Chem 311 2. Major Term 152

1) Worked out solution of 0 Version

2–5) Solutions of Versions 1–4

1. The combustion of ethane (C_2H_6) is represented by the equation:

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$$

In this reaction:

A) CO_2 is formed twice as fast as ethane is consumed.
B) the rate of consumption of ethane is seven times faster than the rate of consumption of oxygen.
C) the rate of formation of CO_2 equals the rate of formation of water.
D) water is formed at a rate equal to two-thirds the rate of formation of CO_2.
E) the rate of consumption of oxygen equals the rate of consumption of water.

2. The initial rate of the reaction between substances **A** and **B** is measured in a series of experiments as follows

Expt	Initial rate/mol dm^{-3} s^{-1}	Initial [A]/mol dm^{-3}	Initial [**B**]/mol dm^{-3}
1	1.5×10^{-2}	0.30	0.30
2	6.0×10^{-2}	X	0.60

Given the order with respect to each reactant is one, the X-value of the initial concentration of the reactant A in experiment 2 should be

A) 0.60
B) 0.11
C) 0.25
D) 0.40
E) 0.30

(12) 001 in 2 it is 3×10^{-2} $\frac{M}{s}$

→ x = 0.30 M

1/s 1/s

3. For the reaction $A + B \longrightarrow C$, the rate constant at 215 °C is 5.0×10^{-3} and the rate constant at 452° C is 1.2×10^{-1}. What is the rate constant at 100° C.

A) 2.50×10^{-4} s^{-1}

B) 1.20×10^{-4} s^{-1}

Q1

$$R = \frac{1}{\nu_i}\frac{d[i]}{dt}$$

$\nu_{C_2H_6} = -2$ $\nu_{O_2} = -7$ $\nu_{CO_2} = 4$ $\nu_{H_2O} = 6$

$$R = -\frac{1}{2}\frac{d[C_2H_6]}{dt} = -\frac{1}{7}\frac{d[O_2]}{dt} = \frac{1}{4}\frac{d[CO_2]}{dt} = \frac{1}{6}\frac{d[H_2O]}{dt}$$

$$\frac{1}{4}\frac{d[CO_2]}{dt} = -\frac{1}{2}\frac{d[C_2H_6]}{dt}$$

$$\frac{d[CO_2]}{dt} = -2\frac{d[C_2H_6]}{dt}$$ Ⓐ

$$-\frac{1}{2}\frac{d[C_2H_6]}{dt} = -\frac{1}{7}\frac{d[O_2]}{dt}$$

$$-\frac{d[C_2H_6]}{dt} = -\frac{2}{7}\frac{d[O_2]}{dt}$$ B wrong $\left(\frac{7}{2}\right)$

$$\frac{1}{4}\frac{d[CO_2]}{dt} = \frac{1}{6}\frac{d[H_2O]}{dt}$$

$$\frac{d[CO_2]}{dt} = \frac{2}{3}\frac{d[H_2O]}{dt}$$ C wrong $\left(\frac{2}{3}\right)$

$$\frac{1}{6}\frac{d[H_2O]}{dt} = \frac{1}{4}\frac{d[CO_2]}{dt}$$

$$\frac{d[H_2O]}{dt} = \frac{3}{2}\frac{d[CO_2]}{dt}$$ D wrong $\left(\frac{3}{2}\right)$

~~$\frac{1}{7}\frac{d[O_2]}{dt} =$~~ no O_2 is consumed: $-\frac{1}{7}$

H_2O is formed $+\frac{1}{6}$

(Q2)

$$R_0 = k_0\,[A]_0\,[B]_0$$

<u>Expt 1:</u> $1.5\cdot10^{-2}\,\frac{M}{s} = k\ 0.3\,M\cdot 0.3\,M$

$$k = \frac{1.5\cdot10^{-2}\,\frac{M}{s}}{0.3\cdot0.3\,M^2}$$

$$= 0.1667\,\frac{1}{Ms}$$

<u>Expt 2:</u> $6.0\cdot10^{-2}\,\frac{M}{s} = k\,X\cdot0.6\,M$

$$X = \frac{6.0\cdot10^{-2}\,\frac{M}{s}}{0.6\,M\cdot0.1667\,\frac{1}{Ms}}$$

$$= 0.60\,M$$ Ⓐ

Q3

$$A + B \to C$$

① 215°C : $k_1 = 5.0 \cdot 10^{-3} \frac{1}{s}$, 488,15K

② 452°C : $k_2 = 1,2 \cdot 10^{-1} \frac{1}{s}$, 725,15K

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

$$\frac{k_1}{k_2} = e^{-E_a/RT_1} \cdot e^{E_a/RT_2}$$

$$= e^{E_a\left(\frac{1}{RT_2} - \frac{1}{RT_1}\right)}$$

$$\ln \frac{k_1}{k_2} = E_a\left(\frac{1}{RT_2} - \frac{1}{RT_1}\right)$$

$$E_a = \frac{1}{\frac{1}{RT_2} - \frac{1}{RT_1}} \ln \frac{k_1}{k_2}$$

$$= \frac{1}{\frac{RT_1 - RT_2}{R^2 T_1 T_2}} \ln \frac{k_1}{k_2}$$

$$= R \frac{T_1 T_2}{T_1 - T_2} \ln \frac{k_1}{k_2}$$

$$= 8,314 \frac{J}{K\,mol} \frac{488,15 \cdot 725,15\,K^2}{(488,15 - 725,15)\,K} \ln \frac{5 \cdot 10^{-3}}{1,2 \cdot 10^{-1}}$$

