CHEM 311 (141) **Second Major Exam** **2 HOURS**

Version 000

Thursday, December 11, 2014, 7:00-9:00 PM

Sec # 03: Dr. Khaled Sec# 02: Dr. Morsy Sec # 04: Dr. Foerner
Sec# 01: Dr. Oweimreen

Please give your section number below

STUDENT NAME: ______________________

STUDENTIDNUMBER: ______________________

STUDENTSECTIONNUMBER: ______________________

Number of Correct Answers	Your Score out of 100%

1. Find the correct choice: The Transition State in a reaction …

   [✓ A.] … must have at least one weak bond.

   B. … can have only strong bonds. would be stable molecule not TS

   C. … is a stable molecule. TS is not stable

   D. … is at a minimum of the potential energy diagram. maximum

   E. … is a stable intermediate. TS is not stable

2. In equilibrium,

   [✓ A.] forward and backward reaction rates are equal.

   B. all rates are zero. nonsense

   C. the backward reaction is faster than the forward reaction. nonsense

   D. forward and backward rates are almost equal. not almost, equal

   E. reactant concentrations are zero. nonsense

3. For the parallel reactions

   A → B rate constant k_1

   A → C rate constant $k_2 = 2.3\ k_1$

   A → D rate constant $k_3 = 4.0\ k_1$

   What is the yield of C?

   [✓ A.] 31.5%

   B. 13.7%

   C. 54.8%

   D. 45.2%

   E. 86.3%

$$\phi_C = \frac{k_2}{k_1+k_2+k_3}$$

$$= \frac{2.3k_1}{k_1+2.3k_1+4.0k_1}$$

$$= \frac{2,3}{7,3} = 0,31507$$

$$\hat{=}\ 31.5\%$$

$$k_1 = Ae^{-E_1/RT}$$

$$k_2 = Ae^{-E_2/RT}$$

4. Reactions 1 and 2 follow the Arrhenius law and have the same pre-exponential factor. If the activation energy of reaction no. 1 is 20 J/mol and that of reaction no. 2 is 200 J/mol, what is the ratio k_1/k_2 of their rate constants at 300K?

   [✓ A.] 1.075

   B. 0.930

   C. 1.083

   D. 0.922

   E. 1.037

$$\frac{k_1}{k_2} = e^{-(E_1-E_2)/RT} = e^{-(20-200)\frac{J}{mol}/RT}$$

$$= e^{180\frac{J}{mol}/(8,314\frac{J}{Kmol}\cdot 300K)}$$

$$= e^{180/2494,2} = e^{0,072167}$$

$$= 1,07483$$

$$= 1,075$$

formation of I consumption of I

$$\frac{d(I)}{dt} = 0 = k_1[A] - k_2(I)$$

5. For the reaction mechanism

   $A \rightarrow I$ rate constant k_1

   $I \rightarrow P$ rate constant k_2

   the steady state approximation yields

   [✓ A.] $k_1[A] - k_2[I] = 0$

   B. $k_1[A] + k_2[I] = 0$

   C. $k_1[A] = 0$

   D. $k_2[I] = 0$

   E. $d[P]/dt = k_2[I]$

6. In the mechanism,

(1) $2\,[N_2O_5 \rightleftarrows NO_2 + \underline{NO_3}]$ equilibirium

(2) $NO_2 + \underline{NO_3} \rightarrow NO + O_2 + NO_2$

(3) $NO + \underline{NO_3} \rightarrow 2\,NO_2$

for the decomposition of N_2O_5 into NO_2 and O_2,

[✓ (A)] both NO and NO_3 are intermediates.
(B) only NO is an intermediate.
(C) only NO_3 is an intermediate.
(D) only NO_3 is a catalyst.
(E) both NO and NO_3 are catalysts.

intermediate

$$R = \frac{d[C]}{dt} = k_3[A_3][B]$$

intermediate

$$SSA_1: \frac{d[A_3]}{dt} = 0 = k_2[A_2][A] - k_3[A_3][B]$$

$$SSA_2: \frac{d[A_2]}{dt} = 0 = k_1[A]^2 - k_{-1}[A_2] - k_2[A_2][A]$$

7. A possible mechanism for the reaction, $2A + B \rightarrow C + D$, is:

(1) $A + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A_2$ fast, equilibrium
(2) $A_2 + A \xrightarrow{k_2} A_3$ slow
(3) $A_3 + B \xrightarrow{k_3} A + C + D$ Fast

SSA_2:

$$[A_2] = \frac{k_1[A]^2}{k_{-1} + k_2[A]}$$

SSA_1:

$$[A_3] = \frac{k_2[A_2][A]}{k_3[B]}$$

$$[A_3][B] = \frac{k_2[A_2][A]}{k_3}$$

According to this mechanism, the rate law (rate of formation of one of the final products) will be (k is an effective rate constant k_{eff}):

$$[A_3] = \frac{k_1[A]^2[A]}{k_3(k_{-1} + k_2[A])[B]}$$

$$k_3[A_3][B] = \frac{k_1[A]^3 k_2}{k_3(k_{-1} + k_2[A])}$$ 4

$$= \frac{k_1 k_2}{\cdots}[A]^3$$ (2) slow ⇒ $k_2[A] \ll k_{-1}$ (fast)

[✓ (a)] Rate = $k[A]^3$ $\qquad k = \frac{k_1 k_2}{k_{-1}}$

(b) Rate = $k[A][B]$

(c) Rate = $k[A]^2[B]$

(d) Rate = $k[A]$

(e) Rate = $k[A]^2$ $\qquad R_{max} = \frac{1}{26.557}\ \frac{M}{s}$

Lineweaver - Burk:

$$\frac{1}{R_0} = \frac{1}{k_2[E]_0} + \frac{K_m}{k_2[E]_0}\frac{1}{[S]_0}$$

$$R_{max} = k_2[E]_0$$

$$= \frac{1}{R_{max}} + \frac{K_m}{R_{max}}\frac{1}{[S]_0}$$

8. The decomposition of hydrogen peroxide (substrate S) is catalyzed by the enzyme catalase (E). At an initial catalase concentration of $3.5 \times 10^{-9}\ M$ the variation of $1/R_0$ (the reciprocal of the initial rate) with $1/[S]_0$, the reciprocal of the initial concentration of the substrate S is given by (Lineweaver-Burk equation), $R_{max} = 0.03765\ \frac{M}{s}$

$$\mathbf{(1/R_0) = 0.6977\ s\ (1/[S]_0) + 26.557\ s/M} \qquad = 3.77\cdot 10^{-2}\ \frac{M}{s}$$

Based on this experimental result which one of the following choices is correct? (from left to right: maximum rate R_{max} in M/s, Michaelis constant K_m in M, and the turnover number k_2 in 1/s)

[✓ A] 3.77×10^{-2} ✓, 2.63×10^{-2} ✓, 1.08×10^{7} ✓

B $\quad 0.6977,\ 26.557,\ 1.99\times10^{8}$

C $\quad 2.63\times10^{-2}$, 3.77×10^{-2}, 7.51×10^{6}

D $\quad 26.557,\ 0.6977,\ 7.59\times10^{6}$

E $\quad 3.77\times10^{-2}$, 2.63×10^{-2}, 7.51×10^{7}

$$K_m = R_{max}\cdot 0.6977\ s$$
$$= 0.03765\ \frac{M}{s}\cdot 0.6977\ s$$
$$= 0.02627\ M = 2.63\cdot10^{-2}\ M$$
$$R_{max} = k_2[E]_0$$
$$k_2 = \frac{0.03765\ \frac{M}{s}}{3.5\cdot10^{-9}\ M}$$
$$= 1.0757\cdot10^{7}\ s^{-1}$$
$$= 1.08\cdot10^{7}\ s^{-1}$$

9. The adsorption of Kr on charcoal at 193.5 K, closely follows the Langmuir adsorption isotherm and in turn the linear relation, $\quad \theta = \frac{V_{ads}}{V_m} = \frac{KP}{1+KP}$

$$\mathbf{(1/V_{ads}) = 0.03258\ g/cm^3 + 0.34076\ (torr\ g/cm^3) \times (1/P)}$$

$$\frac{1}{V_{ads}} = \frac{1}{V_m K}\frac{1}{P} + \frac{1}{V_m}$$

where V_{ads} $(in\ cm^3\ g^{-1})$ is the volume of Kr adsorbed per gram charcoal at the equilibrium Kr pressure $P\,(in\ torr)$. $\quad V_m = \frac{1}{0.03258}\ \frac{cm^3}{g} = 30.69\ \frac{cm^3}{g}$

Which one of the following choices is correct (from left to right: volume of Ar needed to form a monolayer per gram charcoal, V_m, and the adsorption equilibrium constant K at 193.5 K)? $\quad = 30.7\ \frac{cm^3}{g}$

1 $\quad$ 1 (in torr^{-1})

$$K = \frac{1}{0.34076\ \frac{torr\ g}{cm^3}\cdot 30.69\ \frac{cm^3}{g}} = 0.09562\ \frac{1}{torr}$$
$$= 9.56\cdot10^{-2}\ torr^{-1}$$

✓ ✓

[✓ (A)] 30.7, 9.56×10^{-2}

(B) 30.7, 2.93

(C) 2.93, 30.7

(D) 28.7, 0.341

(E) 9.56×10^{-2}, 28.7

10. The mechanism suggested for the reaction,

$$2\,A + B \rightarrow 2\,C$$

is,

$A + A \rightleftarrows I$ forward rate constant k_1, backward rate constant k_{-1}

$I + B \rightarrow 2\,C$ rate constant k_2

The rate law obtained on applying the steady state approximation is,

intermediate ↓

$$R = \frac{1}{2}\frac{d[C]}{dt} = k_2[I][B]$$

$$\text{SSA:}\quad \frac{d[I]}{dt} = k_1[A]^2 - k_{-1}[I] - k_2[I][B] = 0$$

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

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

[✓ (A)] Rate = $k_1k_2[A]^2[B]/(k_{-1} + k_2[B])$

(B) Rate = $k_1k_2[A]^2/(k_{-1} + k_2[B])$

(C) Rate = $k_1k_2[A]^2[B]$

(D) Rate = $k_1k_2[A]^2[B]/(k_1 + k_2[B])$

(E) Rate = $k_1k_2[A][B]$

11. Using the following graphs, which one shows the rate of change of H_2O_2 with time (assume the reaction to be an elementary one)?

$$2\,H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

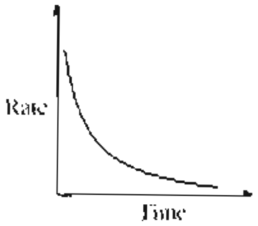
$$R = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = k[H_2O_2]^2$$

H_2O_2 is reactant and thus decreases with time

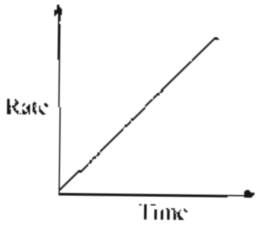
⇒ also R must decrease with time

only the case in A

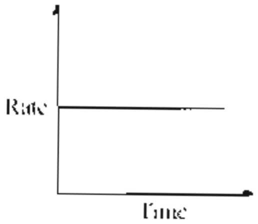
[✓ A]



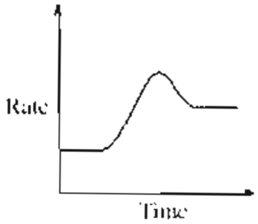
B



C



D.



