

VERSION 1.

Enter your version number in the correct column on your scan sheet (see p. 2 for details).

The correct answers are highlighted in blue.

The answer key is at the end.

1. The **effect on pH** of adding 100.0 mL of water to a 1.00 L solution that is 0.30 M $\text{CH}_3\text{COOH}(\text{aq})$ and 0.45 M $\text{CH}_3\text{COONa}(\text{aq})$ is to:

- A) lower the pH by several units
- B) raise the pH by several units
- C) lower the pH slightly
- D) raise the pH slightly
- E) have no measureable effect on pH

We know that dilution of a buffer has no effect on pH. So, is this a buffer?

It is a mixture of a conjugate weak acid/base pair (acetic acid and sodium acetate).

An effective buffer has a base:acid ratio of $0.1 < [\text{A}^-]/[\text{HA}] < 10$. In this case, $[\text{A}^-]/[\text{HA}] = 0.45/0.30 = 1.5$.

This solution is a buffer, and dilution has no effect on pH.

2. A protein has an isoelectric point of 4.31, and is contained in a 100 ml solution of water at pH 7.00. A 200 ml buffer solution with pH = 4.65 containing the protein solution is desired. If only 0.50 M acetic acid and 0.25 M NaOH are available, **what volumes** of acid and base must be added to the protein solution to reach the desired pH?

Data:

$$K_a(\text{acetic acid}) = 1.8 \times 10^{-5}$$

- A) 41 ml acid, 59 ml base
- B) 88 ml acid, 12 ml base
- C) 72 ml acid, 28 ml base
- D) 53 ml acid, 47 ml base
- E) 65 ml acid, 35 ml base

We want to make an acetate buffer with pH 4.65, so we can use a rearranged form of the Henderson-Hasselbalch equation (see Test 1 solutions) to calculate the relative amounts of acetic acid (HA) and acetate (A^-):

$$\begin{aligned} \text{p}K_a &= -\log(K_a) \\ &= -\log(1.8 \times 10^{-5}) \\ &= 4.74 \end{aligned}$$

$$[\text{A}^-]/[\text{HA}] = 10^{(\text{pH} - \text{p}K_a)}$$

$$= 10^{(4.65-4.74)}$$

$$= 0.804 \quad (1)$$

We are making the buffer from acetic acid (HA) and NaOH, so HA is consumed to produce A⁻: $[HA]_{\text{final}} = [HA]_{\text{initial}} - [A^-]$, and $[A^-] = [NaOH]$.

$$[A^-]/[HA]_{\text{final}} = [NaOH]/([HA]_{\text{initial}} - [NaOH]) \quad (2)$$

Combining equations 1 and 2:

$$[NaOH]/([HA]_{\text{initial}} - [NaOH]) = 0.804$$

or

$$[NaOH] = 0.446[HA]_{\text{initial}} \quad (3)$$

Converting to initial volumes (v_{NaOH} and v_{HA}), and given the starting concentrations of HA (0.50 M) and NaOH (0.25 M):

$$v_{\text{NaOH}} = 0.446v_{\text{HA}} \times (0.50 \text{ M}/0.25 \text{ M})$$

$$= 0.891v_{\text{HA}} \quad (3)$$

We are starting from a 100 mL unbuffered solution, and want to make a 200 mL buffer solution, so the total amount of HA and NaOH added will be 100 mL:

$$v_{\text{HA}} + v_{\text{NaOH}} = 100 \text{ mL} \quad (4)$$

Combine 3 and 4:

$$v_{\text{HA}} + 0.891v_{\text{HA}} = 100 \text{ mL}$$

or

$$v_{\text{HA}} = 100 \text{ mL}/1.891$$

$$= 53 \text{ mL}$$

and

$$v_{\text{NaOH}} = 47 \text{ mL}$$

3. In the titration of 50.0 mL of 0.0200 M $\text{C}_6\text{H}_5\text{COOH}(\text{aq})$ with 0.100 M $\text{NaOH}(\text{aq})$, what is/are the **major aqueous species** in the solution after the addition of 5.0 mL of $\text{NaOH}(\text{aq})$?
- A) $\text{C}_6\text{H}_5\text{COOH}$
 B) $\text{C}_6\text{H}_5\text{COO}^-$ and Na^+
 C) $\text{C}_6\text{H}_5\text{COOH}$ and Na^+
 D) $\text{C}_6\text{H}_5\text{COOH}$, $\text{C}_6\text{H}_5\text{COO}^-$ and Na^+
 E) $\text{C}_6\text{H}_5\text{COOH}$, OH^- and Na^+

Use a mole table to determine what species are present after adding 5.0 mL of NaOH .

	$\text{C}_6\text{H}_5\text{COOH}$	+	NaOH	\rightarrow	$\text{C}_6\text{H}_5\text{COO}^-$	+	Na^+
before	1.00×10^{-3}		5.00×10^{-4}		0		0
after	5.00×10^{-4}		0		5.00×10^{-4}		5.00×10^{-4}

From the mole table, we see that this is a buffer solution, and therefore the major aqueous species are $\text{C}_6\text{H}_5\text{COOH}$, $\text{C}_6\text{H}_5\text{COO}^-$ and Na^+ .