$$= -12,418 \frac{kJ}{mol} \cdot \ln(0,04167)$$

$$= -12,418 \frac{kJ}{mol} \cdot (-3,17797)$$

$$= 39.464 \frac{kJ}{mol}$$

$$\textcircled{1}: \quad k_1 = A e^{-E_a/RT_1}$$

$$A = k_1 \, e^{E_a/RT_1}$$

$$= 5{,}0 \cdot 10^{-3} \, \frac{1}{s} \, e^{\frac{39{,}464 \cdot 10^{3} \, \frac{J}{mol}}{8{,}314 \, \frac{J}{K\,mol} \cdot 488{,}15\,K}}$$

$$= 5{,}0 \cdot 10^{-3} \, \frac{1}{s} \, e^{9{,}7238}$$

$$= \overset{83{,}553}{\cancel{8{,}3553 \cdot 10^{7}}} \, \frac{1}{s}$$

$$k = \underset{83{,}553}{\overset{\cancel{83}}{\cancel{8{,}3553 \cdot 10^{7}}}} \, \frac{1}{s} \, e^{-\frac{39{,}464 \cdot 10^{3} \, \frac{J}{\cancel{K}\,mol}}{8{,}314 \, \frac{J}{K\,mol} \cdot 373{,}15\,K}}$$

$$= \underset{83{,}553}{\cancel{8{,}3553 \cdot 10^{7}}} \, \frac{1}{s} \, e^{-12{,}721}$$

$$= 2{,}49(6) \cdot 10^{-4} \, \frac{1}{s}$$

$$= 2{,}50 \cdot 10^{-4} \, \frac{1}{s}$$

C) $5.51 \times 10^{-4}\ s^{-1}$

D) $2.15 \times 10^{-4}\ s^{-1}$

E) $7.11 \times 10^{-4}\ s^{-1}$

4. The decomposition of dimethylether at 504 °C is first order with a half-life of 1570 seconds. What fraction of an initial amount of dimethylether remains after 4710 seconds?

A) 1/8
B) 1/3
C) 1/6
D) 1/16
E) 1/32

5. The gas phase decomposition data of hydrogen iodide are

***t*, hours**	0	2.0	4.0	6.0
[HI], M	1.00	0.50	0.33	0.25

What are the order and rate constant (k, include units) of this reaction?

A) Second order and $k = 0.50\ M^{-1}h^{-1}$
B) First order and $k = 0.25\ h^{-1}$
C) Second order and $k = 0.25\ Mh^{-1}$
D) First order and $k = 0.50\ h^{-1}$
E) Second order and $k = 2.0\ M^{-1}h^{-1}$

6. Given that a reaction absorbs energy and has an activation energy of 50 kJ/mol, which of the following statements are **correct**?

I. The reverse reaction has an activation energy equal to 50 kJ/mol.
II. The reverse reaction has an activation energy less than 50 kJ/mol.
III. The reverse reaction has an activation energy greater than 50 kJ/mol.
IV. The change in internal energy is less than zero.
V. The change in internal energy is greater than zero.

A) II and V
B) I and IV
C) II and IV
D) III and IV

Q4

A = dimethylether

$$A \xrightarrow{k} P$$

504 °C : 1. order, 777,15K

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{1570\,s} = 4{,}415 \cdot 10^{-4}\ s^{-1}$$

$$-\frac{d[A]}{dt} = k[A]$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \ln\frac{[A]}{[A]_0} = -kt$$

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

4710 s: $e^{-kt} = e^{-4{,}415 \cdot 10^{-4} \cdot 4710} = e^{-2{,}0795}$

$= 0{,}125$

$= 1/8$ Ⓐ

(Q5)

$HI \rightarrow P \quad A = HI$

2h : $[HI] = 0.5\,[HI]_0$ 1. half life $t_{1/2}^{(1)}$

6h : $[HI] = 0.25\,[HI]_0$ 2. half life $t_{1/2}^{(2)}$

1. order $t_{1/2} = \frac{\ln 2}{k}$ independent of $[A]_0$

2. order $t_{1/2} = \frac{1}{k[A]_0}$

$$t_{1/2}^{(2)} = \frac{1}{k\,[A]_0/2} = \frac{2}{k[A]_0} = 2t_{1/2}^{(1)}$$

$\Rightarrow$ 2. order!

$$\frac{d[A]}{dt} = -k[A]^2 \quad , \quad R = -\frac{d[A]}{dt}$$

when the second halflife with $\frac{[A]_0}{2}$ as start is double long as the first, then the reaction is 2.-order

