

Name: _____

Student number: _____

Chemistry 1AA3**Second Test****March 11th, 2005****McMaster University****VERSION 1 Solutions**

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Duration: 110 minutes

This test contains 22 numbered pages. There are **25** multiple-choice questions appearing on pages numbered 3 to 18. Pages 19 and 20 are for your rough work. Page 21 includes some useful data and equations, and there is a periodic table on page 22. You may tear off the last page to view the periodic table and the data provided.

You must enter your name and student number on this question sheet, as well as on the answer sheet. Your invigilator will be checking your student card for identification. **You are responsible** for ensuring that your copy of the question paper is complete. Bring any discrepancy to the attention of your invigilator.

Questions 1 to 20 are each worth 2 marks, questions 21 – 25 are each worth 3 marks; the total marks available are 55. There is **no** additional penalty for incorrect answers.

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

ANSWER ALL QUESTIONS ON THE ANSWER SHEET, IN PENCIL.

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

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

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

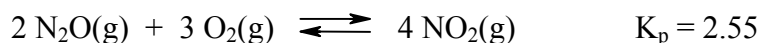
Only Casio FX 991 electronic calculators may be used; but they must NOT be transferred between students. Use of periodic tables or any aids, other than those provided, is not allowed.

continued on next page

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

Questions 1 through 20 are worth two (2) marks each.

1. At 25°C, the gas phase equilibrium is studied by measuring partial pressures.



Calculate K_c for this reaction at the same temperature.

(A) 1.53×10^3

(B) 530.

(C) 62.4

(D) 6.50

(E) 0.104

$$P_i = n_i RT/V = [i]RT; \quad R = 0.08206 \text{ atm}\cdot\text{L/mol}\cdot\text{K}, T \text{ in K}$$

$$\begin{aligned} K_p &= P(\text{NO}_2)^4 P(\text{N}_2\text{O})^{-2} P(\text{O}_2)^{-3} \\ &= [\text{NO}_2]^4 (RT)^4 [\text{N}_2\text{O}]^{-2} (RT)^{-2} [\text{O}_2]^{-3} (RT)^{-3} \\ &= [\text{NO}_2]^4 [\text{N}_2\text{O}]^{-2} [\text{O}_2]^{-3} (RT)^{-1} = K_c / RT \end{aligned}$$

$$K_c = K_p \cdot RT = 2.55 (0.08206)(298.15) = 62.5$$

2. Solid lead iodide, PbI_2 , is added to 0.500 L of water. After equilibrium has been established, 0.020 mol of $\text{PbI}_2(\text{s})$, 0.00076 mol of $\text{Pb}^{2+}(\text{aq})$ and 0.00152 mol of $\text{I}^{-}(\text{aq})$ are present. What is the **equilibrium constant, K_c** , for the dissolution (dissolving) of lead iodide in water?

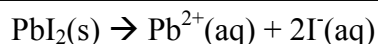
(A) 1.8×10^{-9}

(B) 3.5×10^{-9}

(C) 1.4×10^{-8}

(D) 3.5×10^{-7}

(E) 4.6×10^{-6}



$$K_c = [\text{Pb}^{2+}] [\text{I}^{-}]^2 \quad (\text{no solids included})$$

$$[\text{Pb}^{2+}] = (0.00076 \text{ mol} / 0.500\text{L}) = 0.00152 \text{ M}$$

$$[\text{I}^{-}] = (0.00152 \text{ mol} / 0.500 \text{ L}) = 0.00304 \text{ M}$$

$$K_c = (0.00152) (0.00304)^2 = 1.4 \times 10^{-8}$$

3. How many of the following substances will form **basic solutions** when dissolved in water? KCN LiI IOH NaClO_4 NaNO_2 K_2CO_3

- (A) 1 Salts can be analysed in terms of the neutralization reaction that forms them (strong \rightarrow neutral; weak \rightarrow conjugate weak):
 (B) 2
 (C) 3 KOH (strong base) + HCN (weak acid) \rightarrow KCN (weak base) + H_2O
 (D) 4 LiOH (strong base) + HI (strong acid) \rightarrow LiI (neutral) + H_2O
 IOH is a weak acid (hypoiodous acid)
 (E) 5 NaOH (strong base) + HClO_4 (strong acid) \rightarrow NaClO_4 (neutral) + H_2O
 NaOH (strong base) + HNO_2 (weak acid) \rightarrow NaNO_2 (weak base) + H_2O
 KOH (strong base) + KHCO_3 (weak acid) \rightarrow K_2CO_3 (weak base) + H_2O
 or $2\text{KOH} + \text{H}_2\text{CO}_3 \rightarrow \text{K}_2\text{CO}_3 + 2\text{H}_2\text{O}$

4. The titration of 10.00 mL of a weak base with 0.200 M hydrochloric acid solution reaches the half-equivalence point after adding 4.67 mL of acid. The pH at the half equivalence point is 9.57. Calculate the **initial concentration** and the **K_b** value for the base.