That is all the information we need to answer the question.

But what about H_3O^+ and OH^- ? They are both present, of course, but their concentrations are very small.

Consider that the major species' concentrations are 0.018 M, while $[\text{H}_3\text{O}^+] = 6.3 \times 10^{-5}$ M, and $[\text{OH}^-] = 1.6 \times 10^{-10}$ M. Thus H_3O^+ and OH^- are not considered major species.

4. A buffer was prepared by adding 2.4 g of ammonium nitrate to 100.0 mL of 0.30 M ammonia. To this solution was then added 10.0 mL of 0.30 M sodium hydroxide. What was the **pH change** after addition of NaOH ?

Data:

$$K_b(\text{NH}_3) = 1.8 \times 10^{-5}$$

$$\text{mol wt}(\text{NH}_4\text{NO}_3) = 80.0 \text{ g/mol}$$

- A) 0.15 pH units
 B) 0.09 pH units
 C) 3.0 pH units
 D) 0.90 pH units
 E) 0.30 pH units

Solution 1 pH:

$$\begin{aligned} [\text{NH}_4\text{NO}_3] &= 2.4 \text{ g} \div 80.0 \text{ g/mol} \div 0.1000 \text{ L} \\ &= 0.30 \text{ M} \end{aligned}$$

Therefore $[\text{NH}_3] = [\text{NH}_4^+] = 1$, and $\text{pH} = \text{p}K_a$:

$$K_b(\text{NH}_3) = 1.8 \times 10^{-5}, \text{p}K_b(\text{NH}_3) = 4.74$$

$$\begin{aligned}\text{p}K_a(\text{NH}_4^+) &= 14 - \text{p}K_b(\text{NH}_3) \\ &= 9.26 = \text{solution 1 pH}\end{aligned}$$

Solution 2 pH:

Create a mole table:

	$\text{NH}_4^+ +$	$\text{NaOH} \rightarrow$	$\text{NH}_3 +$	$\text{Na}^+ +$	H_2O
before	0.030	0.0030	0.030	0	-
after	0.027	0	0.033	0.0030	-

Use the Henderson-Hasselbalch equation to calculate the new pH. Because we only need the ratio $[\text{NH}_3]/[\text{NH}_4^+]$, we can use the values from the mole table directly, without converting to concentrations.

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log([A^-]/[HA]) \\ &= 9.26 + \log(0.033/0.027) \\ &= 9.35 = \text{solution 2 pH}\end{aligned}$$

Change in pH:

$$\begin{aligned}\text{pH}_2 - \text{pH}_1 &= 9.26 - 9.35 \\ &= 0.09\end{aligned}$$

5. The average half-life of caffeine in healthy adults is 4.9 h. What is the **rate constant, k** , for the disappearance of caffeine?

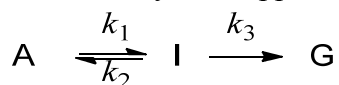
- A) $1.9 \times 10^{-5} \text{ s}^{-1}$
- B) $1.9 \times 10^{-6} \text{ s}^{-1}$
- C) $7.8 \times 10^{-6} \text{ s}^{-1}$
- D) $3.9 \times 10^{-5} \text{ s}^{-1}$
- E) $7.8 \times 10^{-5} \text{ s}^{-1}$

The fact that we are given a half-life indicates that this is a first order reaction.

$$\begin{aligned}t_{1/2} &= 4.9 \text{ h} \times (3600 \text{ s/h}) \\ &= 17640 \text{ s}\end{aligned}$$

$$\begin{aligned}k &= \ln(2) / t_{1/2} \\ &= 0.69 / 17640 \text{ s} \\ &= 3.9 \times 10^{-5} \text{ s}^{-1}\end{aligned}$$

6. In the steady state approximation, which of the following statements is **incorrect**?

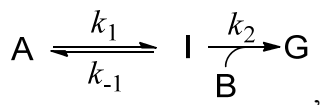


- A) If $k_1 \ll k_3$, then $[I] \approx 0$ throughout the course of the reaction.
- B) If $k_1 \gg k_3$, then the rate limiting step is $I \rightarrow G$.
- C) The steady state approximation is invalid if $k_2 < k_3$.
- D) In the steady state approximation, $d[I]/dt = 0$.
- E) If $k_1 \ll k_2$, then $[I] \approx 0$ throughout the course of the reaction.

The two assumptions in the steady state approximation are that $v_0 = k_3[I]$, and that $d[I]/dt = 0$.

The relative magnitudes of k_2 and k_3 do not affect the validity of the steady state approximation. It is valid when $k_2 = 0$, and when $k_2 \gg k_3$, and at all values in between.

7. For this reaction:



the steady state approximation gives this rate equation:

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

If the reverse reaction for the first step is very, very slow, what will the **rate equation simplify to**?

