VERSION **1**.

Section #1 – These questions are worth two marks each.

1. What is the **percent dissociation** of 0.010 M acetic acid?

   Data: $K_a = 1.8 \times 10^{-5}$

   A) 1.3 %
   B) 3.3%
   C) 13 %
   D) 2.6 %
   E) 4.2 %

   This is a straightforward weak acid ionization problem. We can use an ICE table and the small x approximation. The small x approximation is only valid when the percent ionization is < 5%, so we can probably eliminate (C) before we start.

   HA = acetic acid
   A^- = acetate

	HA +	H_2O	$\rightleftharpoons$	A^-	+ H_3O^+
I	0.010 M	-		0	0
C	-x M	-		+x M	+x M
E	0.010 - x M	-		x M	x M

   K_a = $[A^-][H_3O^+]/[HA] = x^2/[HA]$, therefore $x = \sqrt{\{K_a \times [HA]\}}$

   x = $\sqrt{\{(1.8 \times 10^{-5}) \times (0.010)\}}$
         = 4.2×10^{-4} M

   % ionization = 4.2×10^{-4} M / 0.010 M × 100 %

              = 4.2 %

2. Indicate the **FALSE** statement below regarding pH indicators.

   A) The smallest amount of indicator that allows good visual observation of the equivalence point should be used in order to minimize indicator effects on the amount of titrant needed.
   B) pH indicators cannot easily be used to directly indicate the mid-point of a buffer range.
   C) pH indicators useful for titration of weak acids with strong bases can also be used in titrations of weak bases with strong acids.
   D) pH indicators with more than one pK_{HIn} value may be used in different pH ranges.
   E) Indicators should be chosen so that their pK_{HIn} values match the pH at the equivalence point.

   A) True. pH indicators are weak acids/bases, so in high enough concentrations they could act as buffers (i.e., if $[HA]/K_a > 100$). Therefore, we use only enough to be able to

see the colour change.

B) True. The mid-point of a buffer's range is the point at which its buffering capacity is maximal and therefore the pH change is slowest. Colour changes with pH indicators can only be detected over a range of 2 pH units (pK_a -1 to pK_a +1), so they only work where the pH is changing rapidly. Thus, they will not work in a buffer region.

C) False. Titration of a weak base with a strong acid forms a weak acid at the equivalence point, with pH < 7. Titration of a weak acid with a strong base forms a weak base at the equivalence point, with pH > 7. Thus, no pH indicator could work for both types of titration.

D) True. Some pH indicators like thymol blue go through two colour changes (red to yellow to blue).

E) True. pH indicators are chosen so their colour change coincides with the rapid pH change that occurs at the equivalence point. The indicator's pK_{HIn} should, if anything, be slightly past the equivalence point pH.

3. Sodium hydroxide (1.20 g) and 3-chloropropanoic acid (5.40g, $ClCH_2CH_2COOH$) are dissolved in 0.100 L of distilled water. The resulting solution has a pH of 4.18. **What is the pK_a of 3–chloropropanoic acid?**

   A) 4.18
   B) 4.35
   C) 4.20
   D) 4.00
   E) 3.82

A limiting amount of strong base with a weak acid will give us a buffer. (Excess strong base would just give us a strongly basic solution, but then we wouldn't be able to calculate pK_a.) Calculate the number of moles of strong base and weak acid, then use the ratio in the Henderson-Hasselbalch equation, as usual, but turn it around to give pK_a instead pH. There's no need to calculate concentrations, just the ratio of moles of the acid and base forms is sufficient.

mol NaOH   = 1.20 g / (40 g/mol)
                    = 0.030 mol

mol $ClCH_2CH_2COOH$ = 5.40 g / (108.52 g/mol)
                    = 0.050 mol

Stoichiometry table.

HA = 3-chloropropanoic acid
A^- = 3-chloropropanoate

	NaOH	HA	A^-
Before	0.030 mol	0.050 mol	0
After	0	0.020 mol	0.030 mol

2

4. Acetic acid (0.10 L, 1.2 M, aq.) is titrated to the equivalence point with 1.0 M NaOH.
    What is the pH of the solution at the equivalence point?

    Data: $pK_a = 1.8 \times 10^{-5}$.

    A) 9.34
    B) 9.24
    C) 9.14
    D) 9.44
    E) 9.04

(N.B. the data should be $K_a = 1.8 \times 10^{-5}$, not pK_a.)

In other words, what is the pH of a solution of a solution of a weak base, sodium acetate (NaOAc)? In order to calculate the weak base's concentration at the equivalence point, we need the total solution volume, which requires, in turn, the volume of NaOH. The volume of NaOH depends on the number of moles of acetic acid (HOAc).

mol HOAc   = 0.10 L × 1.2 M
         = 0.12 mol

therefore:
vol NaOH   = 0.12 mol ÷ 1 M
        = 0.12 L

Therefore total volume at equivalence point = 0.10 L + 0.12 L = 0.22 L.

[NaOAc]   = 0.12 mol / 0.22 L
       = 0.545 M

In order to calculate the pH of a weak base solution, we need to work in terms of pOH and K_b.