12. Consider the following reaction:

$$\frac{1}{4}\frac{d(H_2O)}{dt} = \frac{d[C_2H_8)}{dt}$$

$$C_2H_{8(g)} + 4O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(g)}$$

If 1.0 mol C_2H_8 is consumed in 4.0 minutes, the rate of production of H_2O in mol/min is

$$\frac{\Delta[C_2H_8]}{\Delta t} = \frac{1.0}{4} \text{ mol/min}$$

$$\Rightarrow \frac{d(H_2O)}{dt} = 4 \cdot \frac{1.0}{4} \text{ mol/min}$$

$$= 1.0 \text{ mol/min}$$

[✓ A.] 1.0
B. 4.0
C. 0.25
D. 4.0
E. 8.0

$$\int \frac{dx}{x^2} = -\frac{1}{x} + C$$

13.A second order reaction with initial reactant concentration of 0.80 M has a rate constant of 0.05 $M^{-1}s^{-1}$. How long it will take in seconds for the reactant to lose 50% of the initial concentration?

$$-\frac{d(A)}{dt} = k[A]^2_t$$

$$-\int_{(A)_0}^{(A)} \frac{d(A)}{(A)^2} = \frac{1}{(A)} - \frac{1}{(A)_0} = k\int_0^t dt = kt$$

$$kt = \frac{1}{\frac{1}{2}(A)_0} - \frac{1}{(A)_0} = \frac{2}{(A)_0} - \frac{1}{(A)_0} = \frac{1}{(A)_0}$$

$$t = \frac{1}{k(A)_0} = \frac{1}{0.05\frac{1}{Ms} \cdot 0.80 M} = 25 s$$

[✓ A.] 25

B. 50

C. 10

D. 125

E. 8

14. Consider the following reaction: $\frac{1}{2}\frac{\Delta(B)}{\Delta t} = -\frac{1}{3}\frac{\Delta(A)}{\Delta t}$

3A → 2B $\frac{\Delta[B)}{\Delta t} = \frac{2}{3}\left(-\frac{\Delta(A)}{\Delta t}\right)$

The relationship of the rate of appearance of B and the rate of disappearance of A is: $(\Delta[B]/\Delta t) = C \times \{-\Delta[A]/\Delta t)$. The factor C is

[✓ A.] +0.667 $C = \frac{2}{3} = 0{,}667$
B. -2/3
C. +0.334
D. +1
E. +3/2

15. Determine the rate expression for the following reaction:

$2MnO_4^-(aq) + 6H^+(aq) + 5ClO_3^-(aq) \rightarrow 2Mn^{2+}(aq) + 3H_2O(l) + 5ClO_4^-(aq)$

	$[MnO_4^-]$/M	$[ClO_3^-]$/M	$[H^+]$/M	Initial Rate Ms^{-1}
1	0.10	0,10	0.10	5.2x10-3
2	0.25	0.10	0.10	3.3x10-2
3	0.10	0.30	0.10	1.6x10-2
4	0.10	0.10	0.20	7.4x10-3

[✓ A.] $k[MnO_4^-]^2[ClO_3^-][H^+]^{1/2}$

B. $k[MnO_4^-][ClO_3^-]^{1/2}[H^+]^2$

C. $k[MnO_4^-]^{1/2}[ClO_3^-][H^+]^2$

D. $k[MnO_4^-][ClO_3^-][H^+]^2$

E. $k[MnO_4^-]^2[H^+]^{1/2}$

please turn page

16. The mechanism of the chain reaction $C_2H_6 \rightarrow C_2H_4 + H_2$ is:

$$C_2H_6 \xrightarrow{k_1} \underline{2CH_3} \quad CH_3^\bullet$$

$$C_2H_6 + \overline{CH_3} \xrightarrow{k_2} \boxed{C_2H_5} + CH_4 \quad C_2H_5^\bullet$$

$$\boxed{C_2H_5} \xrightarrow{k_3} C_2H_4 + \textcircled{H}$$

$H^\bullet$

$$C_2H_6 + \textcircled{H} \xrightarrow{k_4} C_2H_5 + H_2$$

$$\boxed{2C_2H_5} \xrightarrow{k_5} C_4H_{10}$$

The reactive intermediates of the mechanism are the species:

Q 15 $\quad R = k[MnO_4^-]^m [ClO_3^-]^n [H^+]^k$

$$\frac{R_1}{R_2} = \left(\frac{[MnO_4^-]_1}{[MnO_4^-]_2}\right)^m \quad [ClO_3^-]_1 = [ClO_3^-]_2,\ [H^+]_1 = [H^+]_2 \text{ and cancel}$$

$$\frac{R_1}{R_2} = \frac{5.2}{33} = 0.1576 = \left(\frac{0.10}{0.25}\right)^m = (0.4)^m$$

$$\ln\frac{R_1}{R_2} = m \ln 0.4,\quad m = \frac{\ln 0.1576}{\ln 0.4} = \frac{-1.8477}{-0.9163}$$

$$m = 2.016 = 2$$

$$\frac{R_1}{R_3} = \left(\frac{[ClO_3^-]_1}{[ClO_3^-]_3}\right)^n \quad [MnO_4^-]_1 = [MnO_4^-]_3,\ [H^+]_1 = [H^+]_3 \text{ and cancel}$$

$$\frac{R_1}{R_3} = \frac{5.2}{16} = 0.325 = \left(\frac{0.1}{0.3}\right)^n = \left(\frac{1}{3}\right)^n$$

$$\ln\frac{R_1}{R_2} = n \ln\frac{1}{3} \qquad n = \frac{\ln 0.325}{\ln\frac{1}{3}} = \frac{-1.1239}{-1.0986} = 1.023$$
$$= 1$$

$$\frac{R_1}{R_4} = \left(\frac{[H^+]_1}{[H^+]_4}\right)^k \quad [MnO_4^-]_1 = [MnO_4^-]_4,\ [ClO_3^-]_1 = [ClO_3^-]_4 \text{ and cancel}$$

$$\frac{R_1}{R_4} = \frac{5.2}{7.4} = 0.7027 = \left(\frac{0.10}{0.20}\right)^k = \left(\frac{1}{2}\right)^k$$

$$\ln\frac{R_1}{R_4} = k \ln\frac{1}{2} \qquad k_0 = \frac{\ln 0.7027}{\ln 1/2} = \frac{-0.3528}{-0.69315} = 0.509$$
$$= 1/2$$

$$\rightarrow R = k[MnO_4^-]^2 [ClO_3^-][H^+]^{1/2}$$

[✓ A)] H, CH_3 and C_2H_5
B) H, CH_4 and C_4H_{10}
C) H, CH_3 and C_4H_{10}
D) CH_3, CH_4 and C_2H_5
E) H, CH_4 and C_2H_5

17. The gas-phase chain mechanism of the reaction $Cl_2 + CH_4 \rightarrow CH_3Cl +$ $+HCl$ is:

$$\begin{aligned} Cl_2 &\xrightarrow{k_1} 2Cl \\ Cl + CH_4 &\xrightarrow{k_2} HCl + CH_3 \\ Cl_2 + CH_3 &\xrightarrow{k_3} CH_3Cl + Cl \\ 2Cl &\xrightarrow{k_{-1}} Cl_2 \end{aligned}$$

turn page

$R = \frac{d[HCl]}{dt} = k_2[Cl][CH_4]$

$SSA_1: \frac{d[Cl]}{dt} = 0 = 2k_1[Cl_2] - k_2[Cl][CH_4] + k_3[CH_3][Cl_2] - k[Cl]^2 \; 2$

$SSA_2: \frac{d[CH_3]}{dt} =$

The overall rate of reaction in terms of the rate of formation of HCl is(k_{eff}: is an effective rate constant)

[✓ A)] $k_{eff}[Cl_2]^{1/2}[CH_4]$
B) $k_{eff}[Cl_2][CH_4]^{1/2}$
C) $k_{eff}[Cl_2]^{1/2}[CH_3Cl]$
D) $k_{eff}[Cl_2][CH_3Cl]^{1/2}$
E) $[CH_4][CH_3Cl]$

18. If $\tau_f = 1 \times 10^{-10}$ s and $k_{ic} = 5 \times 10^8\ s^{-1}$, what is Φ_f? Assume that the rate constants for intersystem crossing and quenching are sufficiently small that these processes can be neglected.

$\phi_f = k_f \tau_f$

[✓ A)] 0.95

B) 0.81

C) 0.62

D) 0.27

E) 0.77

$\tau_f = \frac{1}{k_f + k_{ic}}$ $\quad k_{isc}$, $k_q[Q]$ neglected

$\frac{1}{\tau_f} = k_f + k_{ic}$, $\quad k_f = \frac{1}{\tau_f} - k_{ic}$

$= 1\cdot10^{10}s^{-1} - 5\cdot10^{8}s^{-1}$

$= 9.5\cdot10^{9}s^{-1}$

$\phi_f = k_f\tau_f = 9.5\cdot10^{9}s^{-1}\cdot 1\cdot10^{-10}s = 0.95$

19. The chlorination reaction of ethane ($Cl_2 + H_3CCH_3 \rightarrow ClH_2CCH_2Cl + H_2$) processes via a chain reaction mechanism. Which one of the following is not a chain propagation reaction in the chlorination of ethane?