- A) $v_0 = \frac{k_1 k_2 [A]}{k_{-1} + k_2}$
- B) $v_0 = k_1 [A]$
- C) $v_0 = \frac{k_1 k_2 [A][B]}{k_{-1}}$
- D) $v_0 = \frac{k_1 k_2 [A][B]}{k_{-1}}$ Same as (C); this is an oversight.
- E) $v_0 = k_1 k_2 [A][B]$

If k_{-1} is very, very slow, then we can assume that the denominator of the rate equation can be simplified:

If $k_{-1} \ll k_2 [B]$,

then

$k_{-1} + k_2 [B] \approx k_2 [B]$,

and the rate equation simplifies to:

$$v_0 = \frac{k_1 k_2 [A][B]}{k_2 [B]},$$

which further simplifies to:

$$v_0 = k_1 [A].$$

8. For the reaction $aA + bB \rightarrow gG + hH$, which of the following statements **must be incorrect**?

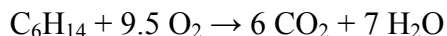
- A) $v_0 = k[B]^2$
- B) $v_0 = 1/g \times d[G]/dt$
- C) average rate = $1/h \times \Delta[H]/\Delta t$
- D) $v_0 = -1/a \times d[A]/dt$
- E) $\Delta[A]/\Delta t = -h/a \times \Delta[H]/\Delta t$

A) Could be correct.

B, C, D) are always correct.

E) Is incorrect. The correct expression would be: $\Delta[A]/\Delta t = -a/h \times \Delta[H]/\Delta t$

9. Combustion of hexane in the gas phase is described by the equation:



If the rate of O_2 consumption is $7.5 \text{ g}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$, which of the following statements is **incorrect**?

- A) $-d[O_2]/dt = 1.58 \cdot d[CO_2]/dt$
- B) The reaction rate is $0.025 \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$.
- C) The rate of hexane consumption is $2.6 \text{ g}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$.
- D) CO_2 production is $6.5 \text{ g}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$.
- E) $\Delta[H_2O]/\Delta t = 0.17 \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$

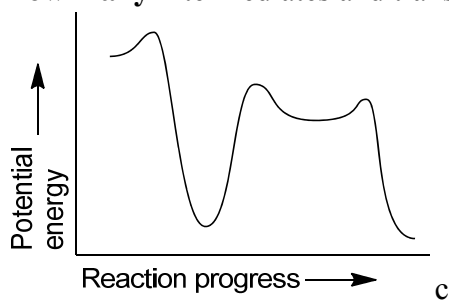
The reaction rate is:

$$\begin{aligned} v &= -1/9.5 \times -d[O_2]/dt \\ &= -1/9.5 \times -(7.5 \text{ g}\cdot\text{L}^{-1}\cdot\text{s}^{-1}) \div 32 \text{ g/mol} \\ &= 0.025 \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \end{aligned}$$

The rate of hexane consumption is:

$$\begin{aligned} \text{rate} &= 0.025 \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \times 86 \text{ g/mol} \\ &= 2.1 \text{ g}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \end{aligned}$$

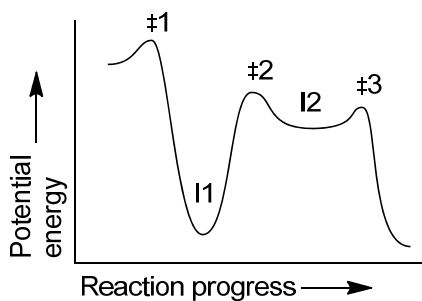
10. **How many** intermediates and transition states are there in this reaction?



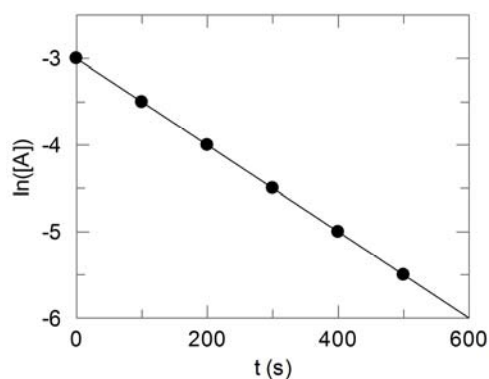
	Intermediates	Transition states
A)	3	3
B)	2	2
C)	3	2
D)	2	3
E)	1	3

Intermediates correspond to valleys in the reaction profile; there are two (I1, I2).

Transition states correspond to peaks in the reaction profile; there are three (\ddagger 1, \ddagger 2, \ddagger 3).



11. What are $[A]_0$ and k for the first order reaction: $A \rightarrow G$?



	$[A]_0$ (M)	k (s^{-1})
A)	0.005	0.005
B)	0.05	0.05
C)	0.05	0.005
D)	0.0005	0.3
E)	0.005	0.05

The equation: $\ln([A]_t/[A]_0) = -kt$ can be rearranged to: $\ln[A]_t = \ln[A]_0 - kt$.