~~$\ln R = \ln k + 2\ln[A]$~~

2. order $\Rightarrow \frac{1}{k[A]_0} = t_{1/2}^{(1)}$

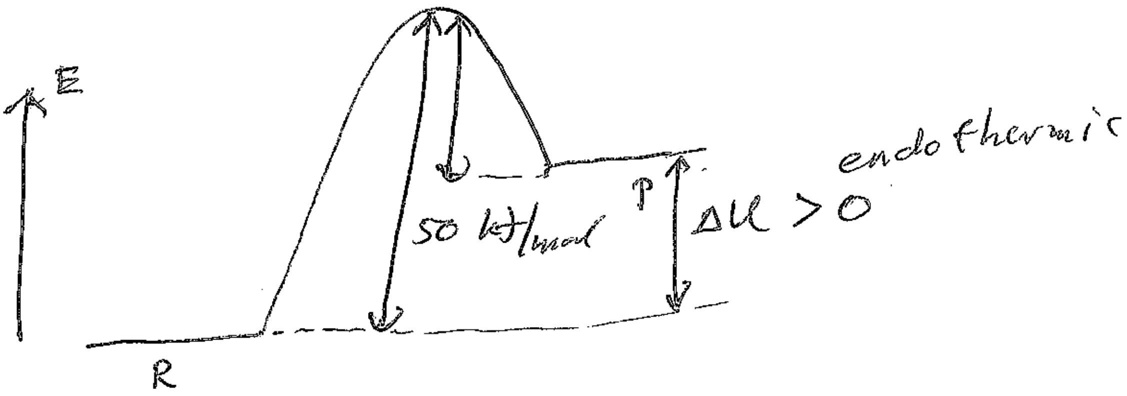
$$k = \frac{1}{t_{1/2}^{(1)}[A]_0} = \frac{1}{2.0h \cdot 1M} = 0.50\,\frac{1}{Mh}$$

$\Rightarrow$ Ⓐ: 2. order, $k = 0.50\,\frac{1}{Mh}$

(Q6)

absorbing energy

=> endothermic



endothermic => $E(R) \neq E(P)$

=> E_a (forward) $\neq$ E_a (backward)

I incorrect

=> E_a (forward) > E_a (backward)

=> II ~~this~~ is correct, III incorrect

$\Delta U(P) - \Delta U(R) \gtrless 0$

endothermic => ~~U(R) hig~~ U(P) higher U(R)

=> $\Delta U > 0$

=> II & V correct (A)

E) III and V

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

$$\begin{array}{llll} (1) & A + A \rightleftharpoons A_2 & & \text{fast, equilibrium} \\ (2) & A_2 + A \longrightarrow A_3 & & \text{slow} \\ (3) & A_3 + B \longrightarrow A + C + D & & \text{fast} \end{array}$$

According to the mechanism, the rate law will be:

A) Rate = $k_{eff}[A]^3$
B) Rate = $k_{eff}[A]^2$
C) Rate = $k_{eff}[A][B]$
D) Rate = $k_{eff}[A]^2[B]$
E) Rate = $k_{eff}[A]$

8. An enzyme-substrate system obeys the simple Michaelis-Menten mechanism:

$$S + E \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [S.E]$$

$$[S.E] \xrightarrow{k_2} E + \text{Products}$$

The rate of product formation at large substrate concentration has the limiting value 0.02 mol sec^{-1}. The rate is half of this value at a substrate concentration of 200 mg L^{-1}. Calaculate k_1/k_{-1} assuming that $k_2 << k_{-1}$.

A) 0.005 L mg^{-1}
B) 0.110 L mg^{-1}
C) 5 L mg^{-1}
D) 10 L mg^{-1}
E) 0.001 L mg^{-1}

9. The oxidation of HSO_3^- by O_2 in aqueous solution is a reaction of importance to processes of acid rain formation and flue gas desulfurization, which is reported to be

$$2HSO_3^- + O_2 \xrightarrow{k} 2\,SO_4^{-2} + 2\,H^+$$

The rate law of this process is found to be

Q7

$$2A + B \xrightarrow{k_{eff}} C + D$$

(1) $2A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_2$ fast

(2) $A_2 + A \xrightarrow{k_2} A_3$ slow

(3) $A_3 + B \xrightarrow{k_3} A + C + D$ fast

$$\text{Rate} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

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

SSA for A_3 (fast decay)

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

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

$$k_3[A_3][B] = k_2[A_2][A]$$

$$\frac{[A_2]}{[A]^2} = K_1 \qquad [A_2] = K_1 [A]^2$$

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

$$k_3[A_3][B] = k_2 K_1 [A]^2 [A]$$

$$\Rightarrow \text{Rate} = \frac{d[C]}{dt} = k_2 K_1 [A]^3$$

$$= k_{eff} [A]^3 \quad ⓐ$$

$$k_{eff} = k_2 K_1$$

(Q8)

Lineweaver – Burk equation:

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

$$K_m = \left(\frac{1}{R_0} - \frac{1}{R_{max}}\right) R_{max} \cdot [S]$$

$$= \left(\frac{1}{0{,}01} - \frac{1}{0.02}\right) \frac{s}{mol} R_{max} \cdot [S]$$

$$= 50 \frac{s}{mol}\ 0.02 \frac{mol}{s} \cdot 200 \frac{mg}{L}$$

$$= 200 \frac{mg}{L}$$

$$K_m = \frac{k_{-1} + k_2}{k_1} = \frac{k_{-1}}{k_1}$$

since $k_2 << k_{-1}$

$$\frac{k_1}{k_{-1}} = \frac{1}{K_m} = \frac{1}{200} \frac{L}{mg} = 0.005 \frac{L}{mg}$$

Ⓐ

$$\text{Rate} = k\,[HSO_3^-]^2[H^+]^2$$

Given pH = 5.6 and an oxygen molar concentration of 2.4×10^{-4} mol dm^{-3} (both presumed constant), an initial HSO_3^- molar concentration 5×10^{-5} mol dm^{-3}, and rate constant of 3.6×10^{6} dm^{9} mol^{-3} s^{-1}, how long would it take for HSO_3^- to reach half its initial concentration?

A) [illegible]yr 14-yr ✓ [illegible]

B) 1 yr

C) 4.0×10^{5} s

D) 11 days

E) 150 days

10. For the consecutive reactions;

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

the rate of concentration changes of the intermediate I is given by,

$$\frac{d[I]}{dt} = k_1[A] - k_2[I].$$

The maximum intermediate concentration is reached when d[I]/dt = 0.
Given

$$[A]=[A]_0 e^{-k_1 t} \quad \text{and} \quad [I]=\frac{k_1}{k_2-k_1}\left(e^{-k_1 t}-e^{-k_2 t}\right)[A]_0$$

the time, t_{max}, at which [I] is at a maximum should be given by

A) $t_{max} = \{1/(k_1-k_2)\} \ln (k_1/k_2)$
B) $t_{max} = \{k_1/(k_1-k_2)\} \ln (k_1/k_2)$
C) $t_{max} = k_1/(k_1-k_2)$
D) $t_{max} = \{k_2/(k_1-k_2)\} \ln (k_1/k_2)$
E) $t_{max} = k_1/(k_2-k_1)$

11. The following free radical mechanism has been proposed for the thermal decomposition of acetaldehyde (ethanal):

Ⓠ8

$$2 HSO_3^- + O_2 \xrightarrow{k} 2 SO_4^{2-} + 2H^+$$

$$Rate = k [HSO_3^-]^2 [H^+]^2 \qquad -\frac{1}{2}\frac{d[HSO_3^-]}{dt} = Rate$$

$pH = 5.6 = const.$

$[O_2] = 2.4 \cdot 10^{-4} M = const$ $\qquad -\frac{d[HSO_3^-]}{dt} = \cancel{2 Rate}$ $2 \cdot Rate$

$[HSO_3^-]_0 = 5 \cdot 10^{-5} M$

$$k = 3.6 \cdot 10^{6} \frac{1}{M^3 s}$$

2. order with reespect to HSO_3^-

$$\Rightarrow \quad t_{1/2}(HSO_3^-) = \frac{1}{2 k_{eff} [HSO_3^-]_0}$$

$$\cancel{= \frac{1}{3.6 \cdot 10^6 \frac{1}{M^3 s}}}$$

$k_{eff} = k [H^+]^2 \qquad [H^+] = const$

$pH = -\log_{10} [H^+]$

$$[H^+] = 10^{-pH} M = 10^{-5.6} M = 2.512 \cdot 10^{-6} M$$

$$k_{eff} = 3.6 \cdot 10^{+6} \frac{1}{M^3 s} (2.512 \cdot 10^{-6} M)^2$$

$$= 22.72 \cdot 10^{-6} \frac{1}{Ms} = 2.272 \cdot 10^{-5} \frac{1}{Ms}$$

$$t_{1/2}(H_2SO_3^-) = \frac{1}{2 k_{eff} [HSO_3^-]_0} = \frac{1}{2 \cdot 2.272 \cdot 10^{-5} \frac{1}{Ms} \cdot 5 \cdot 10^{-5} M}$$

$$= \overset{4.4015}{\cancel{8.803}} \cdot 10^{8} s = \overset{1.223}{\cancel{2.445}} \cdot 10^{5} h$$

$$= \overset{5094}{\cancel{10190}} d = \overset{13.9}{\cancel{28}} y = 14 y$$

(Q10)