- (A) 0.187 M $K_b = 3.7 \times 10^{-5}$
 (B) 0.0934 M $K_b = 2.7 \times 10^{-10}$
 (C) 0.200 M $K_b = 4.4$
 (D) 0.187 M $K_b = 2.7 \times 10^{-10}$
 (E) 0.200 M $K_b = 1.8 \times 10^{-5}$

$\text{HCl} + \text{B} \rightarrow \text{HB}^+ + \text{Cl}^-$
 At the half-equivalent point, $[\text{B}] = [\text{HB}^+]$,
 $K_b = [\text{OH}^-][\text{HB}^+] / [\text{B}] = [\text{OH}^-] = 10^{-\text{pOH}}$
 $\text{pOH} = 14.00 - 9.57 = 4.43$
 $K_b = 10^{-4.43} = 3.7 \times 10^{-5}$
 OR $\text{pH} = \text{pK}_a = 9.57 = 14.00 - \text{pK}_b$
 $K_b = 10^{-\text{pK}_b} = 10^{-4.43}$

At the half-equivalence point, moles HCl added = $\frac{1}{2}$ moles B added.
 Moles $\text{HCl} = 4.67 \times 10^{-3} \text{ L} \times 0.200 \text{ M} = 9.34 \times 10^{-4} \text{ moles} = \frac{1}{2} \text{ moles B}$.
 $[\text{B}] = 2 \times (9.34 \times 10^{-4} \text{ moles}) / 10.00 \times 10^{-3} \text{ L} = 0.1868 \text{ M}$

5. Select the **TRUE** statements about the effects of dilution.

(K_a for HCOOH (formic acid) = 1.8×10^{-4})

- (i) Diluting 15 mL of a buffer that is 1.0 M each in HCOOH and HCOONa by adding 15 mL of H₂O causes little or no change in the pH.
- (ii) Diluting 15 mL of 1.0 M HCOOH by adding 15 mL of H₂O would cause the pH to increase.
- (iii) Diluting 15 mL of 1.0 M HCOOH by adding 15 mL of H₂O would cause the percent ionization of HCOOH to decrease.

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

See lab 7, Part C tables. Use small-x approximation.

(i) Ratio of $[HCOOH]/[HCOO^-]$ is essentially unchanged,
 $[H^+] = K_a[HCOOH]/[HCOO^-] \approx \text{constant}$.

(ii) $[H^+] = x = (K_a[HCOOH])^{1/2}$.
 As $[HA]$ decreases, $[H^+]$ decreases and pH increases.

(iii) % ionization = $[H^+] / [HCOOH] =$
 $(K_a[HCOOH])^{1/2} / [HCOOH] = (K_a/[HCOOH])^{1/2}$.
 As $[HA]$ decreases, % ionization increases.

Le Châtelier: Equilibrium shifts to side of more aqueous moles as volume of water (solvent) increases.

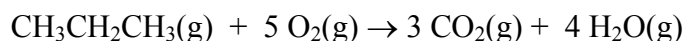
6. Which of the following statements are **TRUE**?

- (i) I^- is a stronger base than F^- .
- (ii) NO_2^- is a stronger base than NO_3^- .
- (iii) $H_2PO_3^-$ is the conjugate base of HPO_3^{2-} .
- (iv) A 0.1 M solution of H_2SO_4 will have a higher pOH than a 0.1 M solution of H_3PO_4 .
- (v) The strongest base that will be present in water at equilibrium is OH^- .

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

(i) HI is a stronger acid than HF $\rightarrow I^-$ is a weaker base than F^- .
 (ii) HNO_3 is a stronger acid than $HNO_2 \rightarrow NO_2^-$ is the stronger base.
 (iii) $H_2PO_3^-$ is the conjugate acid of HPO_3^{2-} (it has one more H^+).
 (iv) Same initial concentrations. H_2SO_4 is a strong acid, first proton is 100% ionized, 2nd is mostly ionized $\rightarrow [H^+] \approx 0.2M$. H_3PO_4 is a weak acid, first proton is partially ionized, others can be ignored $\rightarrow H^+ < 0.1 M$, so it is less 'acidic' than H_2SO_4 . For the stronger acid, the pH is lower and the pOH is higher.
 (v) True, any stronger base will immediately accept a proton from water to form OH^- .

7. The combustion of propane ($\text{CH}_3\text{CH}_2\text{CH}_3$) is described by the equation



If the rate of production of carbon dioxide is $d[\text{CO}_2]/dt = 64.0 \text{ mol L}^{-1} \text{ s}^{-1}$, which of the following statements is/are **TRUE**?

- (i) The rate of consumption of oxygen is $107 \text{ mol L}^{-1} \text{ s}^{-1}$.
- (ii) The rate of production of water is $48.0 \text{ mol L}^{-1} \text{ s}^{-1}$.
- (iii) The rate of consumption of propane is $192 \text{ mol L}^{-1} \text{ s}^{-1}$.
- (iv) The rate of production of water is $85.3 \text{ mol L}^{-1} \text{ s}^{-1}$.

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

$$\begin{aligned} -d[\text{O}_2]/dt &= 64.0 \text{ mol CO}_2/\text{Ls} * (5 \text{ mol O}_2 / 3 \text{ mol CO}_2) \\ &= 106.7 \text{ mol O}_2 / \text{Ls}. \\ d[\text{H}_2\text{O}]/dt &= 64.0 \text{ mol CO}_2/\text{Ls} * (4 \text{ mol H}_2\text{O} / 3 \text{ mol CO}_2) \\ &= 85.3 \text{ mol O}_2 / \text{Ls}. \\ -d[\text{CH}_3\text{CH}_2\text{CH}_3]/dt &= 64.0 \text{ mol CO}_2/\text{Ls} * (1 \text{ mol CH}_3\text{CH}_2\text{CH}_3 / 3 \text{ mol CO}_2) \\ &= 21.3 \text{ mol CH}_3\text{CH}_2\text{CH}_3 / \text{Ls}. \end{aligned}$$