Thus, in a plot of $\ln[A]$ versus time, $\ln[A]_0 = y$ -intercept, and $k = -\text{slope}$.

$$\begin{aligned}
 [A]_0 &= e^{\text{y-intercept}} \\
 &= e^{-3} \\
 &= 0.05 \text{ M}
 \end{aligned}$$

$$\begin{aligned}
 k &= -\text{slope} = -(\text{vertical distance}/\text{horizontal distance}) \\
 &= -(-6 - -3)/(600 \text{ s} - 0 \text{ s}) \\
 &= 3/600 \text{ s}^{-1} \\
 &= 0.005 \text{ s}^{-1}
 \end{aligned}$$

12. What is the **rate constant**, k , for a reaction that gives the following initial velocities, v_0 ?

$[A]$ (M)	$[B]$ (M)	v_0 (M/s)
0.5	1.0	4.1
1.0	0.5	4.1
2.0	2.0	32.8

- A) 8.2 Ms^{-1}
- B) 8.2 s^{-1}
- C) 16.4 s^{-1}
- D) $8.2 \text{ M}^{-1}\text{s}^{-1}$
- E) $16.4 \text{ M}^{-1}\text{s}^{-1}$

It is first necessary to determine the rate law for this reaction. The first two lines

imply that A and B have the same reaction order as each other. The last line supports the reaction being first order for both A and B,* therefore:

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

or

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

Substitute in the values from any line of the table (in this case, the first line):

$$\begin{aligned} k &= 4.1 \text{ M/s} / (0.5 \text{ M} \times 1.0 \text{ M}) \\ &= 8.2 \text{ M}^{-1}\text{s}^{-1} \end{aligned}$$

(* The units for (A) are Ms^{-1} , which are the units for a zero order reaction. The data in the table show that it is not a zero order reaction. The units for (B,C) are for a first order reaction (s^{-1}), while (D,E) are for a second order reaction ($\text{M}^{-1}\text{s}^{-1}$). Given the limited possibilities, it is possible to find the overall rate law by straightforward trial-and-error.)

13. One form of DNA damage, methylation of adenosine residues, destabilizes them. At 37°C , the $t_{1/2}$ for residue breakdown decreases from 37 y to 37 min. By how much does the **activation energy decrease** upon adenosine methylation? (Assume that A is constant.)

- A) 24 kJ/mol
- B) 7.8 kJ/mol
- C) 18 kJ/mol
- D) 4.4 kJ/mol
- E) 34 kJ/mol

Convert the $t_{1/2}$ values to k (in the same time units):

Adenosine (reaction 1):

$$\begin{aligned} t_{1/2} &= 37 \text{ y} \times (5.3 \times 10^6 \text{ min/y}) \\ &= 1.9 \times 10^7 \text{ min} \end{aligned}$$

$$\begin{aligned} k_1 &= 0.69/t_{1/2} \\ &= 3.5 \times 10^{-8} \text{ min}^{-1} \end{aligned}$$

Methyladenosine (reaction 2):

$$t_{1/2} = 37 \text{ min}$$

$$\begin{aligned} k_2 &= 0.69/t_{1/2} \\ &= 1.9 \times 10^{-2} \text{ min}^{-1} \end{aligned}$$

Rearrange $k = Ae^{-E_a/RT}$, and cancel out A, which we assume is constant:

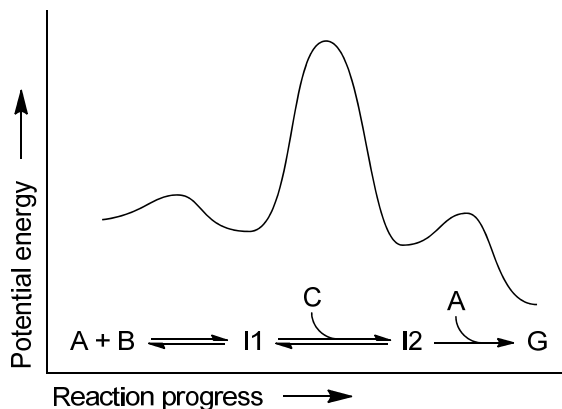
$$E_{a1} - E_{a2} = RT \ln(k_1) - RT \ln(k_2)$$

$$\begin{aligned}
 &= RT \ln(k_1/k_2) \\
 &= 0.0083 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 310 \text{ K} \times \ln(3.5 \times 10^{-8} \text{ min}^{-1} / 1.9 \times 10^{-2} \text{ min}^{-1}) \\
 &= -34 \text{ kJ/mol}
 \end{aligned}$$

or, a 34 kJ/mol decrease.

(The numbers may look fake (37 °C, 37 y, 37 min), but those are the real values for adenosine and 3-methyladenosine residues in DNA.)

14. Based on the reaction profile (below) for the reaction $2A + B + C \rightarrow G$ what is the **overall rate law** for this reaction?



- A) $v_0 = k[C]$
- B) $v_0 = k[I1][C]$
- C) $v_0 = k[A]^2[B][C]$
- D) $v_0 = k[A][B]$
- E) $v_0 = k[A][B][C]$

The rate limiting step is $I1 + C \rightarrow I2$, so steps up to this point contribute to the rate law. The $I2 + A \rightarrow G$ step occurs after the rate-limiting step, so it does not affect the rate law.