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

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

$$[A] = [A]_0 \, e^{-k_1 t}$$

$$[I] = \frac{k_1}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t}\right)[A]$$

$$t_{max} \equiv t_m$$

$$\left.\frac{d[I]}{dt}\right|_{t=t_m} = 0 \quad \text{at } t_m$$

$$\overset{\checkmark}{k_1} \overset{\checkmark}{[A]_0} \, e^{-k_1 t_m} = \frac{k_2 \overset{\checkmark}{k_1}}{k_2 - k_1} \left(e^{-k_1 t_m} - e^{-k_2 t_m}\right)\overset{\checkmark}{[A]_0}$$

$$e^{-k_1 t_m} = \frac{k_2}{k_2 - k_1} \left(e^{-k_1 t_m} - e^{-k_2 t_m}\right)$$

$$\left(1 - \frac{k_2}{k_2 - k_1}\right) e^{-k_1 t_m} = -\frac{k_2}{k_2 - k_1} e^{-k_2 t_m}$$

$$\frac{k_2 - k_1 - k_2}{k_2 - k_1} e^{-k_1 t_m} = -\frac{k_2}{k_2 - k_1} e^{-k_2 t_m}$$

$$-\frac{k_1}{k_2 - k_1} e^{-k_1 t_m} = -\frac{k_2}{k_2 - k_1} e^{-k_2 t_m}$$

$$-\frac{k_1}{k_2} e^{-k_1 t_m} = -e^{-k_2 t_m}$$

$$+\frac{k_1}{k_2} = e^{(k_1 - k_2) \cdot t_m}$$

~~$\ln \frac{k}{k_2}$~~

$$\ln \frac{k_1}{k_2} = (\cancel{k_2} k_1 - k_2)\, t_m$$

$$t_m = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$ Ⓐ

$$CH_3CHO \xrightarrow{k_1} \bullet CH_3 + CHO$$

$$\bullet CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + \bullet CH_2CHO$$

$$\bullet CH_2CHO \xrightarrow{k_3} \bullet CH_3 + CO$$

$$\bullet CH_3 + \bullet CH_3 \xrightarrow{k_4} CH_3CH_3$$

Based on the proposed mechanism, the apparent rate constant expression and the order of the formation of ethane (CH_3CH_3) should be

$\frac{k_1}{2k_1}$

→ A) k_1 and first order
B) k_1/k_4 and half order
C) $(k_1/k_4)^{1/2}$ and half order
D) k_1 and zero order
E) k_1k_2/k_3 and second order

12. The thermal decomposition of phosphine (PH_3) into phosphorous and molecular hydrogen is a first order process.

$$2PH_3\,(g) \longrightarrow 2P\,(s) + 3H_2\,(g)$$

At 680° C the rate constant for this reaction is $0.0198\ s^{-1}$. You would expect the half-life of phosphine at room temperature (25° C) to be _____ than at 680° C.

A) longer
B) shorter
C) the same
D) Not enough information given. Must know ΔH to answer this.
E) Not enough information given. Must know E_a to answer this.

acetone

13. Iodine and ~~propan~~e react in acid solution according to the equation

$$I_2 + CH_3COCH_3 \longrightarrow CH_3COCH_2I + HI$$

The rate equation for the reaction is found to be

$$\text{rate} = k\,[CH_3COCH_3][H^+]$$

At the start of the experiment, the rate of reaction was found to be 2.00×10^{-5} mol dm^{-3} s^{-1} when the concentrations of the reactants were

(Q11)

ethane C_2H_6 only in 1 step

$$\Rightarrow \frac{d[C_2H_6]}{dt} = k_4[CH_3\cdot]^2$$

SSA for $CH_3\cdot$:

$$\frac{d[CH_3\cdot]}{dt} = k_1[CH_3CHO] - k_2[CH_3\cdot][CH_3CHO]$$

$$+ k_3[\cdot CH_2CHO] - 2k_4[CH_3\cdot]^2 \quad (1)$$

SSA ~~for~~ $\cdot CH_2CHO$:

$$\frac{d[\cdot CH_2CHO]}{dt} = 0 = k_2[\cdot CH_3][CH_3CHO] - k_3[\cdot CH_2CHO] \quad (2)$$

$$(1) + (2): \quad k_1[CH_3CHO] - 2k_4[CH_3\cdot]^2 = 0$$

$$2k_4[CH_3\cdot]^2 = k_1[CH_3CHO]$$

$$\Rightarrow \frac{d[C_2H_6]}{dt} = \frac{k_1}{2\,\text{[illegible]}}[CH_3CHO]$$

$$\Rightarrow k_{eff} = \frac{k_1}{2\,\text{[illegible]}}$$, 1. order (A)

with correction $\frac{k_1}{2k_2}$

(Q12)

$$2PH_3(g) \rightarrow 2P(s) + 3H_2(g)$$

1. order, 680°C: $k = 0.0198\ s^{-1}$

$$t_{1/2} = \frac{\ln 2}{k}$$

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

$\Rightarrow$ k ~~de~~increasing when T increases

exponent E_a/RT decreases when T increases

$\Rightarrow$ $e^{-E_a/RT}$ increases when T increases

$\rightarrow$ k increases when T increases

$\Rightarrow$ $t_{1/2}$ decreases when T increases

$\Rightarrow$ $t_{1/2}$ increase at T decrease

$\Rightarrow$ $t_{1/2}$ ~~too~~ larger at 25°C than at 680°C

Ⓐ

(Q13)