[✓ A)] $Cl + Cl \longrightarrow Cl_2$ stable molecule, no propagation
B) $Cl + H_3CCH_3 \longrightarrow ClH_2CCH_3 + H$ $H\cdot$, propagation
C) $Cl + H_3CCH_3 \longrightarrow H_3CCH_2 + HCl$ $C_2H_5\cdot$, propagation
D) $H + Cl_2 \longrightarrow HCl + Cl$ $Cl\cdot$
E) $Cl_2 + H_2CCH_3 \longrightarrow ClH_2CCH_3 + Cl$ $Cl\cdot$ } propagation

Q1:

$$R = \frac{d[HCl]}{dt} = k_2[Cl][CH_4]$$

$$SSA_1: \frac{d[Cl]}{dt} = 0 = 2k_1[Cl_2] \underline{- k_2[Cl][CH_4]} \boxed{+ k_3[Cl_2][CH_3]} - k_{-1}[Cl]^2$$

$$SSA_2: \frac{d[CH_3]}{dt} = 0 = \underline{+k_2[Cl][CH_4]} \boxed{- k_3[Cl_2][CH_3]}$$

$$SSA_1 + SSA_2: \quad 0 = 2k_1[Cl_2] - k_{-1}[Cl]^2$$

$$[Cl]^{\cancel{2}} = \sqrt{2\frac{k_1}{k_{-1}}}\sqrt{[Cl_2]}$$

$$R = \sqrt{2\frac{k_1}{k_{-1}}}\, k_2 [Cl_2]^{1/2}[CH_4]$$

$$k_{eff} = k_2\sqrt{\frac{2k_1}{k_{-1}}}$$

20. A reactant can be photo-chemically converted to a cis-product. In an experiment, 4.15 mmol of reactant are converted when irradiated with 100. W of 280. nm light for 27.0 s. All of the light is absorbed by the sample. What is the overall quantum yield for this photochemical process? $P = 100.\ W = 100.\ VA = 100.\ \frac{VAs}{s} = 100.\ J/s$

[✓ a)] 0.66

b) 0.40

c) 0.10

d) 0.78

e) 0.21

$$E_{light} = 100.\ \frac{J}{s} \cdot 27,0\ s = 2700\ J$$

$$E_{Phot} = h\nu = \frac{hc}{\lambda} = \frac{6,626 \cdot 10^{-34}\ Js \cdot 2,998 \cdot 10^{8}\ \frac{m}{s}}{280. \cdot 10^{-9}\ m}$$

$$= 7,0946 \cdot 10^{-19}\ J$$

$$N_{Phot} = \frac{E_{light}}{E_{Phot}} = \frac{2700\ J}{7,0946 \cdot 10^{-19}\ J} = 3,8057 \cdot 10^{21}$$

$$n_{Phot} = \frac{N_{Phot}}{N_A} = \frac{3,8057 \cdot 10^{21}}{6,022 \cdot 10^{23}\ mol^{-1}} = 6,3197 \cdot 10^{-3}\ mol$$

$$= 6,3197\ mmol$$

$$\phi = \frac{n_{molecules}}{n_{Phot}} = \frac{4.15}{6,3197} = 0,6567$$

$$= 0,66$$

CHEM 311 (141) **Second Major Exam** **2 HOURS**
Thursday, December 11, 2014, 7:00-9:00 PM

STUDENT NAME: ....

STUDENT ID NUMBER: ....

Test Code (001)

(20 Questions)

Dr. Mazen Khaled	Section 1
Dr. Mohamed Morsy	Section 2
Dr. G. Oweimreen	Section 3
Dr. W. Foerner	Section 4

Physical constants, conversion factors, and useful equations

Physical Constants

R = 8.314 J mol^{-1} K^{-1}
= 0.08206 L atmK^{-1} mol^{-1}
= 0.08314 L bar K^{-1} mol^{-1}

N_A = 6.022 x 10^{23} mol^{-1}

k_B = 1.381 x 10^{-23} J K^{-1}

h = 6.626 x 10^{-34} J s

F = 96,500 C mol^{-1}

c = 2.998 x 10^{8} m s^{-1}

g = 9.81 m s^{-2}

B = 0.51mol$^{-1/2}$dm$^{3/2}$
(in H_2O. 25°C)

Sequential reactions:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$[B]=(k_1/(k_2-k_{-1}))\, f(t)[A]_0$

$f(t)=\exp(-k_1t)-\exp(-k_2t)$

Parallel reactions:

$\Phi_i = k_i/S$

Where S is the sum of all rate constants of the paral-lel reactions

Other Units

1dm^3 = 1 L

1dm^3 = 1000 cm^3

1 J = 1 kg m^2 s^{-2}

1 atm = 1.101325 x 10^5 Pa

1 atm = 760 mmHg

1 Torr = 1 mmHg

1 Torr = 133.322 Pa

1 bar = 10^5 Pa

1 nm = 10^{-9} m

Eyring equation:

$k = k_BT/(hc^0) \times f$

$f = \exp(\Delta S^{\#}/R) \times$

$\times \exp(-\Delta H^{\#}/RT)$

$\ln(1 - \theta) = -\theta$
if $\theta << 1$

Important Equations

$E = h\nu$

$c = \nu\lambda$

$PV = nRT$

$\Delta G = \Delta H - T\Delta S$

$k = A e^{E_a/RT}$

$$k = \frac{k_BT}{h} e^{-\Delta^{\ddagger}G/RT}$$

$A = e\,(k_BT/h) \exp(\Delta^{\ddagger}S/R)$

$$k = \frac{k_BT}{h} e^{-\Delta^{\ddagger}G/RT}$$

$E_a = \Delta^{\ne}H^o - P\Delta^{\ne}V^o + RT$ (sol)
$= \Delta^{\ne}H^o - \Sigma\nu RT + RT$ (gas)

$\log k = \log k_o + 1.02\, z_Az_B \sqrt{I}$

$$\log k = \log k_o - \frac{\Delta^{\ne}V}{RT} P$$

$\Delta G^o = -RT \ln K_c$

$$\upsilon = \frac{V[S]}{K_m + [S]}$$

$$V = k_2[E]_0 \text{ and } K_m = \frac{k_{-1} + k_2}{k_1}$$

$\theta = KP/(1 + KP)$, at T=const

$t_f = (k_f + k_q[Q])^{-1}$, Q is quencher

Note:
Quantum yield/efficiency = Φ = moles of product formed / moles of photons absorbed

From the Michaelis-Menten kinetics

$R_o = R_{max}[S]_o(K_m + [S]_o)$, $R_{max} = k_2[E]_o$

The Lineweaver-Burk equation is obtained by taking the inverse

1. Consider the following reaction:

$$3A \rightarrow 2B$$

The relationship of the rate of appearance of B and the rate of disappearance of A is:

$$(\Delta[B]/\Delta t) = C \times \{- \Delta[A]/\Delta t)\}$$

The factor C is

A) +0.667

B) +1

C) +0.334

D) +3/2

E) -2/3

2. For the parallel reactions

$A \rightarrow B$ rate constant k_1

$A \rightarrow C$ rate constant $k_2 = 2.3\ k_1$

$A \rightarrow D$ rate constant $k_3 = 4.0\ k_1$

What is the yield of C?

A) 31.5%

B) 13.7%

C) 45.2%

D) 86.3%

E) 54.8%

3. The chlorination reaction of ethane ($Cl_2 + H_3CCH_3 \Diamond ClH_2CCH_2Cl + H_2$) processes via a chain reaction mechanism. Which one of the following is not a chain propagation reaction in the chlorination of ethane?

A) $Cl + H_3CCH_3 \longrightarrow H_3CCH_2 + HCl$

B) $H + Cl_2 \longrightarrow HCl + Cl$

C) $Cl + H_3CCH_3 \longrightarrow ClH_2CCH_3 + H$

D) $Cl_2 + H_2CCH_3 \longrightarrow ClH_2CCH_3 + Cl$

E) $Cl + Cl \longrightarrow Cl_2$

4. The mechanism suggested for the reaction,

$$2\,A + B \rightarrow 2\,C$$

is,

$A + A \rightleftharpoons I$ forward rate constant k_1, backward rate constant k_{-1}

$I + B \rightarrow 2\,C$ constant k_2

The rate law obtained on applying the steady state approximation is,

A) Rate = $k_1k_2[A]^2[B]$
B) Rate = $k_1k_2[A]^2[B]/(k_{-1} + k_2[B])$
C) Rate = $k_1k_2[A][B]$
D) Rate = $k_1k_2[A]^2/(k_{-1} + k_2[B])$
E) Rate = $k_1k_2[A]^2[B]/(k_1 + k_2[B])$

5. The mechanism of the chain reaction $C_2H_6 \rightarrow C_2H_4 + H_2$ is:

$$C_2H_6 \xrightarrow{k_1} 2CH_3$$

$$C_2H_6 + CH_3 \xrightarrow{k_2} C_2H_5 + CH_4$$

$$C_2H_5 \xrightarrow{k_3} C_2H_4 + H$$

$$C_2H_6 + H \xrightarrow{k_4} C_2H_5 + H_2$$

$$2C_2H_5 \xrightarrow{k_5} C_4H_{10}$$

The reactive intermediates of the mechanism are the species:

A) CH_3, CH_4 and C_2H_5
B) H, CH_4 and C_2H_5
C) H, CH_3 and C_2H_5
D) H, CH_4 and C_4H_{10}
E) H, CH_3 and C_4H_{10}

6. For the reaction mechanism

$$\begin{array}{ll} A \rightarrow I & \text{rate constant } k_1 \\ I \rightarrow P & \text{rate constant } k_2 \end{array}$$

the steady state approximation yields

A) $k_1[A] - k_2[I] = 0$
B) $k_2[I] = 0$
C) $k_1[A] = 0$
D) $d[P]/dt = k_2[I]$
E) $k_1[A] + k_2[I] = 0$

7. If $\tau_f = 1 \times 10^{-10}$ s and $k_{ic} = 5 \times 10^{8}\ s^{-1}$, what is Φ_f? Assume that the rate constants for intersystem crossing and quenching are sufficiently small that these processes can be neglected.

A) 0.27
B) 0.81
C) 0.77
D) 0.95
E) 0.62

8. The adsorption of Kr on charcoal at 193.5 K, closely follows the Langmuir adsorption isotherm and in turn the linear relation,

$$(1/V_{ads}) = 0.34076\ (torr\ g/cm^3) \times (1/P) + 0.03258\ g/cm^3$$

where V_{ads} $(in\ cm^3\ g^{-1})$ is the volume of Kr adsorbed per gram charcoal at the equilibrium Kr pressure, $P(in\ torr)$. Which one of the following choices is correct (left to right: Volume of Ar needed to form a monolayer per gram charcoal, V_m, and the adsorption equilibrium constant K in $torr^{-1}$ at 193.5 K)?