Bearing in mind that the order of a reaction is equal to the stoichiometry of the species present in the rate-limiting step, it is possible to initially write $v_0 = k_2[I1][C]$. We must remove I1 from the rate law because its concentration is unknown. The elementary process that forms [I1] is the bimolecular association of A and B, so we can write:

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

(Note that k may be a complex combination of the rate constants for the individual forward and reverse steps in the reaction (k_1 , k_{-1} , and k_2), but the form of the rate law will still be first order in A, B, and C.)

15. ^{14}C is a radioactive isotope of carbon, with a half-life of 5730 y. If a mastodon tusk contains 2.65% of the ^{14}C it did when the animal was alive, **how old** is the tusk?

- A) 200 000 y
- B) 180 000 y
- C) 40 000 y
- D) 20 000 y
- E) 30 000 y

Radioactive decay is a first order process. We first need to determine k for ^{14}C decay, then use the integrated rate equation to find t for $[A]_t/[A]_0 = 0.0265$:

$$\begin{aligned}k &= 0.69/t_{1/2} \\&= 0.69 / 5730 \text{ y} \\&= 1.2 \times 10^{-4} \text{ y}^{-1}\end{aligned}$$

$\ln([A]_t/[A]_0) = -kt$, therefore:

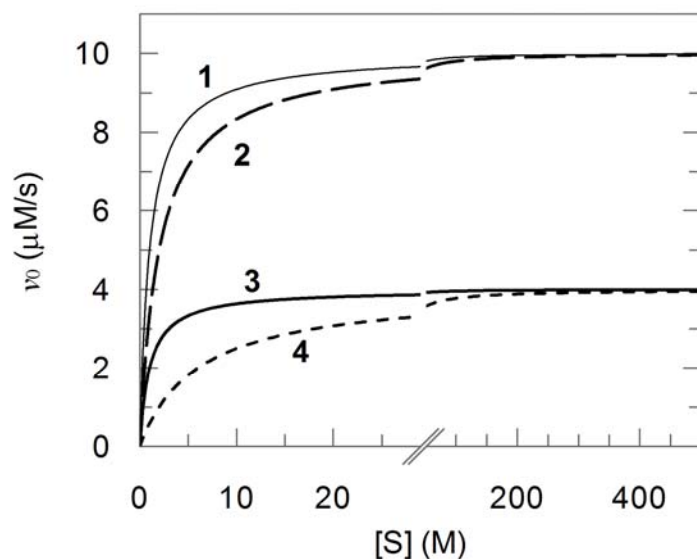
$$\begin{aligned}t &= -\ln([A]_t/[A]_0)/k \\&= -\ln(0.0265) / 1.2 \times 10^{-4} \text{ y}^{-1} \\&= 3.0 \times 10^4 \text{ y}\end{aligned}$$

16. A student is attempting to determine the rate law for the reaction of $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$ under the same conditions as experiment # 8 in Chemistry 1AA3. They are able to measure only the absorbance of B. Which statement regarding the experiment is **incorrect**?

- A) The student can determine the overall order of the reaction.
- B) The slope of a plot of absorbance versus time is directly proportional to the rate of the reaction.
- C) The slope of a plot of absorbance versus time will be negative.
- D) Both relative rates between trials and absolute rates for an individual trial can be determined.
- E) The absolute rate constant cannot be obtained unless the proportionality between absorbance and concentration is known.

The absolute reaction rate cannot be determined without the proportionality constant between absorbance and concentration, as stated in (E). This value was not known in experiment #8, so (D) is incorrect.

17. The effects of mutations on enzyme X were studied. *Mutation a* caused K_M to increase. *Mutation b* caused k_{cat} to decrease. *Mutation c* caused both K_M to increase and k_{cat} to decrease. In the figure below, curve 1 is for the non-mutant (wild-type) enzyme X. Curves 2 through 4 correspond to **which mutations**?



($[S] = 400 \text{ M}$ is ridiculous, of course. (Pure water only contains 55.5 mol/L of H_2O .) The x-axis should be in units of mM, μM , or nM. This does not affect the answer.)

	Curve		
	2	3	4
A)	<i>c</i>	<i>a</i>	<i>b</i>
B)	<i>b</i>	<i>a</i>	<i>c</i>
C)	<i>a</i>	<i>b</i>	<i>c</i>
D)	<i>b</i>	<i>c</i>	<i>a</i>
E)	<i>a</i>	<i>c</i>	<i>b</i>

k_{cat} is an enzyme's maximal rate at high $[S]$, when it is fully saturated with substrate. K_M is the substrate concentration at which the rate is half-maximal. (We cannot determine k_{cat} directly from the graph because $k_{cat} = [E]_0 \times v_0$ when $[S] \gg K_M$, but we are not given $[E]_0$. However, v_0 is directly proportional to k_{cat} at high $[S]$, so we will look at v_0 .)

Wild type enzyme X is curve 1.

Curve 2 is for an enzyme that has the same maximal rate as wild type, i.e., the same k_{cat} value, but requires a higher $[S]$ to achieve that rate. That is, it has a higher K_M value. That corresponds to *mutation a*.

Curves 3 and 4 correspond to mutations which never reach the same rate as wild type, regardless of $[S]$, i.e., k_{cat} is lower for both curves.