8. The bromination of acetone in the presence of acid goes according to the equation:



In the chemistry lab you found that the order of the reaction with respect to Br_2 was zero, and that the orders with respect to acetone and hydrochloric acid were both one. The reaction was monitored by the change in bromine concentration over time. The **rate law** for the reaction is:

- (A) $\text{Rate} = d[\text{Br}_2]/dt = -k [\text{BrCH}_2\text{COCH}_3] [\text{HBr}] / [\text{CH}_3\text{COCH}_3] [\text{Br}_2]$
- (B) $\text{Rate} = -d[\text{Br}_2]/dt = k [\text{Br}_2] / [\text{CH}_3\text{COCH}_3] [\text{H}^+]$
- (C) $\text{Rate} = d[\text{Br}_2]/dt = k [\text{CH}_3\text{COCH}_3] [\text{Br}_2] [\text{H}^+]$
- (D) $\text{Rate} = -d[\text{Br}_2]/dt = k [\text{CH}_3\text{COCH}_3] [\text{H}^+]$
- (E) $\text{Rate} = -d[\text{HBr}]/dt = k [\text{CH}_3\text{COCH}_3] [\text{Br}_2]$

Order = exponent in rate law.
Experimental, not stoichiometry!
 $\text{Rate} = k[\text{Br}_2]^0[\text{acetone}]^1[\text{HCl}]^1$

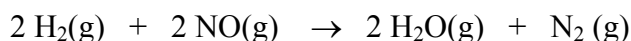
9. Which of the following rate laws is/are **fourth order** processes overall?

- (i) Rate = $k [A]^2[B]^2$
- (ii) Rate = $k [A]^4[B]^1[C]^0$
- (iii) Rate = $k [A]^2[B]^{1.5}[C]^{-0.5}$
- (iv) Rate = $k [A]^{-1}[B]^2[C]^2$
- (v) Rate = $k [A]^3[B]^2[C]^{-1}$

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

(i) $2 + 2 = 4$
 (ii) $4 + 1 + 0 = 5$
 (iii) $2 + 1.5 - 0.5 = 3$
 (iv) $-1 + 2 + 2 = 3$
 (v) $3 + 2 - 1 = 4$
 Sum the individual orders.

10. The reduction of nitric oxide by hydrogen is represented by the equation:



A series of experiments was performed in order to determine the rate law.

The following data were recorded:

	<u>Initial [NO]</u> mol L ⁻¹	<u>Initial [H₂]</u> mol L ⁻¹	<u>Initial rate</u> mol L ⁻¹ s ⁻¹
Experiment 1	1.5×10^{-3}	1.5×10^{-3}	6.8×10^{-4}
Experiment 2	0.5×10^{-3}	1.5×10^{-3}	7.5×10^{-5}
Experiment 3	1.5×10^{-3}	1.0×10^{-3}	4.5×10^{-4}

The **rate law** for the reaction is:

- (A) Rate = $k [\text{NO}]$
- (B) Rate = $k [\text{NO}] [\text{H}_2]$
- (C) Rate = $k [\text{NO}]^2 [\text{H}_2]$
- (D) Rate = $k [\text{NO}]^2 [\text{H}_2]^{1.5}$
- (E) Rate = $k [\text{NO}]^2 [\text{H}_2]^2$

Rate = $k[\text{NO}]^a[\text{H}_2]^b$
 Rate 1/ Rate 2 = $k(1.5)^a(1.5)^b / k(0.5)^a(1.5)^b$
 $6.8 \times 10^{-4} / 7.5 \times 10^{-5} = (1.5 / 0.5)^a$
 $9 = 3^a \rightarrow a = 2$
 Rate 1/ Rate 3 = $k(1.5)^2(1.5)^b / k(1.5)^2(1.0)^b$
 $6.8 \times 10^{-4} / 4.5 \times 10^{-4} = (1.5 / 1.0)^b$
 $1.5 = 1.5^b \rightarrow b = 1$
 Rate = $k[\text{NO}]^2[\text{H}_2]^1$

11. For a reaction with a rate law, $\text{rate} = k[A]^1[B]^{1.5}$ the **units of the rate constant**, k , are:

- (A) $\text{mol L}^{-1} \text{s}^{-1}$
- (B) $\text{mol}^{2.5} \text{L}^{-2.5} \text{s}^{-1}$
- (C) $\text{mol}^{-2.5} \text{L}^{2.5} \text{s}$
- (D) $\text{mol}^{1.5} \text{L}^{-1.5} \text{s}^{-1}$
- (E) $\text{mol}^{-1.5} \text{L}^{1.5} \text{s}^{-1}$

$\text{Rate} = k[A]^1[B]^{1.5}$
 Let all the 'values' = 1, solve for k .
 $1 \text{ M/s} = k (1\text{M})^1(1\text{M})^{1.5}$
 $k = (1\text{M/s}) / (1\text{M})^{2.5} = 1 \text{ M}^{-1.5}\text{s}^{-1}$
 units of k are $\text{mol}^{-1.5}\text{L}^{1.5}\text{s}^{-1}$.

12. The radioisotope ^{18}F is used extensively in a radio-imaging method called PET (Positron Emission Tomography). If the decomposition of an ^{18}F -containing sample is 25% complete after 45 minutes, **how long** will it take to complete **four half-lives** of radioactive decay?