K_b = K_w/K_a
    = $10^{-14} / (1.8 \times 10^{-5})$
    = 5.56×10^{-10}

HA = acetic acid
A⁻ = acetate

	A⁻ +	H₂O ⇌	HA	+ HO⁻
I	0.545 M	-	0	0
C	-x M	-	+x M	+x M
E	0.545 - x M	-	x M	x M

K_b = [HA][HO⁻]/[A⁻]
    = x^2/[A⁻],

3

therefore $x = \sqrt{\{K_b \times [A^-]\}}$

$x \quad = \sqrt{\{(5.56 \times 10^{-10}) \times (0.545\}}$
$\quad = 1.74 \times 10^{-5}$ M

therefore $[HO^-] = 1.74 \times 10^{-5}$ M,
and pOH = 4.76,

pH = 14 - pOH, therefore,

pH = 9.24.

5. Which of the following reactions are **third order overall**?

(i) $v_0 = k[A][B][C]$
(ii) $v_0 = k[A][B]^2[C]$
(iii) $v_0 = k[A]^0[B]^{-1}[C]^3$
(iv) $v_0 = k[A]^2[B]^0[C]$
(v) $v_0 = k[A][B][C]^0$

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

(i) 3rd order

(ii) 4th order

(iii) 2nd order (0 + -1 + 3 = 2)

(iv) 3rd order

(v) 2nd order

6. For this reaction:

$$A \xrightleftharpoons[k_{-1}]{k_1} \quad I \xrightarrow{k_2} G$$

,

where the second step shows A below the arrow,
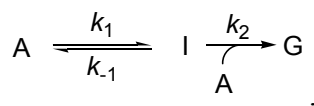
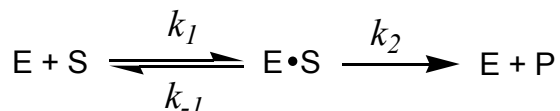the steady state approximation gives this rate equation:

$$v_0 = \frac{k_1 k_2 [A]^2}{k_{-1} + k_2 [A]} .$$

If the first step is fast and rapidly reversible, what will the **rate equation simplify to**?

A) $v_0 = \dfrac{k_1 k_2 [A]}{k_{-1}}$

B) $v_0 = k_1 [A]$

C) $v_0 = k_1 k_2 [A]^2$

D) $v_0 = \dfrac{k_1 k_2 [A]^2}{k_{-1}}$

E) $v_0 = \dfrac{k_1 k_2 [A]^2}{k_2 [A]}$

If the first step is fast, that implies that $k_1 > k_2$; however, that does not affect the rate law. If the first step is rapidly reversible, that implies that $k_{-1} > k_2[A]$. In that case, the denominator simplifies to k_{-1}, making (D) the correct answer.

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7. Which of the following statements regarding the steady state approximation and the Michaelis-Menten equation is **INCORRECT**?

$$E + S \xrightleftharpoons[k_{-1}]{k_1} \quad E{\bullet}S \xrightarrow{k_2} E + P$$

A) $k_{cat} = k_2$.
B) If $[S] \ll K_M$, then $[E{\bullet}S] \ll [E]_0$.
C) The steady state approximation is not valid if $k_{-1} = 0$.
D) The steady state approximation is that $d[E{\bullet}S]/dt = 0$.
E) $k_1 [E]_{free}[S] = [E{\bullet}S](k_{-1} + k_2)$

A) Correct. k_{cat} is the rate-limiting step. In our derivation of the Michaelis-Menten equation, k_2 was defined as being the slow step.

B) Correct. When $[S] \ll K_M$, the enzyme exists mostly in the free form, $[E]_{free}$, and the concentration of the Michaelis complex, $[E{\bullet}S]$, is very low.

C) Incorrect. The steady state approximation is that $d[E{\bullet}S]/dt = 0$. If the formation rate is $k_1[E]_{free}[S]$ and the breakdown rate is $k_2[E{\bullet}S]$, then the approximation can be true, even if there is no breakdown of $[E{\bullet}S]$ to $[E]_{free}$ and $[S]$. (See the concept check in the course notes.)

D) Correct.

8. What is the **enzyme concentration** for a reaction where $v_0 = 10^{-5}$ M/s, $k_{cat} = 100$ s^{-1}, $K_M = 2$ mM, and [S] = 1 mM?

A) 3 mM
B) 0.3 μM
C) 6.7×10^{-7} M
D) 6.7 μM
E) 3×10^{-8} M

This involves the straightforward application of the Michaelis-Menten equation, re-arranged to solve for $[E]_0$.

Michaelis-Menten equation:

$$v_0 = \frac{k_{cat}[E]_0[S]}{K_M + [S]}$$

Re-arranged Michaelis-Menten equation:

$$[E]_0 = \frac{v_0(K_M + [S])}{k_{cat}[S]}$$

$$= \{ 10^{-5} \text{ M/s} \times (2 \times 10^{-3} + 1 \times 10^{-3}) \} / (100 \text{ s}^{-1} \times 1 \times 10^{-3} \text{ M})$$
$$= 3 \times 10^{-7} \text{ M}$$

Recall that 1 μM = 10^{-6} M, therefore 3×10^{-7} M = 0.3 μM.

9. A reaction between a red dye and household bleach was followed visually. The reaction was first order with respect to [dye], with a half life of 18 s. Indicate the **FALSE** statement regarding this reaction.

A) Changing the temperature of this experiment would change the half life.
B) Determining the reaction order with respect to dye in this experiment requires knowing the exact initial concentration of red dye.
C) Using less dye would not affect the half life.
D) We know this reaction is first order with respect to the dye because successive half lives were observed to be constant.
E) Using less bleach would allow us to test the reaction order with respect to bleach.