Curve 3 appears to have the same K_M value as curve 1. The maximal value of v_0

is 4 $\mu\text{M/s}$, and the half-maximal rate, 2 $\mu\text{M/s}$, occurs at $[\text{S}] = 1 \text{ M}$, the same as curve 1. Curve 4 has the same k_{cat} value as curve 3, but requires a higher $[\text{S}]$ to achieve saturation, therefore the enzyme for curve 4 has a higher K_{M} value than curve 3. Therefore, curve 3 corresponds to *mutation b*, and curve 4 corresponds to *mutation c*.

18. The rate of a reaction with an activation energy of 15 kJ/mol doubles when the temperature is increased. If the starting temperature was 300 K, what is the **new temperature**?

- A) 349 K
- B) 393 K
- C) 323 K
- D) 339 K
- E) 279 K

Use the equation $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$, with $k_2/k_1 = 2$:

$$\begin{aligned} 1/T_2 &= 1/T_1 - \ln(k_2/k_1)R/E_a \\ &= 1/300 \text{ K} - \ln(2) \times 0.0083 \text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} / 15 \text{ kJ}\cdot\text{mol}^{-1} \\ &= 2.95 \times 10^{-3} \text{ K}^{-1} \end{aligned}$$

so,

$$T_2 = 339 \text{ K}$$

19. In the pseudo-first order hydrolysis of an ester, $[\text{ester}] = 0.060 \text{ M}$ at $t = 600 \text{ s}$, and 0.018 M at $t = 1200 \text{ s}$. What was $[\text{A}]_0$?

- A) 0.33 M
- B) 0.64 M
- C) 0.14 M
- D) 0.061 M
- E) 0.20 M

We can treat this as a first order reaction, and determine k by adjusting the integrated rate equation. With first order reactions, any pair of times can be used to determine k :

$$\ln([A]_2/[A]_1) = -k(t_2 - t_1)$$

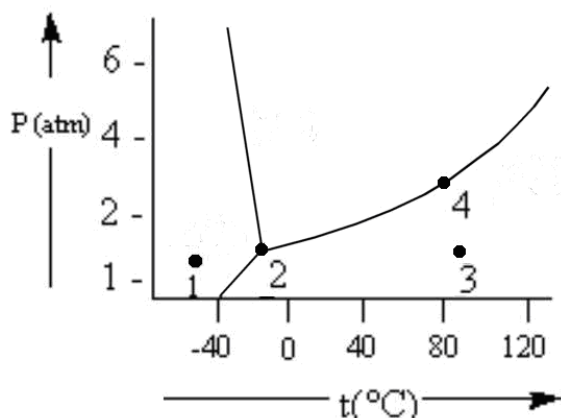
so

$$\begin{aligned} k &= -\ln([A]_2/[A]_1)/(t_2 - t_1) \\ &= -\ln(0.018\text{M}/0.06 \text{ M}) / (1200 \text{ s} - 600 \text{ s}) \\ &= 0.0020 \text{ s}^{-1} \end{aligned}$$

Now rearrange the integrated rate equation again to determine $[A]_0$:

$$\begin{aligned}[A]_0 &= [A]_t / e^{-kt} \\ &= 0.060 \text{ M} / e^{-(0.0020 \text{ 1/s} \times 600 \text{ s})} \\ &= 0.20 \text{ M}\end{aligned}$$

20. According to the phase diagram below for substance Z, which of the following statements is **incorrect**?



- A) If liquid Z is maintained at the pressure of point 4 while the temperature is decreased by 30 °C, the liquid will vaporize.
- B) It is possible to find conditions of temperature and pressure under which solid Z will vaporize without melting first.
- C) At the temperature and pressure of point 3, substance Z exists as a one-phase gaseous system.
- D) If the $Z(s) = Z(l) = Z(g)$ system is maintained at the temperature of point 2 while pressure is decreased, more Z will vaporize.
- E) At the temperature and pressure of point 2, substance Z exists as a three-phase equilibrium system.

(A) In general, cooling a liquid will decrease its vapour pressure and its tendency to vaporize. Liquid Z is no exception; decreasing T while holding P constant will move liquid Z from its boiling/condensation point at pressure P into the one phase liquid region.

(B) Moving in a straight line from 1 to 3 will give sublimation.

(C, D) Correct

(E) Correct. This is the triple point.

21. Which of the following statements regarding intermolecular forces is **incorrect**?

- A) Octanol will have a higher viscosity than pentane because of stronger intermolecular forces in octanol.
- B) Pentanol has a higher vapour pressure than pentane because of hydrogen bonding and dipole-dipole forces in pentanol.
- C) Pentane has a higher boiling point than propane because of stronger London (dispersion) forces.
- D) Pentane has a lower boiling point than 2,3-dibromopentane because pentane has no dipole-dipole forces, and lower London (dispersion) forces than 2,3-dibromopentane.
- E) 2,3-dimethylpentane will have a higher vapour pressure than heptane because of stronger London (dispersion) forces in heptane.

(A) Correct. Octanol is larger and it can form hydrogen bonds.

(B) Incorrect. Pentanol has a **lower** vapour pressure (and higher boiling point) for the reasons stated.

