \\ \frac{k_1}{k_2} &= \exp\{(-E_a / RT_1) - (-E_a / RT_2)\} \\ \ln\left(\frac{k_1}{k_2}\right) &= -\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \end{aligned}$$

The ratio of half-lives is *inverse* to the ratio of rate constants. Recall $\ln 2 = kt_{(1/2)}$

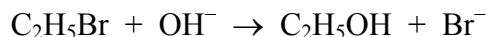
$$\begin{aligned} \ln\left(\frac{\ln 2/t_1}{\ln 2/t_2}\right) &= \ln\left(\frac{t_2}{t_1}\right) = -\frac{E_a}{R} \left(\frac{T_2}{T_2 T_1} - \frac{T_1}{T_1 T_2}\right) \\ \ln\left(\frac{161 \text{ min}}{12.5 \text{ min}}\right) &= -\frac{E_a}{R} \left(\frac{472 \text{ K} - 503 \text{ K}}{503 \text{ K} \cdot 472 \text{ K}}\right) \\ \ln(12.8_8) &= -\frac{E_a}{R} \left(\frac{-31 \text{ K}}{237_{416} \text{ K}^2}\right) \\ 2.555_7 \frac{237_{416} \text{ K}}{31} &= \frac{E_a}{8.3145 \text{ J/mol} \cdot \text{K}} \\ E_a &= 19_{572.8} \text{ K} \times 8.3145 \text{ J/mol} \cdot \text{K} = 16_{2738} \text{ J/mol} \\ E_a &= 163 \text{ kJ/mol} \end{aligned}$$

Note that the activation energy must be positive. A negative E_a suggests an error in calculation. Check the signs at each step.

Continued on next page.

Name:
Student number:

24. The following reaction in aqueous solution was found to be first order in $[\text{OH}^-]$, first order in $[\text{C}_2\text{H}_5\text{Br}]$, and inverse first order in $[\text{Br}^-]$.



Which one of the following mechanisms is consistent with the observed reaction orders?

Observed rate law: $\text{Rate} = k_{\text{obs}}[\text{OH}^-][\text{C}_2\text{H}_5\text{Br}][\text{Br}^-]^{-1} = k_{\text{obs}}[\text{OH}^-][\text{C}_2\text{H}_5\text{Br}]/[\text{Br}^-]$.

- (A) $\text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_5^+ + \text{Br}^-$ slow $\text{Rate} = k_1[\text{C}_2\text{H}_5\text{Br}]$
 $\text{C}_2\text{H}_5^+ + \text{OH}^- \rightarrow \text{C}_2\text{H}_5\text{OH}$ fast
- (B) $\text{C}_2\text{H}_5\text{Br} \rightleftharpoons \text{C}_2\text{H}_5^+ + \text{Br}^-$ fast
 $\text{OH}^- + \text{Br}^- \rightarrow \text{HOBr}^{2-}$ slow $\text{Rate} = k_2[\text{OH}^-][\text{Br}^-]$
 $\text{HOBr}^{2-} + \text{C}_2\text{H}_5^+ \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{Br}^-$ fast
- (C) $\text{C}_2\text{H}_5\text{Br} + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{H}^+ + \text{Br}^-$ slow $\text{Rate} = k_1[\text{C}_2\text{H}_5\text{Br}][\text{H}_2\text{O}]$
 $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ fast *Note that mechanism C involves water as a catalyst, but since water is the solvent, $[\text{H}_2\text{O}]$ is constant and the dependence of rate on this concentration would not be observed.*
- (D) $\text{C}_2\text{H}_5\text{Br} \rightleftharpoons \text{C}_2\text{H}_5^+ + \text{Br}^-$ fast
 $\text{C}_2\text{H}_5^+ + \text{OH}^- \rightarrow \text{C}_2\text{H}_5\text{OH}$ slow $\text{Rate} = k_1[\text{C}_2\text{H}_5^+][\text{OH}^-]$ **3**
- (E) $\text{C}_2\text{H}_5\text{Br} + \text{OH}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{Br}^-$ slow $\text{Rate} = k_1[\text{C}_2\text{H}_5\text{Br}][\text{OH}^-]$ **1**

For all mechanisms *except D* the rate law for the slow (rate determining) step involves reactants and/or products of the overall reaction only.

For mechanism D the rate of the slow step depends on an *intermediate*, C_2H_5^+ . Since the first step is a fast equilibrium we write an expression for the equilibrium constant, and rearrange for the concentration of the intermediate.

$$K_1 = \frac{[\text{C}_2\text{H}_5^+][\text{Br}^-]}{[\text{C}_2\text{H}_5\text{Br}]} \Rightarrow [\text{C}_2\text{H}_5^+] = \frac{K_1[\text{C}_2\text{H}_5\text{Br}]}{[\text{Br}^-]}$$

Now we substitute this expression into our rate law for the slow step.

$$\text{Rate} = k_2[\text{C}_2\text{H}_5^+][\text{OH}^-] = k_2 \frac{K_1[\text{C}_2\text{H}_5\text{Br}]}{[\text{Br}^-]}[\text{OH}^-] = k_2 K_1 \frac{[\text{OH}^-][\text{C}_2\text{H}_5\text{Br}]}{[\text{Br}^-]} = k_{\text{obs}} \frac{[\text{OH}^-][\text{C}_2\text{H}_5\text{Br}]}{[\text{Br}^-]}$$

This rate law matches the observed rate law, so mechanism D is consistent, *but not proven*.

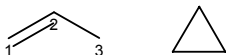
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25. How many **isomers (structural and geometrical)** that contain an **–OH** functional group are possible for the formula C_3H_6O ?

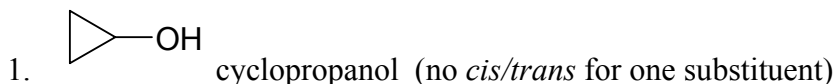
- (A) 7
(B) 6
(C) 5 3
(D) 4 2
(E) 3 1

There is one degree of unsaturation in this molecule. All isomers must have exactly one double bond, *or* exactly one ring. Be sure that all structures include the OH functional group, *i.e.* no ethers or carbonyl groups. Treat –OH as –X, $C_3H_5(OH)$.

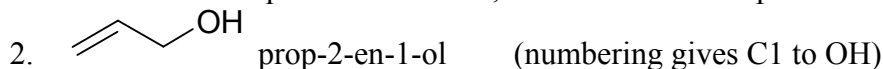
- Start by drawing the possible carbon backbones.
- There is only one possible ring structure and only one possible alkene structure. (For more C atoms there would be more of both.)



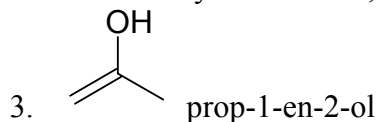
- For each carbon backbone consider the possible *distinct* substitution sites.
- Naming each structure will ensure that they are all different molecules.*
- For the cyclopropane ring all three carbons (and thus all six hydrogen atoms) are equivalent, so there is only one substitution possible.



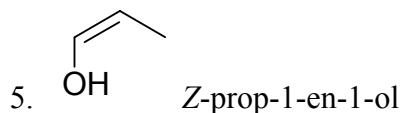
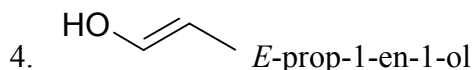
- In the propene chain each of the three C atoms is distinct.
- On 'C3' there are three equivalent H atoms, so one substitution possible.



- On 'C2' there is only one H atom, so one substitution possible.



- On 'C1' there are two distinct H atoms, leading to two *geometric* isomers.



END OF SOLUTIONS

Continued on next page.