- (A) 90 min
- (B) 108 min
- (C) 156 min
- (D) 360 min
- (E) 434 min

$[A]_t = [A]_0 e^{-kt}$ $[A]_t / [A]_0 = e^{-kt}$
 25% complete \rightarrow 75% remaining
 $0.75 = e^{-k(45\text{min})}$ $\ln(0.75) = -k(45 \text{ min})$
 $k = 0.2876 / 45 \text{ min} = 6.393 \times 10^{-3} \text{ min}^{-1}$
 After 4 half lives have $(\frac{1}{2})^4 = 1 / 16$ remaining.
 $\ln(1/16) = -(6.393 \times 10^{-3} \text{ min}^{-1}) t$
 $t = 2.77 / (6.393 \times 10^{-3} \text{ min}^{-1}) = 434 \text{ min}$

13. A reaction has an activation energy of 147 kJ mol^{-1} . **By what factor** will the **reaction rate decrease** after cooling from room temperature (25°C) to the temperature in an industrial freezer (-36°C)?

- (A) 8
- (B) 15
- (C) 4000
- (D) 4×10^6
- (E) 1×10^{55}

$k = Ae^{-E_a/RT}$
 Rate ratio = $k_{\text{fast}} / k_{\text{slow}} = Ae^{-E_a/RT(\text{hot})} / Ae^{-E_a/RT(\text{cold})}$
 $k_{\text{fast}} / k_{\text{slow}} = \exp\{-E_a/RT(\text{hot}) - E_a/RT(\text{cold})\}$
 $k_{\text{fast}} / k_{\text{slow}} = \exp\{-(E_a/R)(1/T(\text{hot}) - 1/T(\text{cold}))\}$
 $= \exp\{-(147000\text{Jmol}^{-1} / 8.3145 \text{ Jmol}^{-1}\text{K}^{-1}) * (1/298.15\text{K} - 1/237.15\text{K})\}$
 $= \exp\{17680 \text{ K} * (298.15\text{K} - 237.15\text{K}) / (298.15\text{K} * 237.15\text{K})\}$
 $= \exp\{15.25\} = 4 \times 10^6 \text{ times faster at the higher T}$
 $\rightarrow 4 \times 10^6 \text{ times slower at the lower T}$

14. Which of the following statements is/are **FALSE**?

Collision theory...

- (i) provides a rationale for the effect of temperature on rate.
- (ii) assumes the reaction rate depends on the frequency with which reactants collide.
- (iii) assumes that reactants must be in a correct orientation to react.
- (iv) assumes that only collisions with energies equal to or greater than the activation energy lead to products.
- (v) assumes the reaction rate depends on the kinetic energy distribution of the reacting molecules.

- (A) i
- (B) i, v
- (C) ii, iii
- (D) iv, v
- (E) None is false.

Collision theory explains the rate laws for elementary reactions, in terms of collision frequencies $\propto [A][B]$. It also explains the Arrhenius equation, $k = Ae^{-E_a/RT}$, which describes the temperature dependence of the rate constant. The collisions must have the correct orientation (accounted for in pre-exponential factor A) and sufficient kinetic energy (E_a) to lead to reaction. The kinetic energy distribution depends on temperature, according to the Boltzmann distribution ($e^{-E/RT}$).

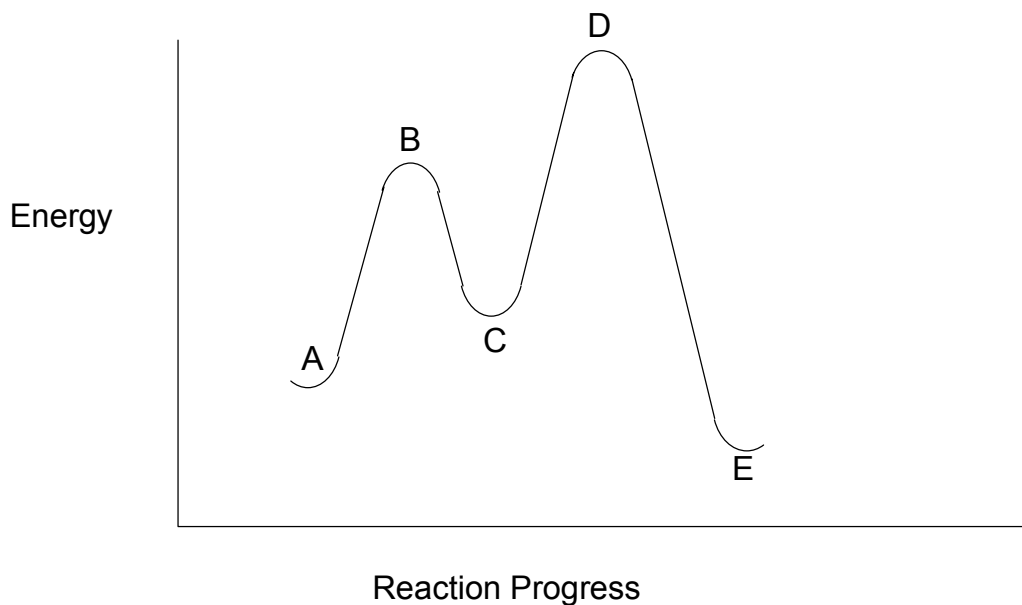
15. Which of the following statements comparing catalyzed and uncatalyzed reactions of the same chemical transformation at the same temperature is/are **FALSE**?

- (i) ΔH_{rxn} is the same for both reactions (with and without catalyst).
- (ii) The distributions of kinetic energies of the reactants (with and without catalyst) are different.
- (iii) The activation energies for the reactions (with and without catalyst) are different.
- (iv) The mechanisms of the reactions (with and without catalyst) are different.
- (v) Only exothermic reactions can be catalyzed.