Although it might have been helpful to remember the in-class demonstration, this question is entirely self-contained.

A) True. Rate constants are temperature dependent, as seen in the equation: $k = A \times \exp(-E_a/RT)$.
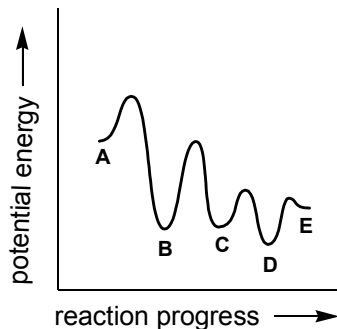
B) False. First order rate constants can be determined from the $t_{1/2}$: $k = \ln(2)/t_{1/2}$. Because $t_{1/2}$ is constant throughout the course of the reaction, k can be derived without knowing the starting concentration. This is true only for first order reactions.

C) True. See (B).

10. Which step is **rate-limiting** in the following reaction?

A) $D \rightarrow E$
B) $B \rightarrow C$
C) $A \rightarrow E$
D) $C \rightarrow D$
E) $A \rightarrow B$

The rate-limiting step is the one with the largest activation energy (i.e., the biggest distance from the bottom of the valley to the transition state). That is the $B \rightarrow C$ step for this reaction.

11. Which of the following reactions **could not** have an overall order of 2?

A, B = reactants, G = product, I = intermediate (not always shown)

A) $A \xrightarrow{\text{fast}} I \xrightarrow[\text{B}]{\text{slow}} G$

B) $2 A + B \rightarrow G$

C) $A \xrightarrow{\text{catalyst}} G$

D) $A + B \rightarrow G$

E) $A \xrightarrow{\text{slow}} I \xrightarrow[\text{B}]{\text{fast}} G$

For some of these reactions, we do not know for sure what the reaction order is, so the question is whether is would be **possible** for the reaction to be second order.

A) The first step would be first order w.r.t. [A], which means that [I] will depend on [A]. B is added in the second, rate-limiting step. Therefore $v_0 = k[A][B]$, and the reaction is second order.

B) Without knowing any of the elementary processes, it is not possible to know the order of this reaction. It could be second order.

C) This reaction could be second order, for example $v_0 = k[A][\text{catalyst}]$, though other

reaction orders are possible.

D) Same as B.

E) Like the S_N1 nucleophilic substitution of tBu-Cl, the first step is rate-limiting and the second step is fast, meaning that it will be zero-order w.r.t. [B]. Overall the rate law will be first order: $v_0 = k[A]$; it cannot be second order overall.

12. The following data were obtained for the reaction $A \rightarrow G$. What is the **rate constant** for this reaction?

time (s)	[A] (µM)
0	1.0
28	0.5
42	0.25
49	0.125

A) 0.0080 s^{-1}
B) 0.018 µM/s
C) 0.018 s^{-1}
D) 0.0040 µMs^{-1}
E) 0.040 s^{-1}

The values of [A] decrease by half in each successive row of the table. The time interval for each row is smaller than the previous one. We know that zero-order reactions have successively shorter half-lives as the reaction proceeds, so that is a good clue that this is a zero order reaction.

We can confirm that by calculating the rate constant, k, for different time intervals.
For example, from 0 to 28 s, $-\Delta A/\Delta t = 0.5 \text{ µM} / 28 \text{ s} = 0.018 \text{ µM/s}$.
From 42 to 49 s, $-\Delta A/\Delta t = 0.125 \text{ µM} / 7 \text{ s} = 0.018 \text{ µM/s}$.

The rate is not changing during the reaction, therefore it is acting like a zero order reaction. For a zero order reaction, the rate constant, k, is the same as the rate, v, and the units - concentration per unit time - are also the same. Because the rate is not changing over time, the average rate, $-\Delta A/\Delta t$, equals the instantaneous rate, v.

13. The kinetic parameter k_{cat}/K_M is important for studying enzymatic reactions. **Under what conditions** would v_0 be directly proportional to k_{cat}/K_M?

A) $[S] \gg K_M$
B) $[E]_0 \gg [S]$
C) $v_0 = k_{cat}$
D) $[S] \ll K_M$
E) $[S] = K_M$

The full Michaelis-Menten equation is:
$$v_0 = \frac{k_{cat}[E]_0[S]}{K_M + [S]}$$
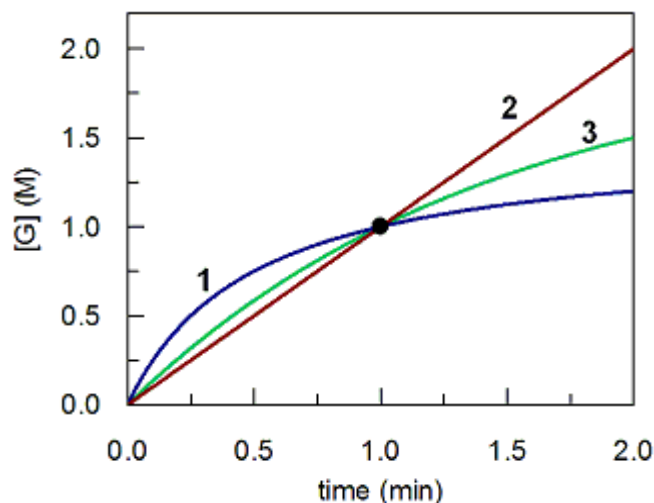.