A) 30.7, 9.56×10^{-2}

B) 2.93, 30.7
C) 28.7, 0.341
D) 30.7, 2.93
E) 9.56×10^{-2}, 28.7

9. Find the correct choice: The Transition State in a reaction …
   A) … is a stable intermediate.
   B) … is a stable molecule.
   C) … must have at least one weak bond.
   D) … can have only strong bonds.
   E) … is at a minimum of the potential energy diagram.

10. At equilibrium,
   A) reactant concentrations are zero.
   B) forward and backward reaction rates are equal.
   C) forward and backward rates are not equal.
   D) all rates are zero.
   E) the backward reaction is faster than the forward reaction.

11. A possible mechanism for the reaction, $2A + B \longrightarrow C + D$, is:

$A + A \rightleftharpoons A_2$ fast, equilibrium
$A_2 + A \longrightarrow A_3$ slow
$A_3 + B \longrightarrow A + C + D$ Fast

According to this mechanism, the rate law (rate of formation of one of the final products) will be (k is an effective rate constant k_{eff}):
   A) Rate = $k[A][B]$
   B) Rate = $k[A]^3$
   C) Rate = $k[A]^2$
   D) Rate = $k[A]$
   E) Rate = $k[A]^2[B]$

12. Determine the rate expression for the following reaction:

$$2MnO_4^-{}_{(aq)} + 6H^+{}_{(aq)} + 5ClO_3^-{}_{(aq)} \rightarrow 2Mn^{2+}{}_{(aq)} + 3H_2O_{(l)} + 5ClO_4^-{}_{(aq)}$$

$[MnO_4^-]/M$	$[ClO_3^-]/M$	$[H^+]/M$	Initial Rate Ms^{-1}
0.10	0.10	0.10	5.2x10-3
0.25	0.10	0.10	3.3x10-2
0.10	0.30	0.10	1.6x10-2
0.10	0.10	0.20	7.4x10-3

A) $k[MnO_4^-]^2[H^+]^{1/2}$
B) $k[MnO_4^-]^2[ClO_3^-][H^+]^{1/2}$
C) $k[MnO_4^-][ClO_3^-][H^+]^2$
D) $k[MnO_4^-][ClO_3^-]^{1/2}[H^+]^2$
E) $k[MnO_4^-]^{1/2}[ClO_3^-][H^+]^2$

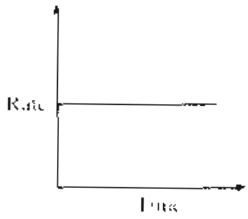
13. Two reactions follow the Arrhenius law and have the same pre-exponential factor. If the activation energy of reaction (1) is 20 *J/mol* and that of reaction (2) is 200 *J/mol*, what would be their rate constant ratio (k_1/k_2) at 300*K*?
A) 1.083
B) 1.075
C) 0.930
D) 0.922
E) 1.037

14. A second order reaction with initial reactant concentration of 0.80 M has a rate constant of 0.05 $M^{-1}s^{-1}$. How long will it take in seconds for the reactant to lose 50% of the initial concentration?
A) 8
B) 10
C) 125
D) 25
E) 50

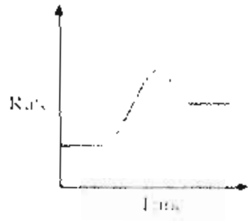
15. Using the following graphs, which one shows the rate of change of H_2O_2 with time (assume the reaction to be an elementary one)?

$$2\,H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

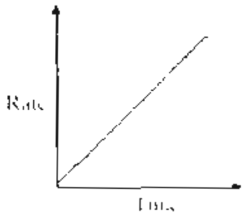
A)



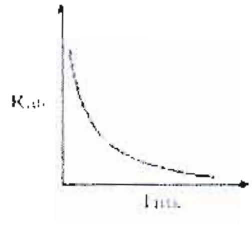
B)



C)



D)



16. A reactant can be photo-chemically converted to a cis-product. In an experiment, 4.15 *mmol* of reactant are converted when irradiated with 100. W of 280. *nm* light for 27.0 *s*. All of the light is absorbed by the sample. What is the overall quantum yield for this photochemical process?
A) 0.40
B) 0.10
C) 0.78
D) 0.21
E) 0.66

17. In the mechanism,

(1) $2\{ N_2O_5 \rightleftharpoons NO_2 + NO_3\}$ equilibrium
(2) $NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$
(3) $NO + NO_3 \rightarrow 2\ NO_2$

for the decomposition of N_2O_5 into NO_2 and O_2,

A) only NO_3 is an intermediate.
B) only NO_3 is a catalyst.
C) only NO is an intermediate.
D) both NO and NO_3 are catalysts
E) both NO and NO_3 are intermediates.

18. The decomposition of hydrogen peroxide (substrate S) is catalyzed by the enzyme catalase (E). At an initial catalase concentration $[S_o]$ of $3.5 \times 10^{-9}\ M$ the variation of $1/R$ (the reciprocal of the initial rate) with $1/[S]$ (the reciprocal of the initial concentration of the substrate) is given by (Lineweaver-Burk equation),

$$(1/R_0) = 0.6977\ s\,(1/[S]_0) + 26.557\ s/M$$

based on this experimental result, which one of the following choices is correct? (left to right: Maximum rate R_{max} in M/s, Michaelis constant K_m in M, and the turnover number k_2 in $1/s$)

A) 2.63×10^{-2}, 3.77×10^{-2}, 7.51×10^{6}
B) 3.77×10^{-2}, 2.63×10^{-2}, 7.51×10^{6}

C) 26.557, 0.6977, 1.08×10^{7}

D) 3.77×10^{-2}, 2.63×10^{-2}, 1.08×10^{7}
E) 0.6977, 26.557, 1.08×10^{7}

19. The gas-phase chain mechanism of the reaction $Cl_2 + CH_4 \rightarrow CH_3Cl +$ +HCl is:

$$Cl_2 \xrightarrow{k_1} 2Cl$$

$$Cl + CH_4 \xrightarrow{k_2} HCl + CH_3$$

$$Cl_2 + CH_3 \xrightarrow{k_3} CH_3Cl + Cl$$

$$2Cl \xrightarrow{k_{-1}} Cl_2$$

The overall rate of reaction in terms of the rate of formation of HCl is (k_{eff} is an effective rate constant)

A) $k_{eff}[Cl_2]^{1/2}[CH_4]$
B) $k_{eff}[CH_4][CH_3Cl]$
C) $k_{eff}[Cl_2][CH_3Cl]^{1/2}$
D) $k_{eff}[Cl_2]^{1/2}[CH_3Cl]$
E) $k_{eff}[Cl_2][CH_4]^{1/2}$

20. Consider the following reaction:

$$C_2H_{8(g)} + 4O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(g)}$$

If 1.0 *mol* C_2H_8 is consumed in 4.0 *min*, the rate of H_2O production in *mol/min* is

A) 8.0
B) 4.0
C) 0.25
D) 4.0
E) 1.0

Answer Key

1. A
2. A
3. E
4. B
5. C
6. A
7. D
8. A
9. C
10. B
11. B
12. B
13. B
14. D
15. D
16. E
17. E
18. D
19. A
20. E

CHEM 311 (141) **Second Major Exam** **2 HOURS**
Thursday, December 11, 2014, 7:00-9:00 PM

STUDENT NAME: ....

STUDENT ID NUMBER: ....

Test Code (002)

(20 Questions)

Dr. Mazen Khaled	Section 1
Dr. Mohamed Morsy	Section 2
Dr. G. Oweimreen	Section 3
Dr. W. Foerner	Section 4

Physical constants, conversion factors, and useful equations

Physical Constants

R = 8.314 J mol^{-1} K^{-1}
= 0.08206 L atmK^{-1} mol^{-1}
= 0.08314 L bar K^{-1} mol^{-1}

N_A = 6.022 x 10^{23} mol^{-1}

k_B = 1.381 x 10^{-23} J K^{-1}

h = 6.626 x 10^{-34} J s

F = 96,500 C mol^{-1}

c = 2.998 x 10^{8} m s^{-1}

g = 9.81 m s^{-2}

B = 0.51$\text{mol}^{-1/2}\text{dm}^{3/2}$
(In H_2O, 25°C)

Sequential reactions.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$[B]=(k_1/(k_2-k_{-1}))\ f(t)[A]_0$

$f(t)=\exp(-k_1t)-\exp(-k_2t)$

Parallel reactions:

$\Phi_i = k_i/S$

Where S is the sum of all rate constants of the paral-lel reactions

Other Units

1dm^3 = 1 L

1dm^3 = 1000 cm^3

1 J = 1 kg m^2 s^{-2}

1 atm = 1.101325 x 10^5 Pa

1 atm = 760 mmHg

1 Torr = 1 mmHg

1 Torr = 133.322 Pa

1 bar = 10^5 Pa

1 nm = 10^{-9} m

Eyring equation:

$k = k_BT/(hc^0) \times f$

$f = \exp(\Delta S^{\neq}/R) \times$

$\times \exp(-\Delta H^{\neq}/RT)$

$\ln(1 - \theta) = -\theta$
if $\theta << 1$

Important Equations

$E = h\upsilon$

$c = \upsilon\lambda$

$PV = nRT$

$\Delta G = \Delta H - T\Delta S$

$k = A\,e^{-E_a/RT}$

$$k = \frac{k_BT}{h} e^{-\Delta^{\neq}G/RT}$$

$A = e\,(k_BT/h)\exp(\Delta^{\ddagger}S/R)$

$$k = \frac{k_BT}{h} e^{-\Delta^{\neq}G/RT}$$

$E_a = \Delta^{\neq}H^{o} - P\Delta^{\neq}V^{o} + RT$ (sol)
$= \Delta^{\neq}H^{o} - \Sigma\nu RT + RT$ (gas)

$\log k = \log k_o + 1.02\, z_A z_B \sqrt{I}$

$$\log k = \log k_o - \frac{\Delta^{\neq}V}{RT}P$$

$\Delta G^{o} = -RT \ln K_c$

$$\upsilon = \frac{V[S]}{K_m + [S]}$$

$$V = k_2[E]_0 \; and \; K_m = \frac{k_{-1} + k_2}{k_1}$$

$\theta = KP/(1 + KP)$, at T=const

$t_f = (k_f + k_q[Q])^{-1}$, Q is quencher

Note:
Quantum yield/efficiency = Φ = moles of product formed / moles of photons absorbed

From the Michaelis-Menten kinetics

$R_o = R_{max}[S]_o(K_m + [S]_o)$, $\quad R_{max} = k_2[E]_o$

The Lineweaver-Burk equation is obtained by taking the inverse

1. For the parallel reactions

$A \rightarrow B$ rate constant k_1
$A \rightarrow C$ rate constant $k_2 = 2.3\ k_1$
$A \rightarrow D$ rate constant $k_3 = 4.0\ k_1$

What is the yield of C?
A) 13.7%
B) 54.8%
C) 86.3%
D) 31.5%
E) 45.2%

2. Two reactions follow the Arrhenius law and have the same pre-exponential factor. If the activation energy of reaction (1) is 20 *J/mol* and that of reaction (2) is 200 *J/mol*, what would be their rate constant ratio (k_1/k_2) at 300*K*?
A) 1.037
B) 0.922
C) 1.083
D) 0.930
E) 1.075

3. At equilibrium.
A) all rates are zero.
B) reactant concentrations are zero.
C) forward and backward reaction rates are equal.
D) the backward reaction is faster than the forward reaction.
E) forward and backward rates are not equal.