$$I_2 + CH_3COCH_3 \rightarrow CH_3COCH_2I + HI$$

$$R = k[CH_3COCH_3][H^+]$$

$$R_0 = 2.00 \cdot 10^{-5} \text{ M/s}$$

$$[CH_3COCH_3]_0 = 1.50 \text{ M}$$

$$[I_2]_0 = 2.00 \cdot 10^{-2} \text{ M}$$

$$[H^+] = 3.00 \cdot 10^{-2} \text{ M}$$

$$k = \frac{R_0}{[CH_3COCH_3]_0 \, [H^+]_0}$$

$$= \frac{2.00 \cdot 10^{-5} \text{ M/s}}{1.50 \text{ M} \cdot 3.00 \cdot 10^{-2} \text{ M}}$$

$$= 4.44 \cdot 10^{-4} \frac{1}{\text{M s}}$$ Ⓐ

Reactant	Concentration / mol dm^{-3}
CH_3COCH_3	1.50
I_2	2.00×10^{-2}
H^+	3.00×10^{-2}

Use these data to calculate a value for the rate constant and deduce its units.

A) 4.44×10^{-4} dm^3 mol^{-1} s^{-1}

B) 1.25×10^{-4} s^{-1}

C) 2.14×10^{-3} dm^6 mol^{-2} s^{-1}

D) 1.32×10^{-2} dm^3 mol^{-1} s^{-1}

E) 2.15×10^{-4} dm^6 mol^{-2} s^{-1}

14. If reaction A has an activation energy of 250 kJ and reaction B has an activation energy of 100 kJ, which of the following statements **must** be correct?

A) At the same temperature the rate of reaction B is greater than the rate of reaction A.
B) If reaction A is exothermic and reaction B is endothermic then reaction A is favored kinetically.
C) The energy of reaction A must be greater than the energy of reaction B.
D) The energy of reaction B must be greater than the energy of reaction A.

E) The rate of reaction A at 25 °C equals the rate of reaction B at 100 °C.

15. The adsorption of CO gas on charcoal at 273 K fit to the Langmuir isotherm,

$$\theta = \frac{Kp}{1 + Kp} = \frac{V}{V_m}$$

Its linear plot of p/V vs. p of the CO gas variation introduced the

Q14

$$E_a(A) = 250 \text{ kJ}$$

$$E_a(B) = 100 \text{ kJ}$$

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

$$\cancel{k(B)})\ Ae^{-E_a(B)/RT} > Ae^{-E_a(A)/RT}$$

$$\Rightarrow k_B > k_A \quad (A)$$

Q15

$$\theta = \frac{Kp}{1+Kp} = \frac{V}{V_m}$$

$$\frac{P}{V}\left(\frac{kPa}{cm^3}\right) = 1.2\,\frac{kPa}{cm^3} + 0.0090\,\frac{P}{cm^3}$$

$$\frac{1}{\theta} = \frac{1+Kp}{Kp} = \frac{V_m}{V} = 1 + \frac{1}{Kp}$$

$$\cancel{\frac{1}{Kp} = \frac{V_m}{V} - 1}$$

$$\cancel{\frac{V}{Kp} = V_m - V}$$

$$Kp = \frac{V}{V_m}(1+Kp)$$

$$\frac{P}{V} = \frac{1}{K \cdot V_m}(1+Kp) = \frac{1}{K \cdot V_m} + \frac{1}{V_m}P$$

$$\frac{1}{K V_m} = 1.2 \frac{kPa}{cm^3}$$

$$\frac{1}{V_m} = 0.0090 \frac{1}{cm^3}$$

$$V_m = 111.11 \ cm^3$$

$$\frac{1}{K} = 1.20 \frac{kPa}{cm^3} \cdot 111.11 \ cm^3 = 133.332 \ kPa$$

$$K = 7.5 \cdot 10^{-3} \frac{1}{kPa}$$

$$V_m = 111.11 \ cm^3$$

for full coverage with CO, the ideal gas equation holds:

$$P V_m = n R T$$

$$n = \frac{P V_m}{R T}$$

$$= \frac{1 \ atm \cdot 111.11 \ cm^3}{0.0821 \frac{L \, atm}{K \, mol} \cdot 273 \ K}$$

$$= \frac{1 \ atm \cdot 111.11 \ cm^3}{0.0821 \cdot 1000 \frac{cm^3 \, atm}{K \, mol} \cdot 273 \ K}$$

$$= 4.963 \cdot 10^{-3} \ mol$$

aerea $A = 4.963 \cdot 10^{-3} \ mol \cdot 818 \cdot (10^{-9} m)^2 \cdot 6.022 \cdot 10^{23} \frac{1}{mol}$

$$= 2.4 \cdot 10^{6} \ m^2$$

$$= 2.4 \cdot 10^{6} \ m^2 \left(10^{-3} \frac{km}{m}\right)^2 = 2.4 \ km^2$$

$1/V_m$

following least square linear equation

$$P/V\,(\text{kPa/cm}^3) = 1.2\ \text{kPa/cm}^3 + \overset{\overset{1/V_m}{\downarrow}}{\boxed{0.0090}}\ \text{cm}^{-3}\ P$$