14. Indicate the **number of FALSE statements** regarding the curves of [G] versus time for the reaction:

A + B → G, shown below:

(i) Curve 1 is consistent with a first order reaction.
(ii) Curve 2 corresponds to a zero order reaction.
(iii) Curve 3 cannot correspond to a zero order reaction.
(iv) All three reactions have an average reaction rate of $\Delta G/\Delta t = 0.0167$ M s^{-1} over the first minute of reaction.
(v) Curves 1 and 3 could arise from exactly the same reaction carried out at the same concentrations but at two different temperatures

A) all statements are correct
B) one statement is false
C) two statements are false
D) three statements are false
E) four statements are false

15. Indicate the **FALSE** statement(s) regarding the reaction $aA + bB \rightarrow gG + hH$.

(i) The reaction rate can be expressed, equivalently, as: $v_o = (1/a)dA/dt$ or $v_o = \Delta G/\Delta t$..

(ii) The reaction rate can be expressed as $v_o = k[A]^m[B]^n$, where m and n can be different from a and b.

(iii) Average rates approach instantaneous rates when Δt approaches zero.

A) iii
B) ii, iii
C) i, ii
D) ii
E) i

(i) False. $v_0 = (1/a)dA/dt$ is correct, but $v_0 = \Delta G/\Delta t$ is incorrect. $\Delta G/\Delta t$ is an average rate, but v_0 is the instantaneous rate at time = 0. It is not equivalent to equate average and instantaneous rates. Also, the expression $\Delta G/\Delta t$ neglects the term for stoichiometry, $1/g$.

(ii) True

(iii) True.

16. Indicate the **INCORRECT** statement regarding vapour pressure:

A) The relationship between vapour pressure and temperature is not necessarily linear.
B) Large, nonpolar molecules can have greater intermolecular forces than small polar molecules.
C) Liquids boil when their vapour pressure equals atmospheric pressure.
D) At 298 K, the vapour pressure of water is higher than that of methanol (CH_3OH).
E) As temperature increases, vapour pressure increases.

A) Correct. The relationship is generally curved:
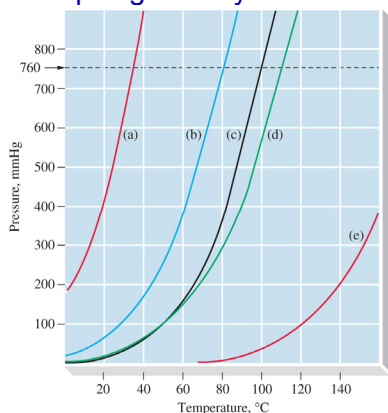
B) Correct. Dispersion forces between individual atoms are weaker than hydrogen bonds, but they are additive and can become large for large molecules. For example, pentacontane ($C_{50}H_{102}$) boils at 575 °C even though it can only form dispersion interactions.

C) Correct. See (A). Water boils at 100 °C at 1 atm pressure, but at lower pressures, it boils at lower temperatures, when its vapour pressure equals the atmospheric pressure.

D) Incorrect. The vapour pressure of water is lower than methanol under all conditions. Methanol can form, on average, two hydrogen bonds (one through the lone pair electrons, one through the proton), while water can form four on average (two through the lone pair electrons, two through the protons). Methanol can form more dispersion interactions through its methyl group, but that does not compensate for the difference in hydrogen bonding.

E) Correct. See (A).

17. Indicate the **FALSE** statement regarding this phase diagram:
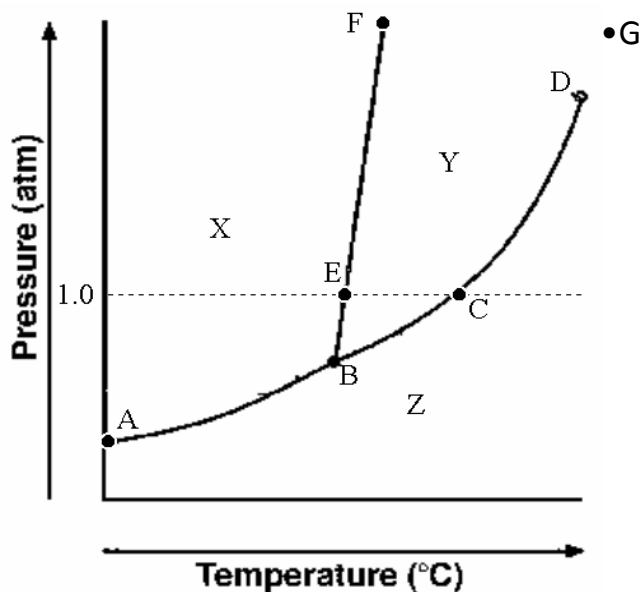
A)   Sublimation occurs along the line from points B to F.
B)   Point C is the normal boiling point of the substance.
C)   In region X, the substance is a solid.
D)   At point G, phases are indistinguishable.
E)   In region Z the substance is a gas.

A) False. X is solid, Y is liquid, so the phase transition along B – F is melting/freezing.

B) True. Y is liquid, Z is gas, and the pressure at C is 1 atm, therefore that is the normal boiling point.

C) True.

D) True. The is the region where supercritical fluids form.

E) True.