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

Catalysts change the mechanism and lower the activation energy of both the forward and the reverse reaction. They cannot change the enthalpies of the products and reactants. The kinetic energy distribution depends only on temperature. If the forward reaction is exothermic then the reverse is endothermic. Both are catalysed.

16. With respect to the reaction progress diagram below, which of the following statements is/are **TRUE**?

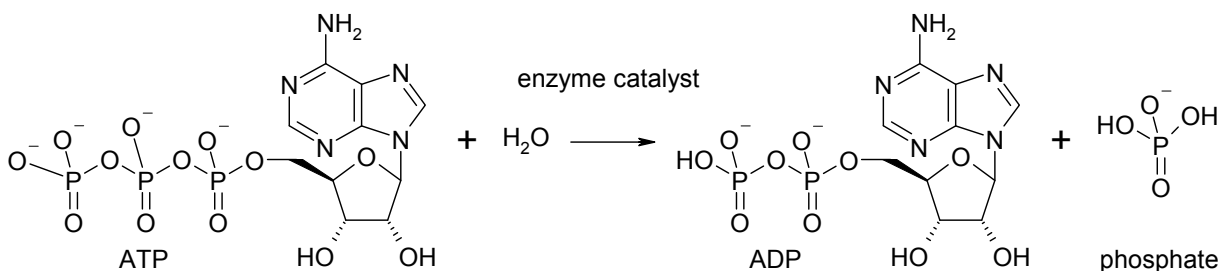


- (i) B, C and D represent transition states.
- (ii) The conversion of $E \rightarrow C$ is endothermic.
- (iii) The rate of the overall reaction does not depend on the energy difference between A and E.
- (iv) The activation energy for the overall reaction is represented by the energy difference from $C \rightarrow D$.

- (A) i, iii
- (B) ii, iii
- (C) ii, iv
- (D) iii, iv
- (E) all are true

B & D are transition states (local energy maxima), C is an intermediate (local minimum).
 C is higher in energy than E, so $E \rightarrow C$ is endothermic.
 The rate of reaction depends on the barrier height, not the reaction enthalpy (or energy).
 The overall activation energy is the energy difference between reactants (A) and the highest transition state (D).

17. Biological cells derive energy from the hydrolysis of adenosine triphosphate (ATP) to adenosine diphosphate (ADP), a reaction catalyzed by many enzymes. The activation energy of uncatalyzed ATP hydrolysis in water is 56.5 kJ mol^{-1} . By how much is the **transition state energy** of ATP hydrolysis **decreased** if an enzyme hydrolyzes ATP 1.0×10^4 times faster than the hydrolysis in water at 37°C ?



- (A) 2.8 kJ mol^{-1}
 (B) 24 kJ mol^{-1}
 (C) 33 kJ mol^{-1}
 (D) 57 kJ mol^{-1}
 (E) 80 kJ mol^{-1}

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

$$\text{Rate ratio} = k_{\text{fast}} / k_{\text{slow}} = Ae^{-E_a(\text{cat})/RT} / Ae^{-E_a(\text{uncat})/RT}$$

$$k_{\text{fast}} / k_{\text{slow}} = e^{-E_a(\text{cat})/RT} / e^{-E_a(\text{uncat})/RT}$$

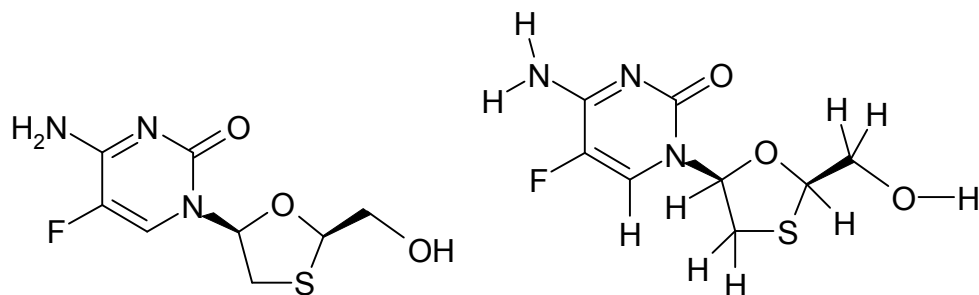
$$\ln(k_{\text{fast}} / k_{\text{slow}}) = -E_a(\text{cat})/RT + E_a(\text{uncat})/RT$$

$$\ln(1.0 \times 10^4) = \{E_a(\text{uncat}) - E_a(\text{cat})\} / (8.3145 \text{ J mol}^{-1} \text{ K}^{-1} * 310.15 \text{ K})$$

$$\{E_a(\text{uncat}) - E_a(\text{cat})\} = 9.21 * 2579 \text{ J/mol} = 23750 \text{ J/mol}$$

The energy difference is 24 kJ/mol .

18. Emtriva[®] is the brand name of emtricitabine, a synthetic drug used to treat HIV/AIDS. The structure of emtricitabine is shown below:



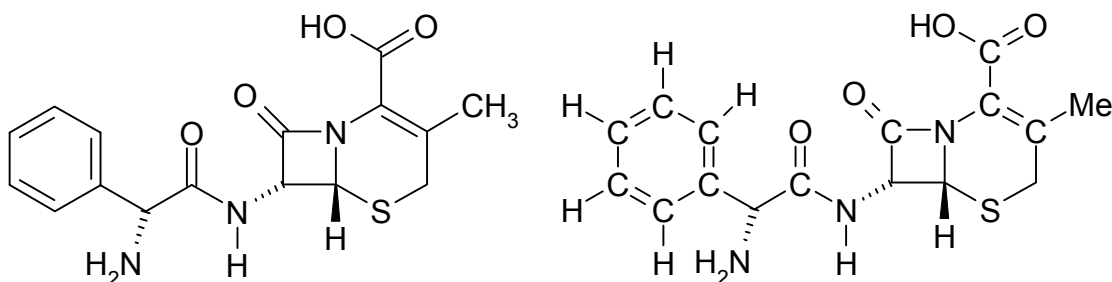
What are the total number of **sigma (σ) bonds** and the total number of **pi (π) bonds** in this molecule?