Based on these results and given the surface area of a CO molecule 818 nm^2, the adsorption isotherm equilibrium constant (K) and the surface area of 1 g charcoal at 273 K and 1 atm should be

$$V_m \rightarrow n = \frac{PV}{RT}$$

$$n = \frac{1 \times 0.111}{0.0821 \times 273}$$

$$\boxed{n \times (818 \times 10^{-18}) \times N}$$

2.4 km^2

A) 7.5 x 10^{-3} kPa^{-1} and 2.4 km^2

B) 1.1 x 10^{-2} kPa^{-1} and 1.6 km^2

C) 7.5 x 10^{-3} kPa^{-1} and 5.1 km^2

D) 3.2 x 10^{-2} kPa^{-1} and 8.2 km^2

E) 1.1 x 10^{-3} kPa^{-1} and 2.4 km^2

16. The quenching of tryptophan fluorescence by dissolved oxygen gas was monitored by measuring emission lifetimes at 348 nm in aqueous solutions. Determine the quenching rate constant for this process from the following data:

$[O_2]/(10^{-2}$ mol dm$^{-3})$	0	2.3	8.0
$\tau/(10^{-9}$ s)	2.6	1.5	0.71

A) 1.3 ~~13~~ x 10^{10} dm^3 mol^{-1} s^{-1} ✓

B) 0.72 x 10^{10} s^{-1}

C) 0.72 x 10^{10} dm^3 mol^{-1} s^{-1}

D) 2.8 x 10^8 dm^3 mol^{-1} s^{-1}

E) 2.8 x 10^8 s^{-1}

$\frac{1}{\tau_f}$ vs $[O_2]$

slope = k_q

intercept = k_f

$$\frac{1}{\tau_f} = k_f + k_q \cdot [Q]$$

(Q 16)

	1	2	3
$[O_2]$ M	0	$2.3 \cdot 10^{-2}$ M	$8.0 \cdot 10^{-2}$ M
τ_f (ns)	2.6	1.5	0.71
$\frac{1}{\tau_f}$ (ns^{-1})	0.385	0.667	1.408

$$\frac{1}{\tau_f} = k_f + k_q [O_2]$$

y x $\frac{1}{\tau_f}$ vs $[O_2]$

~~stope = $[2O_2] - [O_2]$~~

$$slope_{12} = \frac{(0.667 - 0.385)\, ns^{-1}}{(2.3 \cdot 10^{-2} - 0)\, M}$$

$$= \frac{0.282\, (10^{-9} s)^{-1}}{2.3 \cdot 10^{-2}\, M}$$

$$= \frac{0.282 \cdot 10^{+9}\, s^{-1}}{2.3 \cdot 10^{-2}\, M}$$

$$= 1.226 \cdot 10^{10} \frac{1}{Ms}$$

$$slope_{23} = \frac{(1.408 - 0.667) \cdot 10^{+9} \frac{1}{s}}{8 \cdot 10^{-2} - 2.3 \cdot 10^{-2}\, M}$$

$$= \frac{8.13 \cdot 10^{8}}{0.057\, Ms} = 1.\underset{30}{\cancel{43}} \cdot 10^{10} \frac{1}{Ms} = k_q$$

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SAMPLE

1. RIYADH is:

A - a country
B - a mountain
C - an island
D - a city
E - a river

1 A B C [✓ D] E

1 A B C D [✓ E]
2 A [✓ B] C D E
3 A B [✓ C] D E
4 A B [✓ C] D E
5 A [✓ B] C D E
6 [✓ A] B C D E
7 A B [✓ C] D E
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DO NOT USE INK OR BALL POINT PEN

2

SAMPLE

1. RIYADH is:

A - a country *D - a city*
B - a mountain *E - a river*
C - an island

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King Fahd University of Petroleum & Minerals
DHAHRAN 31261, SAUDI ARABIA

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الظهران ٣١٢٦١ المملكة العربية السعودية

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DIRECTIONS:

Read each question and its numbered answers. When you have decided which answer is correct, blacken the corresponding oval on this form with a no. 2 pencil. Make no extra marks. They may be counted as incorrect answers. Erase incorrect answers fully before filling in correct answer.

DO NOT USE INK OR BALL POINT PEN

SAMPLE

1. RIYADH is:

A - a country
B - a mountain
C - an island
D - a city
E - a river

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CHEM 311 (152) **Second Major Exam** **2 HOURS**

Thursday, April 14, 2016, 7:30-9:30 PM

STUDENT NAME: ....

STUDENT ID NUMBER: ....