18. Identify the **FALSE** statement regarding phase changes and supercritical fluids:

    A) It takes longer to completely cook pasta at the top of Mount Everest than in Hamilton.
    B) The density of a supercritical fluid is greater than that of the gas, but less than the liquid.
    C) Deposition is endothermic.
    D) Supercritical fluids have low surface tension.
    E) The probability of a solid subliming rather than melting is increased at low temperatures and pressures.

A) True. Water boils at ~70 °C at the top of Mt. Everest (elevation = 8848 m), so cooking is slower than in Hamilton (elevation = 75 m).

B) True.

C) False. Phase changes in the direction solid → liquid → gas are endothermic. In the opposite direction, they are exothermic. That's why steam burns can be so severe. The steam itself is hot, and when it condenses into water on the skin, it gives off further heat.

D) True. That is why there is no liquid → gas phase transition in the supercritical region. The lack of surface tension means that there is no clear distinction between the phases in that region.

E) True. The liquid phase is less likely to exist at low temperatures and pressures, which increases the likelihood of sublimation being possible (see the phase diagram in question 17 above).

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19. What would the **dominant intermolecular force** be in a pure sample of SF_6 (l)?

    A) dipole-dipole interactions
    B) ionic interactions
    C) dispersion forces
    D) hydrogen bonding
    E) ion-dipole interactions

SF6 is a pure, symmetric molecule with no overall dipole. There are no protons to form hydrogen bonds, and no charges. Therefore, it can only form dispersion interactions.
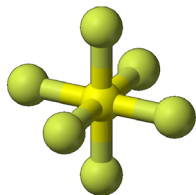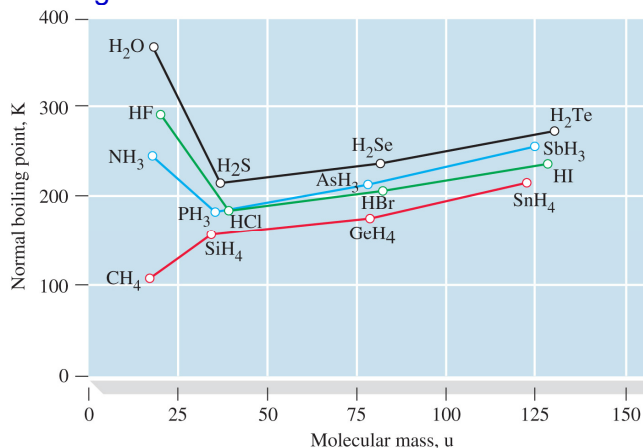

Yellow = S, green = F.

20. Which of the following would have the **highest melting point**?

    A) NH_3
    B) SiH_4
    C) CH_4
    D) PH_3
    E) AsH_3

Only NH_3 can form hydrogen bonds (one through the lone pair of electrons and through one of the protons). Being the strongest individual intermolecular interaction, hydrogen bonding dominates over the other forces.

21. **Which structure** corresponds to the name 3-bromo-5-*tert*-butyloctane?

A)

B)

C)

D)

E)
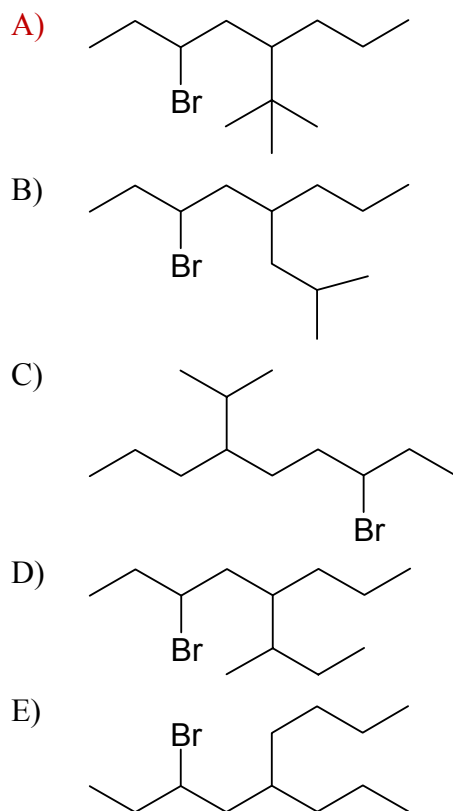
A) Correct.

B) Alkyl substituent is isobutyl.

C) Alkyl substituent is isopropyl, longest chain is a nonane.

D) Alkyl substituent is *sec*-butyl.

E) Alkyl substituent is butyl, or *n*-butyl.

22. Which of the following statements is/are **TRUE** ?

(i) Alkanes are polar molecules because of the large electronegativity difference between C and H.

(ii) It is possible to rotate a C-C bond in butane 360°.

(iii) A compound with the molecular formula C_5H_{10} could be a cycloalkane.

(iv) All cycloalkanes are planar molecules.