- (A) 17 sigma, 3 pi
 (B) 17 sigma, 6 pi
 (C) 20 sigma, 3 pi
 (D) 24 sigma, 6 pi
 (E) 27 sigma, 3 pi

Complete the structure.

Each single bond (24) is a sigma bond.
 Each double bond (3) is a sigma plus a pi bond.

19. Respiratory tract infections caused by *S. pneumoniae* or *S. pyogenes* can be treated with Keflex[®] (also called Cephalexin), whose structure is shown below:



How many **sp²-hybridized carbon atoms** are present in this molecule?

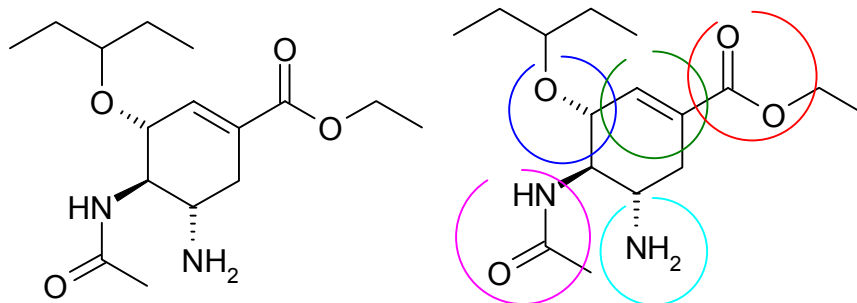
- (A) 6
 (B) 9
 (C) 10
 (D) 11
 (E) 12

Trigonal planar
 C atoms have 2
 single bonds and
 a double bond.

6 in the ring,
 3 carbonyls and
 2 in the alkene
 group = 11.

The other 5 carbon atoms are sp³ hybridized,
 having 4 single bonds. (CH bonds not shown).

20. If you came down with the flu this winter, your doctor might have prescribed Tamiflu[®]. The active ingredient is oseltamivir, whose structure is shown below.



This molecule contains several **functional groups**, including:

- (A) an alkene, an ether, a ketone, and a secondary amine.
- (B) an alkene, an ester, an amide, and a primary amine.
- (C) an alkyne, an ether, an aldehyde, and a secondary amine.
- (D) an alkene, a carboxylic acid, an amide, and a primary amine.
- (E) an ester, an ether, a secondary alcohol, and a secondary amine.

There are five functional groups in this molecule:
 Ether, alkene, ester, amide, primary amine.

Questions 21 through 25 are worth three (3) marks each.

21. A 1.00 L solution with pH = 3.70 has 0.810 M $\text{NaNO}_2(\text{aq})$ and a certain concentration of $\text{HNO}_2(\text{aq})$. How many **moles of $\text{HCl}(\text{g})$** must be added to change the pH of the solution by 0.24 pH units? Assume no volume change on the addition of $\text{HCl}(\text{g})$. (K_a for $\text{HNO}_2 = 7.1 \times 10^{-4}$)

- (A) 0.11 mol
(B) 0.17 mol
(C) 0.27 mol
(D) 0.34 mol
(E) 0.40 mol

Before addition of HCl , $[\text{NO}_2^-] = 0.810 \text{ M}$
 $\text{pH} = 3.70 \rightarrow [\text{H}^+] = 10^{-3.70} = 1.9953 \times 10^{-4} \text{ M}$
 $[\text{HNO}_2] = [\text{H}^+][\text{NO}_2^-] / K_a = 0.2276 \text{ M, since}$
 $[\text{HNO}_2] = (1.9953 \times 10^{-4})(0.810) / (7.1 \times 10^{-4})$

$\text{HCl} + \text{NO}_2^- \rightarrow \text{HNO}_2 + \text{Cl}^-$ Strong acid goes to completion.
 When y moles of HCl are added $[\text{HNO}_2]$ increases by y M,
 and $[\text{NO}_2^-]$ decreases by y M.

The pH decreases to $3.70 - 0.24 = 3.46$, $[\text{H}^+] = 10^{-3.46}$

After addition of HCl , $[\text{NO}_2^-] = 0.810 - y \text{ M}$, $[\text{HNO}_2] = 0.2276 + y \text{ M}$,
 $[\text{H}^+] = 3.467 \times 10^{-4}$. Using the small-x approximation (as above)
 $K_a = [\text{H}^+][\text{NO}_2^-] / [\text{HNO}_2] \rightarrow K_a / [\text{H}^+] = [\text{NO}_2^-] / [\text{HNO}_2]$

$(7.1 \times 10^{-4}) / (3.467 \times 10^{-4}) = (0.810 - y) / (0.2276 + y) = 2.048$
 $(0.810 - y) = (0.2276 + y) * (2.048) = 0.4660 + 2.048 y$
 $0.810 - 0.4660 = 2.048 y + y$
 $0.3440 = 3.048 y \rightarrow y = 0.3440 / 3.048 = 0.1128 = \text{moles of HCl added.}$

Can get the same results in each step by using
 $\text{pH} = \text{p}K_a + \log \{[\text{NO}_2^-] / [\text{HNO}_2]\}$,
 where $\text{p}K_a = -\log K_a$.