4. Consider the following reaction:

$$3A \rightarrow 2B$$

The relationship of the rate of appearance of B and the rate of disappearance of A is:

$$(\Delta[B]/\Delta t) = C \times \{-\Delta[A]/\Delta t)\}$$

The factor C is

A) +0.334
B) +3/2
C) -2/3
D) +0.667
E) +1

5. The gas-phase chain mechanism of the reaction $Cl_2 + CH_4 \rightarrow CH_3Cl + +HCl$ is:

$$Cl_2 \xrightarrow{k_1} 2Cl$$

$$Cl + CH_4 \xrightarrow{k_2} HCl + CH_3$$

$$Cl_2 + CH_3 \xrightarrow{k_3} CH_3Cl + Cl$$

$$2Cl \xrightarrow{k_1} Cl_2$$

The overall rate of reaction in terms of the rate of formation of HCl is (k_{eff} is an effective rate constant)

A) $k_{eff}\,[Cl_2]\,[CH_3Cl]^{1/2}$
B) $k_{eff}\,[Cl_2]^{1/2}[CH_3Cl]$
C) $k_{eff}\,[Cl_2][CH_4]^{1/2}$
D) $k_{eff}[Cl_2]^{1/2}[CH_4]$
E) $k_{eff}\,[CH_4][CH_3Cl]$

6. The decomposition of hydrogen peroxide (substrate S) is catalyzed by the enzyme catalase (E). At an initial catalase concentration $[S_o]$ of 3.5×10^{-9} M the variation of $1/R$ (the reciprocal of the initial rate) with $1/[S]$ (the reciprocal of the initial concentration of the substrate) is given by (Lineweaver-Burk equation),

$$(1/R_0) = 0.6977\ s\,(1/[S]_0) + 26.557\ s/M$$

based on this experimental result, which one of the following choices is correct? (left to right: Maximum rate R_{max} in *M/s*, Michaelis constant K_m in *M*, and the turnover number k_2 in *1/s*)

A) 3.77×10^{-2}, 2.63×10^{-2}, 1.08×10^{7}
B) 0.6977, 26.557, 1.08×10^{7}
C) 3.77×10^{-2}, 2.63×10^{-2}, 7.51×10^{6}

D) 26.557, 0.6977, 1.08×10^{7}

E) 2.63×10^{-2}, 3.77×10^{-2}, 7.51×10^{6}

7. In the mechanism,

(1) $2\{N_2O_5 \rightleftharpoons NO_2 + NO_3\}$ equilibrium
(2) $NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$
(3) $NO + NO_3 \rightarrow 2\,NO_2$

for the decomposition of N_2O_5 into NO_2 and O_2,

A) both NO and NO_3 are catalysts.
B) only NO is an intermediate.
C) only NO_3 is an intermediate.
D) both NO and NO_3 are intermediates.
E) only NO_3 is a catalyst.

8. A second order reaction with initial reactant concentration of 0.80 M has a rate constant of 0.05 $M^{-1}s^{-1}$. How long will it take in seconds for the reactant to lose 50% of the initial concentration?
   A) 25
   B) 125
   C) 8
   D) 50
   E) 10

9. The chlorination reaction of ethane ($Cl_2 + H_3CCH_3$ ◊ $ClH_2CCH_2Cl + H_2$) processes via a chain reaction mechanism. Which one of the following is not a chain propagation reaction in the chlorination of ethane?
   A) $H + Cl_2 \longrightarrow HCl + Cl$
   B) $Cl + Cl \longrightarrow Cl_2$
   C) $Cl + H_3CCH_3 \longrightarrow H_3CCH_2 + HCl$
   D) $Cl + H_3CCH_3 \longrightarrow ClH_2CCH_3 + H$
   E) $Cl_2 + H_2CCH_3 \longrightarrow ClH_2CCH_3 + Cl$

10. A possible mechanism for the reaction, $2A + B \longrightarrow C + D$, is:

$A + A \rightleftharpoons A_2$	fast, equilibrium
$A_2 + A \longrightarrow A_3$	slow
$A_3 + B \longrightarrow A + C + D$	Fast

According to this mechanism, the rate law (rate of formation of one of the final products) will be (*k* is an effective rate constant k_{eff}):
   A) Rate = $k[A]^3$
   B) Rate = $k[A]$
   C) Rate = $k[A]^2[B]$
   D) Rate = $k[A]^2$
   E) Rate = $k[A][B]$

11. The mechanism suggested for the reaction,

$$2\,A + B \rightarrow 2\,C$$

is,

$A + A \rightleftharpoons I$	forward rate constant k_1, backward rate constant k_{-1}
$I + B \rightarrow 2\,C$	constant k_2

The rate law obtained on applying the steady state approximation is,

A) Rate = $k_1k_2[A]^2[B]/(k_1 + k_2[B])$
B) Rate = $k_1k_2[A][B]$
C) Rate = $k_1k_2[A]^2/(k_{-1} + k_2[B])$
D) Rate = $k_1k_2[A]^2[B]$
E) Rate = $k_1k_2[A]^2[B]/(k_{-1} + k_2[B])$

12. The mechanism of the chain reaction $C_2H_6 \rightarrow C_2H_4 + H_2$ is:

$$C_2H_6 \xrightarrow{k_1} 2CH_3$$

$$C_2H_6 + CH_3 \xrightarrow{k_2} C_2H_5 + CH_4$$

$$C_2H_5 \xrightarrow{k_3} C_2H_4 + H$$

$$C_2H_6 + H \xrightarrow{k_4} C_2H_5 + H_2$$

$$2C_2H_5 \xrightarrow{k_5} C_4H_{10}$$

The reactive intermediates of the mechanism are the species:

A) H, CH_3 and C_4H_{10}
B) H, CH_4 and C_4H_{10}
C) CH_3, CH_4 and C_2H_5
D) H, CH_3 and C_2H_5
E) H, CH_4 and C_2H_5

13. Determine the rate expression for the following reaction:

$$2MnO_4^-{}_{(aq)} + 6H^+{}_{(aq)} + 5ClO_3^-{}_{(aq)} \rightarrow 2Mn^{2+}{}_{(aq)} + 3H_2O_{(l)} + 5ClO_4^-{}_{(aq)}$$

$[MnO_4^-]/M$	$[ClO_3^-]/M$	$[H^+]/M$	Initial Rate Ms^{-1}
0.10	0.10	0.10	5.2x10-3
0.25	0.10	0.10	3.3x10-2
0.10	0.30	0.10	1.6x10-2
0.10	0.10	0.20	7.4x10-3

A) $k[MnO_4^-][ClO_3^-][H^+]^2$
B) $k[MnO_4^-]^{1/2}[ClO_3^-][H^+]^2$
C) $k[MnO_4^-][ClO_3^-]^{1/2}[H^+]^2$
D) $k[MnO_4^-]^2[ClO_3^-][H^+]^{1/2}$
E) $k[MnO_4^-]^2[H^+]^{1/2}$

14. If $\tau_f = 1 \times 10^{-10}$ s and $k_n = 5 \times 10^8$ s^{-1}, what is Φ_f? Assume that the rate constants for intersystem crossing and quenching are sufficiently small that these processes can be neglected.
A) 0.95
B) 0.77
C) 0.27
D) 0.62
E) 0.81

15. Consider the following reaction:

$$C_2H_{8(g)} + 4O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(g)}$$

If 1.0 *mol* C_2H_8 is consumed in 4.0 *min*, the rate of H_2O production in *mol/min* is
A) 1.0
B) 4.0
C) 8.0
D) 0.25
E) 4.0

16. For the reaction mechanism

$$\begin{array}{ll} A \rightarrow I & \text{rate constant } k_1 \\ I \rightarrow P & \text{rate constant } k_2 \end{array}$$

the steady state approximation yields

A) $k_2[I] = 0$
B) $k_1[A] + k_2[I] = 0$
C) $d[P]/dt = k_2[I]$
D) $k_1[A] - k_2[I] = 0$
E) $k_1[A] = 0$

17. A reactant can be photo-chemically converted to a cis-product. In an experiment, 4.15 *mmol* of reactant are converted when irradiated with 100. W of 280. *nm* light for 27.0 *s*. All of the light is absorbed by the sample. What is the overall quantum yield for this photochemical process?

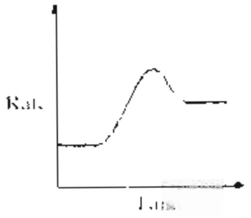
A) 0.66
B) 0.40
C) 0.21
D) 0.10
E) 0.78

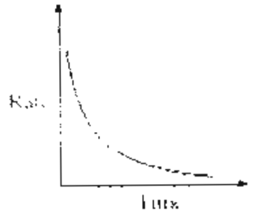
18. Find the correct choice: The Transition State in a reaction …

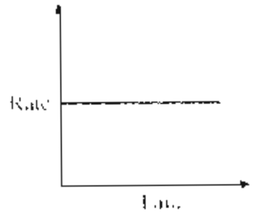
A) … can have only strong bonds.
B) … is at a minimum of the potential energy diagram.
C) … is a stable molecule.
D) … must have at least one weak bond.
E) … is a stable intermediate.