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

(i) False. Carbon is *slightly* more electronegative than hydrogen, but the difference is

small, and alkanes are nonpolar.
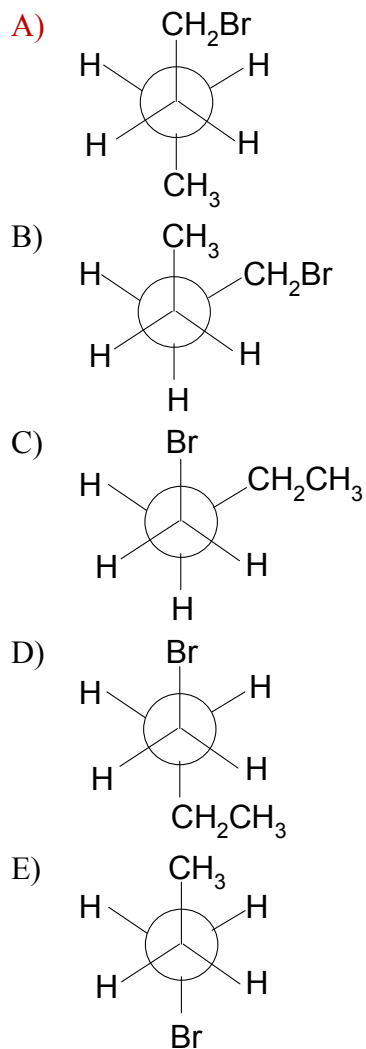
(ii) True. σ-bonds (single bonds) can rotate freely.

(iii) True. The general formula for a cycloalkane is C_nH_{2n} (the same as alkenes), so C_5H_{10} could be a cycloalkane.

(iv) False. Cyclopropane is planar; cyclobutane and large cycloalkanes are puckered.
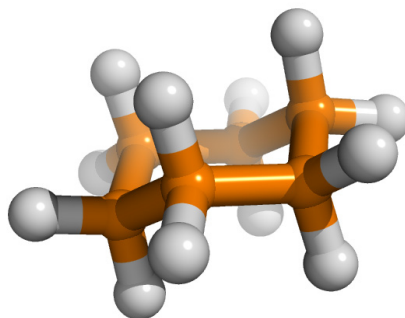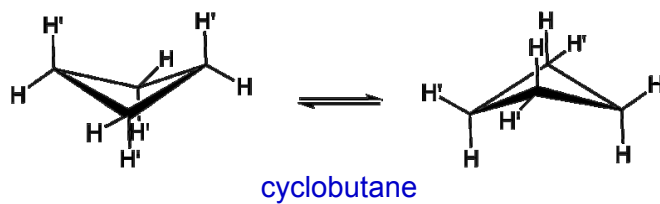
cyclobutane

cyclohexane, chair conformation

23. Which structure below represents the **lowest energy conformation** of 1-bromobutane, looking along the C2-C3 bond?

A)

CH_2Br

H — H
H — H

CH_3

B)

CH_3

H — CH_2Br
H — H

H

C)

Br

H — CH_2CH_3
H — H

H

D)

Br

H — H
H — H

CH_2CH_3

E)

CH_3

H — H
H — H

Br

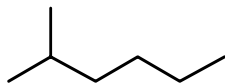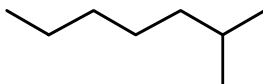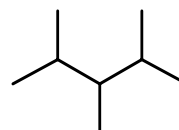|	
A)	*Anti* conformation, most favourable.
B)	Staggered, but *gauche* conformation, so less favourable than *anti*.
C)	Looking down the C1-C2 bond, and *gauche* conformation.
D)	Looking down the C1-C2 bond, though it is an *anti* conformation.
E)	1-Bromopropane, not 1-bromobutane.

24. Which of the following statements regarding compounds (i) to (v) is **FALSE**?
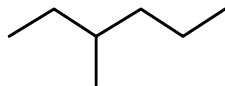

(i) (ii) (iii)

(iv) (v)

A) (iv) and (v) are structural isomers
B) (ii) and (v) are completely different molecules
C) (iii) and (iv) are completely different molecules
D) (i) and (ii) are identical molecules
E) (ii) and (iii) are structural isomers

A) True. Both are alkanes with 7 carbon atoms and the formula C_7H_{16}.

B) True. (ii) contains 8 carbon atoms, (v) contains 7.

C) True. (iii) contains 8 carbon atoms, (iv) contains 7.

D) False. (i) contains 7 carbon atoms, (ii) contains 8.

E) True. Both contain 8 carbon atoms, but have different connectivities.

25. **How many structural isomers** are there of compounds having the molecular formula $C_3H_6Br_2$?

    A) 2
    B) 3
    C) 4 (3 marks)
    D) 5
    E) 1 (3 marks)

UPDATE

There is an error in the 9th edition of the Petrucci text that led some people to believe that there is only one structural isomer of $C_3H_6Br_2$. We will therefore assign full marks to (E), based on people following the text's definition.