(C) Correct. The type of forces is the same for pentane and propane, but pentane is larger (C_5H_{12} vs. C_3H_8), so there is more contact area between molecules for dispersion forces to act.

(D) Correct. Pentane has no dipole-dipole forces, and bromine atoms (atomic wt. 80 g/mol) are much larger than hydrogen (1 g/mol).

(E) Correct. For molecules with the same molecular formula (C_7H_{16}), more highly branched molecules have higher vapour pressures because they are less flexible and are less able to form contacts with other molecules.

22. Arrange in order by **decreasing boiling point** (from highest to lowest):



- A) $HOCH_2CH_2OH > C_4H_{10} > CH_3CH_2OH$
- B) $CH_3CH_2OH > C_4H_{10} > HOCH_2CH_2OH$
- C) $CH_3CH_2OH > HOCH_2CH_2OH > C_4H_{10}$
- D) $C_4H_{10} > HOCH_2CH_2OH > CH_3CH_2OH$
- E) $HOCH_2CH_2OH > CH_3CH_2OH > C_4H_{10}$

Ethylene glycol ($HOCH_2CH_2OH$) can form hydrogen bonds through two hydroxyl groups, acting as both hydrogen bond donors (through the proton) and hydrogen bond acceptors (through the lone pair electrons of oxygen). It also forms dipole-dipole, and dispersion interactions. Ethanol has only one hydroxyl group for hydrogen bonding, and butane has none. Even though butane has more carbon atoms through which to form dispersion interactions, these are weaker than hydrogen bonds or dipole-dipole interactions.

23. What is the **maximum number** of glycerol molecules ($\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$) that could form hydrogen bonds with a single glycerol molecule?

- A) 9
- B) 5
- C) 14
- D) 3
- E) 1

Glycerol can form 9 hydrogen bonds. Each of the three hydroxyl groups can donate one hydrogen bond through its proton, and accept two hydrogen bonds - one through each of the lone pairs of electrons on the oxygen atom.

24. When a liquid is in dynamic equilibrium with its vapour at a given temperature, T, which of the following statements are **correct**?

- i) Increasing temperature will decrease vapour pressure.
- ii) The vapour pressure has a unique value at temperature T.
- iii) Vaporization and condensation proceed at equal rates.
- iv) The concentration of vapour is dependent on time at temperature T.

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

(i) Incorrect. Increasing temperature increases vapour pressure.

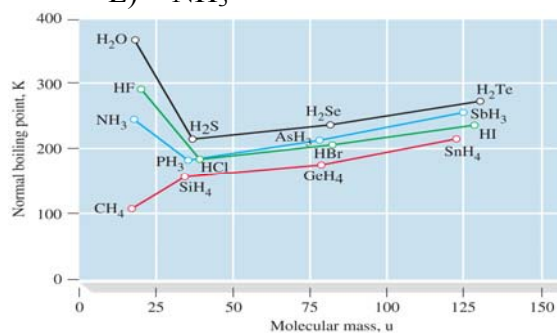
(ii) Correct.

(iii) Correct. When the system is in dynamic equilibrium, vaporization and condensation are both occurring. The fact that the system has reached equilibrium means that the rates are equal to each other, so that the amount of liquid and gas phase are not changing over time.

(iv) Incorrect. Because the system is in equilibrium, the concentrations are not changing over time.

25. Which of the following compounds has the **highest boiling point** at a given pressure?

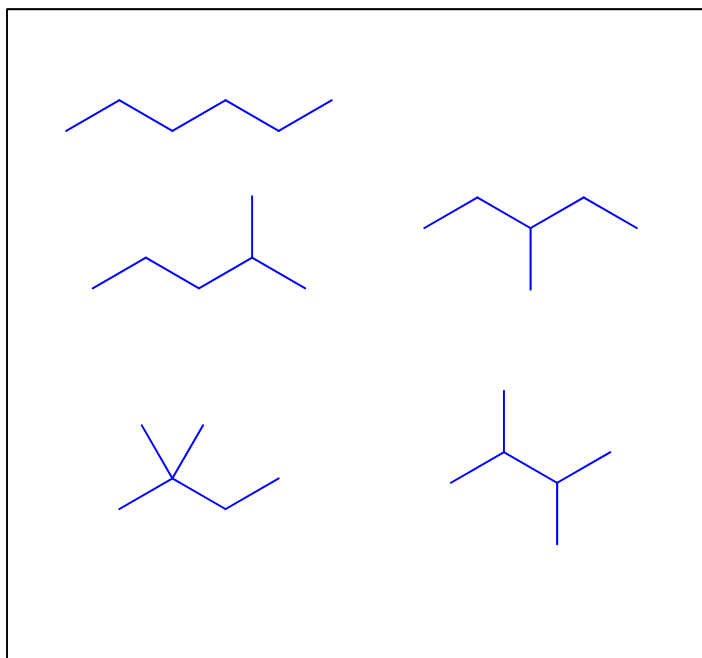
- A) CH_4
- B) HBr
- C) H_2O
- D) HF
- E) NH_3