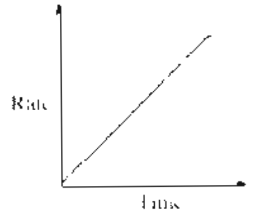
19. Using the following graphs, which one shows the rate of change of H_2O_2 with time (assume the reaction to be an elementary one)?

$$2\ H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

A) 

B) 

C) 

D) 

20. The adsorption of Kr on charcoal at 193.5 K, closely follows the Langmuir adsorption isotherm and in turn the linear relation,

$$(1/V_{ads}) = 0.34076\ (torr\ g/cm^3) \times (1/P) + 0.03258\ g/cm^3$$

where V_{ads} $(in\ cm^3\ g^{-1})$ is the volume of Kr adsorbed per gram charcoal at the equilibrium Kr pressure, $P(in\ torr)$. Which one of the following choices is correct (left to right: Volume of Ar needed to form a monolayer per gram charcoal, V_m, and the adsorption equilibrium constant K in $torr^{-1}$ at 193.5 K)?

A) 28.7, 0.341
B) 9.56×10^{-2}, 28.7
C) 30.7, 2.93
D) 2.93, 30.7
E) 30.7, 9.56×10^{-2}

Answer Key

1. D
2. E
3. C
4. D
5. D
6. A
7. D
8. A
9. B
10. A
11. E
12. D
13. D
14. A
15. A
16. D
17. A
18. D
19. B
20. E

CHEM 311 (141) **Second Major Exam** **2 HOURS**
Thursday, December 11, 2014, 7:00-9:00 PM

STUDENT NAME: ....

STUDENT ID NUMBER: ....

Test Code (003)

(20 Questions)

Dr. Mazen Khaled	Section 1
Dr. Mohamed Morsy	Section 2
Dr. G. Oweimreen	Section 3
Dr. W. Foerner	Section 4

Physical constants, conversion factors, and useful equations

Physical Constants

R = 8.314 J mol^{-1} K^{-1}
= 0.08206 L atmK^{-1} mol^{-1}
= 0.08314 L bar K^{-1} mol^{-1}

N_A = 6.022 x 10^{23} mol^{-1}

k_B = 1.381 x 10^{-23} J K^{-1}

h = 6.626 x 10^{-34} J s

F = 96,500 C mol^{-1}

c = 2.998 x 10^{8} m s^{-1}

g = 9.81 m s^{-2}

B = 0.51mol$^{-1/2}$dm$^{3/2}$
(in H_2O, 25°C)

Sequential reactions:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$[B]=(k_1/(k_2-k_{-1}))\, f(t)[A]_0$

$f(t)=\exp(-k_1 t)-\exp(-k_2 t)$

Parallel reactions:

$\Phi_i = k_i/S$

Where S is the sum of all rate constants of the paral-lel reactions

Other Units

1dm^3 = 1 L

1dm^3 = 1000 cm^3

1 J = 1 kg m^2 s^{-2}

1 atm = 1.101325 x 10^5 Pa

1 atm = 760 mmHg

1 Torr = 1 mmHg

1 Torr = 133.322 Pa

1 bar = 10^5 Pa

1 nm = 10^{-9} m

Eyring equation:

$k = k_B T/(hc^0) \times f$

$f = \exp(\Delta S^{\#}/R) \times$

$\times \exp(-\Delta H^{\#}/RT)$

$\ln(1 - \theta) = -\theta$
if $\theta << 1$

Important Equations

$E = h\nu$

$c = \nu\lambda$

$PV = nRT$

$\Delta G = \Delta H - T\Delta S$

$k = A\, e^{-E_a/RT}$

$$k = \frac{k_B T}{h} e^{-\Delta^{\ddagger} G / RT}$$

$A = e\, (k_B T/h) \exp(\Delta^{\ddagger} S/R)$

$$k = \frac{k_B T}{h} e^{-\Delta^{\ddagger} G / RT}$$

$E_a = \Delta^{\neq}H^o - P\Delta^{\neq}V^o + RT$ (sol)
$= \Delta^{\neq}H^o - \Sigma\nu RT + RT$ (gas)

$\log k = \log k_o + 1.02\, z_A z_B \sqrt{I}$

$$\log k = \log k_o - \frac{\Delta^{\neq} V}{RT} P$$

$\Delta G^o = - RT \ln K_c$

$$\nu = \frac{V[S]}{K_m + [S]}$$

$$V = k_2[E]_0 \text{ and } K_m = \frac{k_{-1} + k_2}{k_1}$$

$\theta = KP/(1 + KP)$, at T=const

$\tau_f = (k_f + k_q[Q])^{-1}$, Q is quencher

Note:
Quantum yield/efficiency = Φ = moles of product formed / moles of photons absorbed

From the Michaelis-Menten kinetics

$R_o = R_{max}[S]_o(K_m + [S]_o)$, $\quad R_{max} = k_2[E]_o$

The Lineweaver-Burk equation is obtained by taking the inverse

1. The adsorption of Kr on charcoal at 193.5 K, closely follows the Langmuir adsorption isotherm and in turn the linear relation,

$$(1/V_{ads}) = 0.34076\ (torr\ g/cm^3) \times (1/P) + 0.03258\ g/cm^3$$

where V_{ads} $(in\ cm^3\ g^{-1})$ is the volume of Kr adsorbed per gram charcoal at the equilibrium Kr pressure, $P(in\ torr)$. Which one of the following choices is correct (left to right: Volume of Ar needed to form a monolayer per gram charcoal, V_m, and the adsorption equilibrium constant K in $torr^{-1}$ at 193.5 K)?

A) 30.7, 9.56×10^{-2}

B) 2.93, 30.7
C) 9.56×10^{-2}, 28.7
D) 28.7, 0.341
E) 30.7, 2.93

2. The mechanism suggested for the reaction,

$$2\,A + B \rightarrow 2\,C$$

is,

$A + A \rightleftarrows I$ forward rate constant k_1, backward rate constant k_{-1}
$I + B \rightarrow 2\,C$ constant k_2

The rate law obtained on applying the steady state approximation is,
A) Rate = $k_1k_2[A]^2[B]/(k_{-1} + k_2[B])$
B) Rate = $k_1k_2[A]^2[B]/(k_1 + k_2[B])$
C) Rate = $k_1k_2[A][B]$
D) Rate = $k_1k_2[A]^2/(k_{-1} + k_2[B])$
E) Rate = $k_1k_2[A]^2[B]$

3. The chlorination reaction of ethane ($Cl_2 + H_3CCH_3$ ◊ $ClH_2CCH_2Cl + H_2$) processes via a chain reaction mechanism. Which one of the following is not a chain propagation reaction in the chlorination of ethane?
A) $Cl + H_3CCH_3 \longrightarrow H_3CCH_2 + HCl$
B) $Cl_2 + H_3CCH_3 \longrightarrow ClH_2CCH_3 + Cl$
C) $Cl + Cl \longrightarrow Cl_2$

D) $H + Cl_2 \longrightarrow HCl + Cl$
E) $Cl + H_3CCH_3 \longrightarrow ClH_2CCH_3 + H$

4. For the parallel reactions

$A \rightarrow B$ rate constant k_1
$A \rightarrow C$ rate constant $k_2 = 2.3\ k_1$
$A \rightarrow D$ rate constant $k_3 = 4.0\ k_1$

What is the yield of C?
A) 54.8%
B) 45.2%
C) 13.7%
D) 86.3%
E) 31.5%

5. A possible mechanism for the reaction, $2A + B \longrightarrow C + D$, is:

$A + A \rightleftarrows A_2$ fast, equilibrium
$A_2 + A \longrightarrow A_3$ slow
$A_3 + B \longrightarrow A + C + D$ Fast

According to this mechanism, the rate law (rate of formation of one of the final products) will be (k is an effective rate constant k_{eff}):
A) Rate = $k[A]^2$
B) Rate = $k[A]^2[B]$
C) Rate = $k[A][B]$
D) Rate = $k[A]$
E) Rate = $k[A]^3$

6. Consider the following reaction:

$$C_2H_{8(g)} + 4O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(g)}$$

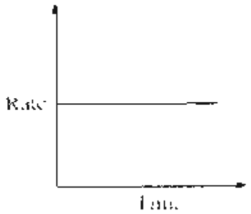
If 1.0 *mol* C_2H_8 is consumed in 4.0 *min*, the rate of H_2O production in *mol/min* is
A) 8.0
B) 4.0
C) 4.0
D) 1.0
E) 0.25

7. Two reactions follow the Arrhenius law and have the same pre-exponential factor. If the activation energy of reaction (1) is 20 *J/mol* and that of reaction (2) is 200 *J/mol*, what would be their rate constant ratio (k_1/k_2) at 300*K*?
A) 1.075
B) 0.930
C) 0.922
D) 1.037
E) 1.083

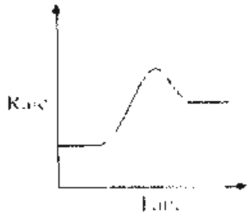
8. Using the following graphs, which one shows the rate of change of H_2O_2 with time (assume the reaction to be an elementary one)?

$$2\ H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

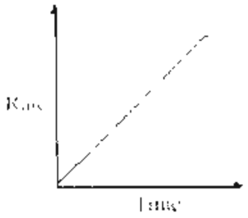
A)



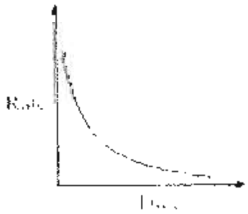
B)



C)



D)



9. Determine the rate expression for the following reaction:

$$2MnO_4^-{}_{(aq)} + 6H^+{}_{(aq)} + 5ClO_3^-{}_{(aq)} \rightarrow 2Mn^{2+}{}_{(aq)} + 3H_2O_{(l)} + 5ClO_4^-{}_{(aq)}$$

$[MnO_4^-]/M$	$[ClO_3^-]/M$	$[H^+]/M$	Initial Rate Ms^{-1}
0.10	0,10	0.10	5.2x10-3
0.25	0.10	0.10	3.3x10-2
0.10	0.30	0.10	1.6x10-2
0.10	0.10	0.20	7.4x10-3

A) $k[MnO_4^-]^2[ClO_3^-][H^+]^{1/2}$
B) $k[MnO_4^-][ClO_3^-]^{1/2}[H^+]^2$
C) $k[MnO_4^-][ClO_3^-][H^+]^2$
D) $k[MnO_4^-]^2[H^+]^{1/2}$
E) $k[MnO_4^-]^{1/2}[ClO_3^-][H^+]^2$