In the 9th edition, Ch. 26, question 9, the text states that positional isomers are different from structural isomers. If you follow their definition, all the isomers of $C_3H_6Br_2$ are positional isomers, not structural isomers. In that case, the answer would be 1. In reality, positional isomers are a subset of structural isomers (see below). We don't discuss them at all in the course because we don't consider that a useful distinction. The 10th edition has dropped positional isomers altogether.
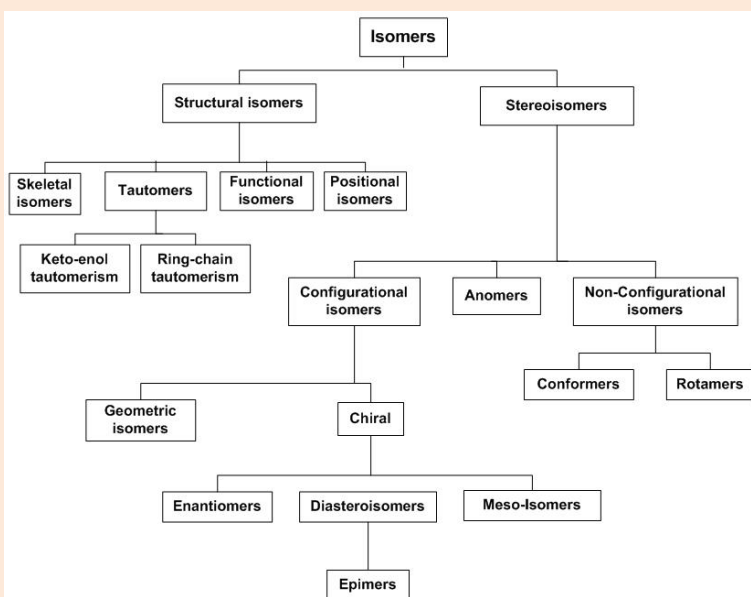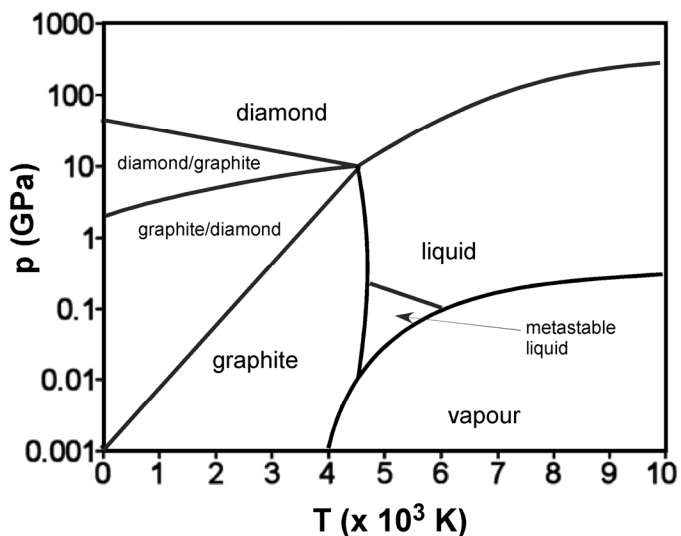

Image from http://www.biocheminfo.org/bnd/isomer_classification.jpeg

26. Consider the phase diagram for carbon below. If you wanted to convert graphite to diamond at room temperature, **what pressure range (in atm)** would be required to ensure pure diamond? $(G = Giga = 10^9; 1 \text{ atm} = 101.3 \text{ kPa})$.

A) 1×10^3 to 1×10^4
B) 1×10^1 to 1×10^2
C) $< 1 \times 10^0$
D) 1×10^2 to 1×10^3
E) $> 1 \times 10^6$

> Room temperature is ~290 K, near the left edge of the graph. Creating pure diamond would require about 100 Gpa of pressure.
>
> 100 Gpa × 10^9 Pa/GPa × (1 × 10^5 Pa/atm) ≈ 10^6 atm.
>
> (10^4 atm ≈ 1 Gpa, so (A) is too low.)

27. The reaction $H_2CO_3 \rightarrow CO_2 + H_2O$ has $t_{1/2} = 5.0$ s at 37 °C in the human body. If the activation energy is 67 kJ mol^{-1}, **what is $t_{1/2}$** for the same reaction with the same E_a in a hibernating frog whose body temperature is 2 °C?

A) 86 s
B) 5.3 s
C) 137 s
D) 54 s
E) 10 s

> The fact that $t_{1/2}$ is quoted means that this is a first order reaction. We can't use $t_{1/2}$ directly in equations; we have to convert it to a rate constant, k_1. We can then re-arrange the Arrhenius equation to calculate k_2, the rate constant at 2 °C, then convert that to $t_{1/2}$.
>
> At 37 °C, k_1 = ln(2)/$t_{1/2}$ = 0.693 / (5 s) = 0.139 s^{-1}.
>
> We know the values of k_1, T_1, T_2 and E_a. Thus, we need to re-arrange the Arrhenius equation to give us k_2 from the known values:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Re-arrange to:

$$\ln k_2 - \ln k_1 = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

and:

$$k_2 = \exp\left(\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \ln(k_1)\right)$$

$$k_2 = \exp\left(\frac{67}{0.0083}\left(\frac{1}{310} - \frac{1}{275}\right) + \ln(0.139)\right)$$

$k_2 = 5.05 \times 10^{-3}$ s^{-1}

$(t_{1/2})_2 = \ln(2)/ (5.05 \times 10^{-3}$ s$^{-1})$
$= 137$ s

28. In the reaction of A + B → G, the absorbance (Abs) of G was monitored as a function of time. Given the following information, determine the **reaction rate**.

For 0.10 M of pure G, Abs = 1.31.

Reactant	Concentration
A	0.10 M
B	0.10 M

Time (s)	Abs of G
0	0
15	0.085
30	0.170

A) 3.28×10^{-5} M s^{-1}
B) 4.33×10^{-4} M s^{-1}
C) 5.56×10^{-3} M s^{-1}
D) 9.21×10^{-4} M s^{-1}
E) 7.19×10^{-4} M s^{-1}

[G] exactly doubles between 15 s and 30 s, so this is behaving like a zero-order reaction. For a zero-order reaction, reactant concentrations do not matter: $v = k$.