22. The half-life for the dissociation of digoxin, a potent heart drug, from heart muscle is 9.6 hours. Shortly after taking digoxin for the first time, the amount of digoxin bound to heart muscle in a patient reached a maximum amount of 0.12 μmole ; then the amount began to decrease slowly. Twenty-four hours later, the same patient took a second dose of digoxin. What will be the **maximum amount** of digoxin bound to heart muscle after the second dose? (Note 1 $\mu\text{mole} = 10^{-6}$ mole.)

- (A) 0.021 μmole
- (B) 0.12 μmole
- (C) 0.14 μmole
- (D) 0.17 μmole
- (E) 0.24 μmole

We assume that the new dose adds to whatever remains from the old dose. Find out what remains of first dose, then add 0.12 μmole .

$$[A]_t / [A]_0 = e^{-kt}, \text{ when } t = t_{1/2}$$

$$1/2 = e^{-k(t_{1/2})} \rightarrow \ln(1/2) = -kt_{1/2}$$

$$k = \ln(2) / t_{1/2} = 0.693 / 9.6 \text{ h} = 0.0722 \text{ h}^{-1}$$

After 24 hours:

$$[A]_t = [A]_0 e^{-kt} = (0.12 \mu\text{mole} / \text{volume}) * \exp(-0.0722 \text{ h}^{-1} * 24 \text{ h})$$

$$[A]_t = (0.12 \mu\text{mole} / V) * \exp(-1.733) = (0.12 \mu\text{mole} / V) * 0.1768$$

0.0212 μmole of the drug remain, then 0.12 μmole are added.

The maximum amount is then 0.14 μmole .

23. *Crime Scene Investigation – Hamilton (CSI-Hamilton)*: A forensics expert examined a body found in a Hamilton park 6.0 days after death and noted the extent of decomposition; assume that the outdoor temperature remained constant at 2°C throughout this 6.0 day period. The same expert while on vacation in a tropical country (assume a constant temperature of 24°C) was asked to examine another body found 2.5 days after death and noted that the extent of decomposition in the two bodies was identical. What is the **activation energy** for this decomposition?

- (A) 0.016 kJ mol⁻¹
- (B) 0.27 kJ mol⁻¹
- (C) 27 kJ mol⁻¹
- (D) 77 kJ mol⁻¹
- (E) 27,000 kJ mol⁻¹

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

Rate ratio = 1/time ratio

$$t_{\text{slow}} / t_{\text{fast}} = k_{\text{fast}} / k_{\text{slow}} = Ae^{-E_a/RT(\text{hot})} / Ae^{-E_a/RT(\text{cold})}$$

$$6 \text{ days} / 2.5 \text{ days} = \exp\{-E_a/RT(\text{hot}) - E_a/RT(\text{cold})\}$$

$$2.4 = \exp\{-(E_a/R) (1/T(\text{hot}) - 1/T(\text{cold}))\}$$

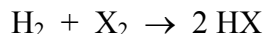
$$\ln(2.4) = -\{(E_a/8.3145 \text{ Jmol}^{-1}\text{K}^{-1}) * (1/297.15\text{K} - 1/275.15\text{K})\}$$

$$0.875 = (E_a/8.3145 \text{ Jmol}^{-1}\text{K}^{-1}) * (297.15\text{K} - 275.15\text{K}) / (297.15\text{K} * 275.15\text{K})$$

$$E_a = 0.875 * (8.3145 \text{ Jmol}^{-1}\text{K}^{-1}) * (297.15\text{K} * 275.15\text{K}) / 22 \text{ K}$$

$$E_a = 27_{052} \text{ J/mol} = 27 \text{ kJ/mol}$$

24. At least three possible mechanisms have been postulated for the reaction of hydrogen with halogens (halogens = X_2)



Which of the following statements about rate laws is/are **TRUE** regarding the proposed mechanisms below?

Mechanism 1) $H_2 + X_2 \rightarrow 2 HX$ slow

Mechanism 2) $X_2 \rightarrow X + X$ slow

$H_2 + X \rightarrow HX + H$ fast

$H + X \rightarrow HX$ fast

Mechanism 3) $X_2 \rightleftharpoons X + X$ fast

$H_2 + X \rightarrow HX + H$ slow

$H + X \rightarrow HX$ fast

- i) The rate law for mechanism 3 is $\text{Rate} = k [H_2][X_2]^{1/2}$.
- ii) The rate laws for mechanisms 1 and 2 are both second order overall.
- iii) If mechanism 2 is correct, increasing the concentration of $[H_2]$ will slow down the overall reaction rate.
- iv) Mechanism 2 is not possible because X is unstable and will reform X_2 faster than reacting with H_2 .
- v) The rate laws for mechanisms 2 and 3 are both first order in X_2 .

(A) i

(B) i, iii

(C) ii, iii, v

(D) ii, iv

(E) iv

Rate = Rate of slow step

Mechanism 1: $\text{Rate} = k [H_2][X_2]$ (2nd order)

Mechanism 2: $\text{Rate} = k_1[X_2]$ (1st order)

Independent of $[H_2]$

X is unstable and will reform X_2 faster than reacting with H_2 , but will *occasionally* react with H_2 , leading to the desired product. This is a possible mechanism.