10. The decomposition of hydrogen peroxide (substrate S) is catalyzed by the enzyme catalase (E). At an initial catalase concentration $[S_o]$ of 3.5×10^{-9} M the variation of $1/R$ (the reciprocal of the initial rate) with $1/[S]$ (the reciprocal of the initial concentration of the substrate) is given by (Lineweaver-Burk equation),

$$(1/R_0) = 0.6977\ s\,(1/[S]_0) + 26.557\ s/M$$

based on this experimental result, which one of the following choices is correct? (left to right: Maximum rate R_{max} in M/s, Michaelis constant K_m in M, and the turnover number k_2 in $1/s$)

A) 2.63×10^{-2}, 3.77×10^{-2}, 7.51×10^6
B) 3.77×10^{-2}, 2.63×10^{-2}, 7.51×10^6

C) 3.77×10^{-2}, 2.63×10^{-2}, 1.08×10^7
D) 0.6977, 26.557, 1.08×10^7
E) 26.557, 0.6977, 1.08×10^7

11. For the reaction mechanism

$$\begin{array}{ll} A \rightarrow I & \text{rate constant } k_1 \\ I \rightarrow P & \text{rate constant } k_2 \end{array}$$

the steady state approximation yields
A) $k_1[A] - k_2[I] = 0$
B) $k_2[I] = 0$
C) $k_1[A] = 0$
D) $d[P]/dt = k_2[I]$
E) $k_1[A] + k_2[I] = 0$

12. In the mechanism,

$$\begin{array}{llcll} (1) & 2\{\ N_2O_5 & \rightleftharpoons & NO_2 + NO_3\} & \text{equilibrium} \\ (2) & NO_2 + NO_3 & \rightarrow & NO + O_2 + NO_2 & \\ (3) & NO + NO_3 & \rightarrow & 2\ NO_2 & \end{array}$$

for the decomposition of N_2O_5 into NO_2 and O_2,
A) both NO and NO_3 are intermediates.
B) only NO_3 is a catalyst.
C) only NO is an intermediate.
D) only NO_3 is an intermediate.
E) both NO and NO_3 are catalysts.

13. A reactant can be photo-chemically converted to a cis-product. In an experiment, 4.15 *mmol* of reactant are converted when irradiated with 100. W of 280. *nm* light for 27.0 s. All of the light is absorbed by the sample. What is the overall quantum yield for this photochemical process?
A) 0.40
B) 0.21
C) 0.10
D) 0.78
E) 0.66

14. The gas-phase chain mechanism of the reaction $Cl_2 + CH_4 \rightarrow CH_3Cl +$ +HCl is:

$$Cl_2 \xrightarrow{k_1} 2Cl$$

$$Cl + CH_4 \xrightarrow{k_2} HCl + CH_3$$

$$Cl_2 + CH_3 \xrightarrow{k_3} CH_3Cl + Cl$$

$$2Cl \xrightarrow{k_1} Cl_2$$

The overall rate of reaction in terms of the rate of formation of HCl is (k_{eff}: is an effective rate constant)

A) $k_{eff}[Cl_2]^{1/2}[CH_4]$
B) $k_{eff}[Cl_2][CH_4]^{1/2}$
C) $k_{eff}[CH_4][CH_3Cl]$
D) $k_{eff}[Cl_2]^{1/2}[CH_3Cl]$
E) $k_{eff}[Cl_2][CH_3Cl]^{1/2}$

15. The mechanism of the chain reaction $C_2H_6 \rightarrow C_2H_4 + H_2$ is:

$$C_2H_6 \xrightarrow{k_1} 2CH_3$$

$$C_2H_6 + CH_3 \xrightarrow{k_2} C_2H_5 + CH_4$$

$$C_2H_5 \xrightarrow{k_3} C_2H_4 + H$$

$$C_2H_6 + H \xrightarrow{k_4} C_2H_5 + H_2$$

$$2C_2H_5 \xrightarrow{k_5} C_4H_{10}$$

The reactive intermediates of the mechanism are the species:

A) H, CH_3 and C_2H_5
B) CH_3, CH_4 and C_2H_5
C) H, CH_3 and C_4H_{10}
D) H, CH_4 and C_2H_5
E) H, CH_4 and C_4H_{10}

16. A second order reaction with initial reactant concentration of 0.80 M has a rate constant of 0.05 $M^{-1}s^{-1}$. How long will it take in seconds for the reactant to lose 50% of the initial concentration?
A) 8
B) 10
C) 125
D) 25
E) 50

17. Consider the following reaction:

$$3A \rightarrow 2B$$

The relationship of the rate of appearance of B and the rate of disappearance of A is:

$$(\Delta[B]/\Delta t) = C \times \{- \Delta[A]/\Delta t)\}$$

The factor C is
A) +3/2
B) +1
C) +0.667
D) +0.334
E) -2/3

18. If $\tau_f = 1 \times 10^{-10}$ s and $k_{ic} = 5 \times 10^{8}\ s^{-1}$, what is Φ_f? Assume that the rate constants for intersystem crossing and quenching are sufficiently small that these processes can be neglected.
A) 0.27
B) 0.62
C) 0.81
D) 0.95
E) 0.77

19. At equilibrium,
A) forward and backward rates are not equal.
B) all rates are zero.
C) reactant concentrations are zero.
D) forward and backward reaction rates are equal.
E) the backward reaction is faster than the forward reaction.

20. Find the correct choice: The Transition State in a reaction …

A) … must have at least one weak bond.
B) … is a stable intermediate.
C) … is at a minimum of the potential energy diagram.
D) … is a stable molecule.
E) … can have only strong bonds.

Answer Key

1. A
2. A
3. C
4. E
5. E
6. D
7. A
8. D
9. A
10. C
11. A
12. A
13. E
14. A
15. A
16. D
17. C
18. D
19. D
20. A

CHEM 311 (141) **Second Major Exam** 2 HOURS
Thursday, December 11, 2014, 7:00-9:00 PM

STUDENT NAME: ....

STUDENT ID NUMBER: ....

Test Code (004)

(20 Questions)

Dr. Mazen Khaled	Section 1
Dr. Mohamed Morsy	Section 2
Dr. G. Oweimreen	Section 3
Dr. W. Foerner	Section 4

Physical constants, conversion factors, and useful equations

Physical Constants

R = 8.314 J mol^{-1} K^{-1}
= 0.08206 L atmK^{-1} mol^{-1}
= 0.08314 L bar K^{-1} mol^{-1}

N_A = 6.022 x 10^{23} mol^{-1}

k_B = 1.381 x 10^{-23} J K^{-1}

h = 6.626 x 10^{-34} J s

F = 96,500 C mol^{-1}

c = 2.998 x 10^{8} m s^{-1}

g = 9.81 m s^{-2}

B = 0.51mol$^{-1/2}$dm$^{3/2}$
(in H_2O, 25°C)

Sequential reactions.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

[B]=(k$_1$/(k$_2$-k$_{-1}$)) f(t)[A]$_0$

f(t)=exp(-k$_1$t)-exp(-k$_2$t)

Parallel reactions:

$\Phi_i = k_i/S$

Where S is the sum of all rate constants of the paral-lel reactions

Other Units

1dm^3 = 1 L

1dm^3 = 1000 cm^3

1 J = 1 kg m^2 s^{-2}

1 atm = 1.101325 x 10^5 Pa

1 atm = 760 mmHg

1 Torr = 1 mmHg

1 Torr = 133.322 Pa

1 bar = 10^5 Pa

1 nm = 10^{-9} m

Eyring equation:

$k = k_BT/(hc^0) \times f$

$f = \exp(\Delta S^{\#}/R) \times$

$\times \exp(-\Delta H^{\#}/RT)$

$\ln(1 - \theta) = -\theta$
if θ << 1

Important Equations

$E = h\upsilon$

$c = \upsilon\lambda$

$PV = nRT$

$\Delta G = \Delta H - T\Delta S$

$k = A\,e^{-E_a/RT}$

$$k = \frac{k_BT}{h} e^{-\Delta^{\ddagger} G/RT}$$

$A = e\,(k_BT/h) \exp(\Delta^{\ddagger}S/R)$

$$k = \frac{k_BT}{h} e^{-\Delta^{\ddagger} G/RT}$$

$E_a = \Delta^{\neq}H^o - P\Delta^{\neq}V^o + RT$ (sol)
$= \Delta^{\neq}H^o - \Sigma\nu RT + RT$ (gas)

$\log k = \log k_o + 1.02\, z_A z_B \sqrt{I}$

$$\log k = \log k_o - \frac{\Delta^{\neq}V}{RT}P$$

$\Delta G^o = -RT \ln K_c$

$$\upsilon = \frac{V[S]}{K_m + [S]}$$

$$V = k_2[E]_0 \; and \; K_m = \frac{k_{-1} + k_2}{k_1}$$

θ = KP/(1 + KP), at T=const

$t_f = (k_f + k_q[Q])^{-1}$, Q is quencher

Note:
Quantum yield/efficiency = Φ = moles of product formed / moles of photons absorbed

From the Michaelis-Menten kinetics

$R_o = R_{max}[S]_o(K_m + [S]_o)$, $\quad\quad R_{max} = k_2[E]_o$

The Lineweaver-Burk equation is obtained by taking the inverse

1. A possible mechanism for the reaction, $2A + B \longrightarrow C + D$, is:

$A + A \rightleftarrows A_2$	fast, equilibrium
$A_2 + A \longrightarrow A_3$	slow
$A_3 + B \longrightarrow A + C + D$	Fast

According to this mechanism, the rate law (rate of formation of one of the final products) will be (k is an effective rate constant k_{eff}):

A) Rate = $k[A]^3$
B) Rate = $k[A]$
C) Rate = $k[A]^2[B]$
D) Rate = $k[A]^2$
E) Rate = $k[A][B]$

2. For the parallel reactions

$A \rightarrow B$	rate constant k_1
$A \rightarrow C$	rate constant $k_2 = 2.3\ k_1$
$A \rightarrow D$	rate constant $k_3 = 4.0\ k_1$

What is the yield of C?