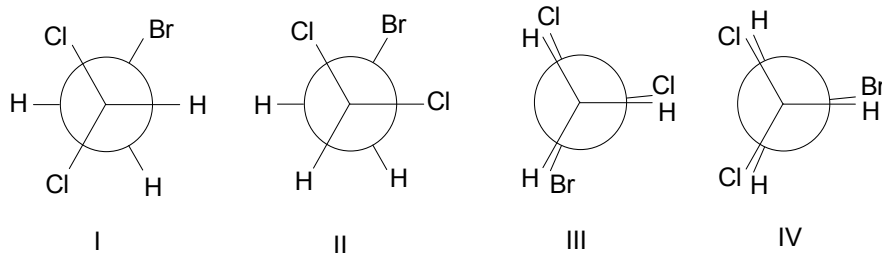
Petrucci, 10th ed., page 501, Fig. 12-5

26. How many **skeletal (or structural) isomers** can be drawn for C_6H_{14} ?

- A) 5
- B) 2
- C) 3
- D) 8
- E) 6



27. Which of the following statements are **incorrect** regarding the Newman projections shown below?



- i) Structure I sits at higher energy than structure II.
- ii) Structures I and II are two different conformations of the same molecule.
- iii) Structures II and IV are two different conformations of the same molecule, related by a 180° rotation about the C1-C2 bond.
- iv) The name of structures I, II, III and IV is 1-bromo-2,2-dichloroethane.
- v) Structure IV sits at higher energy than structure I.

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

(i) Incorrect. In **II**, Br is *gauche* to both Cl atoms, while in **I** it is *gauche* to one Cl atom, and *anti* to the other. *Anti* conformations are more favourable (lower energy) than *gauche*.

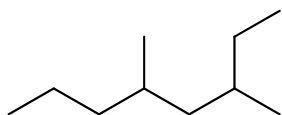
(ii) Correct.

(iii) Correct.

(iv) Incorrect. Structure **III** is 1-bromo-1,1-dichloroethane.

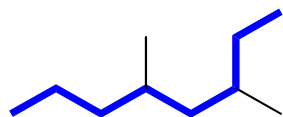
(v) Correct. All eclipsed conformations have higher energy than all staggered conformations.

28. What is the **correct IUPAC name** for the following structure?



- A) 3,5-dimethyloctane
- B) 2-ethyl-3-methyldecane
- C) 2-ethyl-3-methylheptane
- D) 4-methyl-6-ethylheptane
- E) 5,7-dimethyloctane

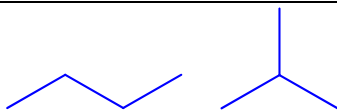
The longest chain (in blue) is 8 carbon atoms long, therefore, the molecule is an octane. (E) is incorrect because it does not use the lowest possible numbering for the substituents.



29. Which of the following statements regarding structural (skeletal) isomers is **incorrect**?

- A) There are only two structural isomers for molecules with formula C_4H_{10} .
- B) Conformational isomers (e.g., *anti* and *gauche*) are also structural isomers.
- C) $CH_3CH_2-O-CH_2CH_3$ is a structural isomer of $CH_3CH_2CH_2CH_2OH$.
- D) Structural isomers have the same chemical formula but differ with respect to the connectivity (bonding sequence) of atoms.
- E) 2,3,3-trimethylpentane is a structural isomer of 3-ethylhexane.

(A) Correct.



(B) Incorrect. Structural isomerism implies different connectivities, while conformations involve only rotations about single bonds without breaking bonds or changing connectivity.

(C) Correct. Both molecules have the molecular formula $C_4H_{10}O$.

(D) Correct.

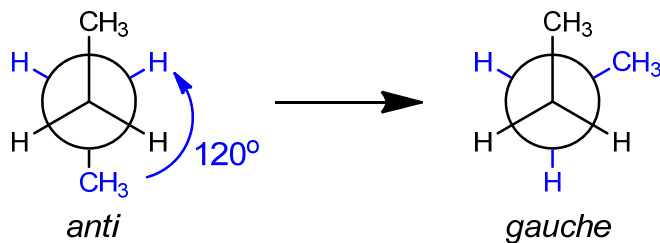
(E) Correct. Both have the molecular formula C_8H_{18} .

30. Choose the **incorrect** statement about organic compounds.

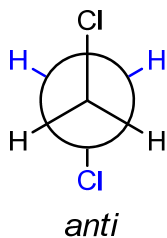
- A) Alkanes have only single C–C and C–H bonds connecting all atoms.
- B) Small cycloalkanes such as cyclopropane experience ring strain because the C–C bond angles are smaller than ideal.
- C) Alkanes have the general formula C_nH_{2n+1} .
- D) In the Newman projection for butane, looking along the C2–C3 bond, a rotation of 120° is required to convert from the *anti* conformation to a *gauche* conformation.
- E) For Newman projections of 1,2-dichloroethane, the lowest energy conformation is the *anti* staggered conformation.

(A, B) Correct.

(C) Incorrect. Alkanes have the general formula C_nH_{2n+2} .



(D) Correct.



(E) Correct.

Version 1 - Answer Key

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

Version 2 - Answer Key

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

Version 3 - Answer Key

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

Version 4 - Answer Key

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