Mechanism 3: $\text{Rate} = k_2 [H_2][X]$, but X is an intermediate,

replace with equilibrium value from first step:

$$K_1 = k_1 / k_{-1} = [X]^2 / [X_2] \rightarrow [X] = (K_1[X_2])^{1/2}$$

$$\text{Rate} = k_2 [H_2] (K_1[X_2])^{1/2} = k_{app} [H_2][X_2]^{1/2} \quad (1/2 \text{ order in } X_2)$$

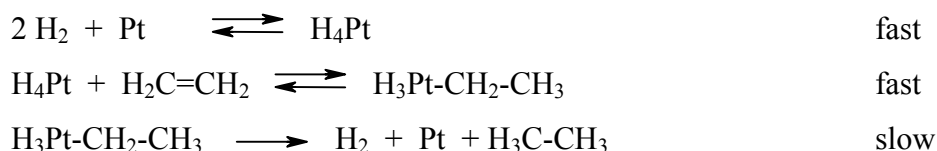
25. The addition of hydrogen to an alkene can be catalyzed by a soluble form of platinum (Pt). Two mechanisms have been proposed for the addition of hydrogen (H_2) to ethene ($\text{H}_2\text{C}=\text{CH}_2$). The rate law has the form: $\text{Rate} = k [\text{Pt}]^X [\text{H}_2]^Y [\text{H}_2\text{C}=\text{CH}_2]^Z$.

Identify the **exponents X, Y, Z for the two rate laws** consistent with these **two mechanisms**. You must match the correct order for **both** mechanisms.

MECHANISM I



MECHANISM II



	<u>MECHANISM I</u>				<u>MECHANISM II</u>		
	X	Y	Z		X	Y	Z
(A)	1	1	0		1	1	1
(B)	1	1	0		1	2	1
(C)	1	1	1		1	2	1
(D)	1	1	1		1	1	1
(E)	1/2	1	1		1	2	0

Both mechanisms require use of the pre-equilibrium approximation. (Twice in mech. II)

I) $K_1 = k_1 / k_{-1} = [\text{PtH}_2] / [\text{H}_2][\text{Pt}] \rightarrow [\text{PtH}_2] = K_1 [\text{H}_2][\text{Pt}]$

Rate = $k_2[\text{PtH}_2][\text{C}_2\text{H}_4] = k_2 K_1 [\text{H}_2][\text{Pt}][\text{C}_2\text{H}_4]$

Rate = $k_{\text{app}} [\text{Pt}][\text{H}_2][\text{C}_2\text{H}_4]$ (1, 1, 1)

II) $K_1 = k_1 / k_{-1} = [\text{H}_4\text{Pt}] / [\text{H}_2]^2 [\text{Pt}] \rightarrow [\text{H}_4\text{Pt}] = K_1 [\text{H}_2]^2 [\text{Pt}]$

$K_2 = k_2 / k_{-2} = [\text{H}_3\text{Pt}-\text{CH}_2-\text{CH}_3] / [\text{H}_4\text{Pt}] [\text{C}_2\text{H}_4] \rightarrow$

$[\text{H}_3\text{Pt}-\text{CH}_2-\text{CH}_3] = K_2 [\text{H}_4\text{Pt}] [\text{C}_2\text{H}_4] = K_2 (K_1 [\text{H}_2]^2 [\text{Pt}]) [\text{C}_2\text{H}_4]$

Rate = $k_3[\text{H}_3\text{Pt}-\text{CH}_2-\text{CH}_3] = k_3 (K_2 (K_1 [\text{H}_2]^2 [\text{Pt}]) [\text{C}_2\text{H}_4])$

Rate = $k_{\text{app}} [\text{Pt}][\text{H}_2]^2 [\text{C}_2\text{H}_4]$ (1, 2, 1)

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Data page

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

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

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

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

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

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

$$[A]_t = [A]_0 e^{-kt}$$

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

$$K_b(\text{NO}_2^-) = 1.4 \times 10^{-11}$$

$$K_a(\text{IOH}) = 2.3 \times 10^{-11}$$

$$K_b(\text{CN}^-) = 1.6 \times 10^{-5}$$

$$K_a(\text{C}_6\text{H}_5\text{COOH}) = 6.3 \times 10^{-5}$$

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

$$K_a(\text{HCOOH}) = 1.8 \times 10^{-4}$$

$$K_b(\text{CO}_3^{2-}) = 2.1 \times 10^{-4}$$

PERIODIC TABLE OF THE ELEMENTS															
ALDRICH®															
Transition Metals															
I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	I	II	III	IV
1 H 1.0079	2 He 4.0026	3 Li 6.941	4 Be 9.0122	5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180	11 Na 22.990	12 Mg 24.305	13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066
17 Cl 35.453	18 Ar 39.948	19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61
33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80	37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 105.42	47 Ag 107.87	48 Cd 112.41
49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29	55 Cs 132.91	56 Ba 137.33	57 *La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25
71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [222]
87 Fr [223]	88 Ra 226.03	89 *Ac 227.03	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]
103 Lr [262]	104 Unq [261]	105 Unp [262]	106 Unh [263]	107 Uuq [264]	108 Uuh [265]	109 Uuq [266]	110 Uuh [267]	111 Uuq [268]	112 Uuh [269]	113 Uuq [270]	114 Uuh [271]	115 Uuq [272]	116 Uuh [273]	117 Uuq [274]	118 Uuh [275]

Atomic weights are based on $^{12}\text{C} = 12$ and conform to the 1987 IUPAC report values rounded to 5 significant digits. Numbers in [] indicate the most stable isotope.

* Lanthanides

** Actinides

END OF TEST