A) 13.7%
B) 54.8%
C) 31.5%
D) 45.2%
E) 86.3%

3. The decomposition of hydrogen peroxide (substrate S) is catalyzed by the enzyme catalase (E). At an initial catalase concentration $[S_o]$ of 3.5×10^{-9} M the variation of $1/R$ (the reciprocal of the initial rate) with $1/[S]$ (the reciprocal of the initial concentration of the substrate) is given by (Lineweaver-Burk equation),

$$(1/R_0) = 0.6977\ s\,(1/[S]_0) + 26.557\ s/M$$

based on this experimental result, which one of the following choices is correct? (left to right: Maximum rate R_{max} in *M/s*, Michaelis constant K_m in *M*, and the turnover number k_2 in *1/s*)

A) 3.77×10^{-2}, 2.63×10^{-2}, 7.51×10^{6}

B) 3.77×10^{-2}, 2.63×10^{-2}, 1.08×10^{7}
C) 26.557, 0.6977, 1.08×10^{7}

D) 2.63×10^{-2}, 3.77×10^{-2}, 7.51×10^{6}
E) 0.6977, 26.557, 1.08×10^{7}

4. For the reaction mechanism

$$A \rightarrow I \qquad \text{rate constant } k_1$$
$$I \rightarrow P \qquad \text{rate constant } k_2$$

the steady state approximation yields

A) $k_1[A] = 0$
B) $d[P]/dt = k_2[I]$
C) $k_2[I] = 0$
D) $k_1[A] + k_2[I] = 0$
E) $k_1[A] - k_2[I] = 0$

5. The mechanism suggested for the reaction,

$$2\,A + B \rightarrow 2\,C$$

is,

$A + A \rightleftharpoons I$ forward rate constant k_1, backward rate constant k_{-1}
$I + B \rightarrow 2\,C$ constant k_2

The rate law obtained on applying the steady state approximation is,
A) Rate = $k_1k_2[A][B]$
B) Rate = $k_1k_2[A]^2/(k_{-1} + k_2[B])$
C) Rate = $k_1k_2[A]^2[B]/(k_1 + k_2[B])$
D) Rate = $k_1k_2[A]^2[B]$
E) Rate = $k_1k_2[A]^2[B]/(k_{-1} + k_2[B])$

6. In the mechanism,

(1) $2\{N_2O_5 \rightleftharpoons NO_2 + NO_3\}$ equilibrium
(2) $NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$
(3) $NO + NO_3 \rightarrow 2\,NO_2$

for the decomposition of N_2O_5 into NO_2 and O_2,
A) only NO_3 is a catalyst.
B) only NO is an intermediate.
C) only NO_3 is an intermediate.
D) both NO and NO_3 are catalysts.
E) both NO and NO_3 are intermediates.

7. A second order reaction with initial reactant concentration of 0.80 M has a rate constant of 0.05 $M^{-1}s^{-1}$. How long will it take in seconds for the reactant to lose 50% of the initial concentration?
A) 25
B) 8
C) 50
D) 125
E) 10

8. The mechanism of the chain reaction $C_2H_6 \rightarrow C_2H_4 + H_2$ is:

$$C_2H_6 \xrightarrow{k_1} 2CH_3$$

$$C_2H_6 + CH_3 \xrightarrow{k_2} C_2H_5 + CH_4$$

$$C_2H_5 \xrightarrow{k_3} C_2H_4 + H$$

$$C_2H_6 + H \xrightarrow{k_4} C_2H_5 + H_2$$

$$2C_2H_5 \xrightarrow{k_5} C_4H_{10}$$

The reactive intermediates of the mechanism are the species:

A) H, CH_4 and C_4H_{10}
B) H, CH_3 and C_2H_5
C) H, CH_4 and C_2H_5
D) CH_3, CH_4 and C_2H_5
E) H, CH_3 and C_4H_{10}

9. The adsorption of Kr on charcoal at 193.5 K, closely follows the Langmuir adsorption isotherm and in turn the linear relation,

$$(1/V_{ads}) = 0.34076\ (torr\ g/cm^3) \times (1/P) + 0.03258\ g/cm^3$$

where V_{ads} $(in\ cm^3\ g^{-1})$ is the volume of Kr adsorbed per gram charcoal at the equilibrium Kr pressure, $P(in\ torr)$. Which one of the following choices is correct (left to right: Volume of Ar needed to form a monolayer per gram charcoal, V_m, and the adsorption equilibrium constant K in $torr^{-1}$ at 193.5 K)?

A) 2.93, 30.7
B) 28.7, 0.341
C) 30.7, 2.93
D) 9.56×10^{-2}, 28.7
E) 30.7, 9.56×10^{-1}

10. A reactant can be photo-chemically converted to a cis-product. In an experiment, 4.15 *mmol* of reactant are converted when irradiated with 100. W of 280. *nm* light for 27.0 *s*. All of the light is absorbed by the sample. What is the overall quantum yield for this photochemical process?
    A) 0.21
    B) 0.66
    C) 0.40
    D) 0.10
    E) 0.78

11. At equilibrium,
    A) reactant concentrations are zero.
    B) forward and backward reaction rates are equal.
    C) all rates are zero.
    D) the backward reaction is faster than the forward reaction.
    E) forward and backward rates are not equal.

12. The chlorination reaction of ethane ($Cl_2 + H_3CCH_3$ ◊ $ClH_2CCH_2Cl + H_2$) processes via a chain reaction mechanism. Which one of the following is not a chain propagation reaction in the chlorination of ethane?
    A) $H + Cl_2 \longrightarrow HCl + Cl$
    B) $Cl + H_3CCH_3 \longrightarrow H_3CCH_2 + HCl$
    C) $Cl_2 + H_2CCH_3 \longrightarrow ClH_2CCH_3 + Cl$
    D) $Cl + H_3CCH_3 \longrightarrow ClH_2CCH_3 + H$
    E) $Cl + Cl \longrightarrow Cl_2$

13. If $\tau_f = 1 \times 10^{-10}$ *s* and $k_{ic} = 5 \times 10^{8}$ s^{-1}, what is Φ_f? Assume that the rate constants for intersystem crossing and quenching are sufficiently small that these processes can be neglected.
    A) 0.95
    B) 0.77
    C) 0.27
    D) 0.62
    E) 0.81

14. Consider the following reaction:

$$C_2H_{8(g)} + 4O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(g)}$$

If 1.0 *mol* C_2H_8 is consumed in 4.0 *min*, the rate of H_2O production in *mol/min* is
A) 1.0
B) 8.0
C) 0.25
D) 4.0
E) 4.0

15. The gas-phase chain mechanism of the reaction $Cl_2 + CH_4 \rightarrow CH_3Cl +$ $+HCl$ is:

$$\begin{aligned} Cl_2 &\xrightarrow{k_1} 2Cl \\ Cl + CH_4 &\xrightarrow{k_2} HCl + CH_3 \\ Cl_2 + CH_3 &\xrightarrow{k_3} CH_3Cl + Cl \\ 2Cl &\xrightarrow{k_1} Cl_2 \end{aligned}$$

The overall rate of reaction in terms of the rate of formation of HCl is (k_{eff} is an effective rate constant)
A) $k_{eff}\,[Cl_2]^{1/2}[CH_3Cl]$
B) $k_{eff}\,[Cl_2]\,[CH_3Cl]^{1/2}$
C) $k_{eff}[Cl_2]^{1/2}[CH_4]$
D) $k_{eff}\,[Cl_2][CH_4]^{1/2}$
E) $k_{eff}\,[CH_4][CH_3Cl]$

16. Determine the rate expression for the following reaction:

$$2MnO_4^-{}_{(aq)} + 6H^+{}_{(aq)} + 5ClO_3^-{}_{(aq)} \rightarrow 2Mn^{2+}{}_{(aq)} + 3H_2O_{(l)} + 5ClO_4^-{}_{(aq)}$$

$[MnO_4^-]/M$	$[ClO_3^-]/M$	$[H^+]/M$	Initial Rate Ms^{-1}
0.10	0.10	0.10	5.2x10-3
0.25	0.10	0.10	3.3x10-2
0.10	0.30	0.10	1.6x10-2
0.10	0.10	0.20	7.4x10-3

A) $k[MnO_4^-][ClO_3^-][H^+]^2$

B) $k[MnO_4^-]^{1/2}[ClO_3^-][H^+]^2$

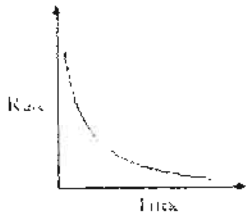
C) $k[MnO_4^-]^2[H^+]^{1/2}$

D) $k[MnO_4^-][ClO_3^-]^{1/2}[H^+]^2$

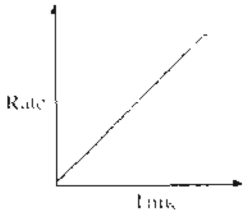
E) $k[MnO_4^-]^2[ClO_3^-][H^+]^{1/2}$

17. Using the following graphs, which one shows the rate of change of H_2O_2 with time (assume the reaction to be an elementary one)?

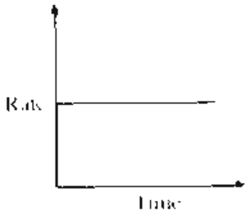
$$2\ H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$



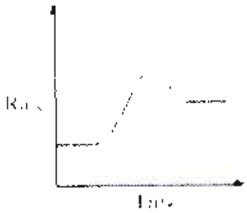
A)



B)



C)



D)

18. Two reactions follow the Arrhenius law and have the same pre-exponential factor. If the activation energy of reaction (1) is 20 *J/mol* and that of reaction (2) is 200 *J/mol*, what would be their rate constant ratio (k_1/k_2) at 300 *K*?

A) 1.083
B) 1.037
C) 0.930
D) 1.075
E) 0.922

19. Find the correct choice: The Transition State in a reaction …
    - A) … is at a minimum of the potential energy diagram.
    - B) … can have only strong bonds.
    - C) … is a stable intermediate.
    - D) … must have at least one weak bond.
    - E) … is a stable molecule.

20. Consider the following reaction:

$$3A \rightarrow 2B$$

The relationship of the rate of appearance of B and the rate of disappearance of A is:

$$(\Delta[B]/\Delta t) = C \times \{- \Delta[A]/\Delta t)\}$$

The factor C is
- A) +0.334
- B) -2/3
- C) +3/2
- D) +1
- E) +0.667

Answer Key

1. A
2. C
3. B
4. E
5. E
6. E
7. A
8. B
9. E
10. B
11. B
12. E
13. A
14. A
15. C
16. E
17. A
18. D
19. D
20. E