The reaction rate can be calculated using any time interval (0 – 15 s, 0 – 30 s, 15 – 30 s). We will use 0 to 30 s.

Convert absorbance to concentration at t = 30 s:
[G] = 0.17 × (0.1 M / 1.31)
     = 0.013 M

v = 0.013 M / 30 s
   = 4.33 × 10^{-4} M/s

29. The hydrolysis rate of 0.200 M methyl acetate was measured in a sodium acetate / acetic acid buffer (0.0500 M each) at 25°C. After 10.0 minutes, the pH had changed to 4.59. If the reaction is first order, what is the **rate constant**?

Hydrolysis reaction: $CH_3COOCH_3 + H_2O \rightarrow CH_3OH + CH_3COOH$
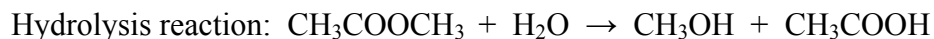
Data: K_a(acetic acid, CH_3COOH) = 1.80 × 10^{-5}

A) 3.32 × 10^{-4} s^{-1}
B) 4.09 × 10^{-4} s^{-1}
C) 7.58 × 10^{-4} s^{-1}
D) 9.46 × 10^{-4} s^{-1}
E) 1.81 × 10^{-4} s^{-1}

We will use the change in pH and the Henderson-Hasselbalch equation to calculate the amount of acetic acid formed in the reaction, then convert that to a rate constant.

At t = 0, the concentrations of sodium acetate, [A$^-$], and acetic acid, [HA], were identical (0.05 M), therefore pH = pK_a = 4.74.

At t = 10 min, pH = 4.59. Acetic acid is being added from methyl acetate hydrolysis; we can calculate the amount from the change in pH. Re-arranging the Henderson-Hasselbalch equation gives the [A$^-$]/[HA] ratio:

[A$^-$]/[HA] = 10$^{(pH - pKa)}$
            = 10$^{(4.59 - 4.74)}$
            = 0.708   (1)

[A$^-$] has not changed, but [HA] has increased by x:

[A$^-$]/[HA] = (0.05) / (0.05 + x)   (2)

Combining equations **1** and **2**:

x   = 0.05/0.708 - 0.05
         = 0.0206 M

Therefore, after 10 min, the product concentration, x, is 0.0206 M.

We can re-arrange this form of the first order integrated rate equation to calculate the rate constant, k:

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

$$k = -ln\left(\frac{[A]_t}{[A]_0}\right) / t$$

$[A]_t$ = 0.200 M - 0.0206 M = 0.1794 M

$[A]_0$ = 0.200 M

t = 10 min × 60 s/min = 600 s.

k = -ln(0.1794/0.200) / 600
= 1.81×10^{-4} s^{-1} to 1.85×10^{-4} s^{-1}, depending on how you rounded the value of x.

30. Dimethyl ether decomposes at 504°C:

$(CH_3)_2O(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$
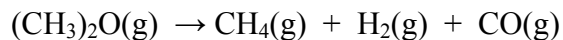
The first order rate constant is $k = 4.3 \times 10^{-4}$ s^{-1}. If 0.411 atm of $(CH_3)_2O(g)$ is introduced into a reaction vessel at 504°C, what is the **total pressure** (atm) in the reaction vessel after 390 s?

A) 0.62
B) 0.40
C) 0.38
D) 0.69
E) 0.54

As 3 moles of products are produced for each mole of reactant consumed, the total pressure, p_{total}, will increase with time.

We can use the integrated rate equation to give $[A]_t/[A]_0$ at 390 s (A is dimethyl ether):

$[A]_t$ = $[A]_0 \cdot e^{-kt}$
= 0.411 atm × exp(-4.3 × 10^{-4} s^{-1} × 390 s)
= 0.347 atm

The partial pressure of the products, $p_{products}$, is 3 times the decrease in partial pressure of A.

$p_{products}$ = 3 × Δp_A
= 3 × (0.411 atm - 0.347 atm)
= 0.192 atm

The total pressure is therefore:

p_{total} = $p_A + p_{products}$
= 0.347 atm + 0.192 atm
= 0.54 atm

Answer key - version 1.
1. E
2. C
3. D
4. B
5. E
6. D
7. C
8. B
9. B
10. B
11. E
12. B
13. D
14. B
15. E
16. D
17. A
18. C
19. C
20. A
21. A
22. C
23. A
24. D
25. C
26. E
27. C
28. B
29. E
30. E

Answer key - version 2.

1. C
2. C
3. E
4. B
5. B
6. A
7. D
8. B
9. E
10. A
11. B
12. D
13. B
14. C
15. A
16. A
17. D
18. A
19. E
20. A
21. A
22. C
23. B
24. D
25. C
26. A
27. C
28. D
29. B
30. E

Answer key - version 3.

1. D
2. B
3. D
4. E
5. E
6. B
7. E
8. E
9. C
10. B
11. B
12. E
13. C
14. D
15. D
16. A
17. E
18. B
19. E
20. B
21. B
22. B
23. A
24. E
25. E
26. E
27. B
28. B
29. E
30. D

Answer key - version 4.

1. C
2. C
3. B
4. C
5. D
6. D
7. B
8. E
9. D
10. C
11. E
12. D
13. E
14. C
15. D
16. C
17. B
18. C
19. E
20. A
21. C
22. E
23. C
24. E
25. A
26. E
27. B
28. C
29. D
30. B