Test Code (001)

(16 Questions)

Dr. M. Wazeer	Section 1
Dr. M. Morsy	Section 2
Dr. W. Foerner	Section 3
Dr. H. Badawi	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)

Parallel reactions:

A -k$_1$-> B
A -k$_2$-> C

Yield of the reaction:

$\Phi_i = k_i/S$

Where S is the sum of all rate constants of the parallel 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:

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

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

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

Sequential reactions:

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

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

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

Important Equations

$E = h\upsilon$

$c = \upsilon\lambda$

$PV = nRT$

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

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

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

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

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

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

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

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

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

$dP/dt = k\theta$

$\theta = KP/(1 + KP)$, 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

1. The following free radical mechanism has been proposed for the thermal decomposition of acetaldehyde (ethanal):

$$CH_3CHO \xrightarrow{k_1} \bullet CH_3 + CHO$$

$$\bullet CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + \bullet CH_2CHO$$

$$\bullet CH_2CHO \xrightarrow{k_3} \bullet CH_3 + CO$$

$$\bullet CH_3 + \bullet CH_3 \xrightarrow{k_4} CH_3CH_3$$

Based on the proposed mechanism, the apparent rate constant expression and the order of the formation of ethane (CH_3CH_3), respectively, should be

A) $(k_1/k_4)^{1/2}$ and half order
B) k_1 and zero order
C) k_1/k_4 and half order
D) k_1k_2/k_3 and second order
[✓ E)] $k_1/2$ and first order

= ⑪ in Version 0

2. For the reaction A + B ⟶ C, the rate constant at 215 °C is 5.0×10^{-3} s^{-1} and the rate constant at 452° C is 3.0×10^{-1} s^{-1}. What is the rate constant at 100° C.

A) 1.82e–2 s^{-1}
[✓ B)] 1.05e–4 s^{-1}
C) 1.85e–8 s^{-1}
D) 2.34e3 s^{-1}
E) 6.11e3 s^{-1}

③ in 00-Version but there $k_2 = 0,12 \frac{1}{s}$, here $k_2 = 0,3\ s^{-1}$

$$\ln \frac{k_1}{k_2} = \ln \frac{5 \cdot 10^{-3}}{0,3} = -4,0943$$

$$E_a = 50,8436 \frac{kJ}{mol}$$

$$A = 1379.37 \frac{1}{s} \rightarrow k(100°C) = 1,05 \cdot 10^{-4} \frac{1}{s}$$

3. The oxidation of HSO_3^- by O_2 in aqueous solution is a reaction of importance to processes of acid rain formation, which is reported to be

$$2HSO_3^- + O_2 \xrightarrow{k} 2\ SO_4^{-2} + 2\ H^+$$

The rate law of this process is found to be

$$\text{Rate} = k\,[HSO_3^-]^2[H^+]^2$$

Given pH = 5 and an oxygen molar concentration of 2.4×10^{-4} mol dm^{-3} (both presumed constant), an initial HSO_3^- molar concentration 5×10^{-5} mol dm^{-3}, and rate constant of 3.6×10^{6} dm^9 mol^{-3} s^{-1}, how long would it take for HSO_3^- to reach half its initial concentration?

A) 3.2e2 yr
B) 1.0e–5 days
[✓ C)] 8.8e–1 yr
D) 8.8e–1 days
E) 4.0e5 s

(3) in version 0

here $[H^+] = 10^{-5}$ M $k_{eff} = 3.6\cdot10^{-4}\ \frac{1}{Ms}$

$t_{1/2} = 2.8\cdot10^{7}$ s $=$ ~~8.8~~ 0.88 y

4. If reaction A has an activation energy of 300 kJ and reaction B has an activation energy of 175 kJ, which of the following statements **must** be correct?

A) If reaction A is exothermic and reaction B is endothermic then reaction A is favored kinetically.
B) The rate of reaction A at 25 °C equals the rate of reaction B at 100 °C.
[✓ C)] At the same temperature the rate of reaction B is greater than the rate of reaction A.
D) The energy of reaction A must be greater than the energy of reaction B.
E) The energy of reaction B must be greater than the energy of reaction A.

(14) in Verion 0 A

5. The thermal decomposition of phosphine (PH_3) into phosphorous and molecular hydrogen is a first order process.

$$2PH_3\,(g) \longrightarrow 2P\,(s) + 3H_2\,(g)$$

At 680° C the rate constant for this reaction is 0.0198 s^{-1}. You would expect the half-life of phosphine at room temperature (25° C) to be _____ than that at 680° C.

A) the same
[✓ B)] longer
C) Not enough information given. Must know ΔH to answer this.
D) Not enough information given. Must know E_a to answer this.
E) shorter

(12) in Version 0

6. An enzyme-substrate system obeys the simple Michaelis-Menten mechanism:

$$S + E \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [SE]$$

$$[SE] \xrightarrow{k_2} E + \text{Products}$$

The rate of product formation at large substrate concentration has a maximum rate value 0.02 mol sec^{-1}. The rate is half of this value at a substrate concentration of 200 mg L^{-1}. Find the equilibrium constant (K_1) of the [SE]-complex formation assuming that $k_2 << k_{-1}$.

[✓ A)] 2.0e2 L mg^{-1} = ⑧ in version O

B) 10 L mg^{-1}

C) 2.5e1 L mg^{-1}

D) 5.0e2 L mg^{-1}

[✓ E)] 5.0e–3 L mg^{-1}

$K_1 = \frac{k_1}{k_{-1}} = \frac{1}{K_m} = 200 \frac{L}{mg}$

7. The gas phase decomposition data of hydrogen iodide are

***t*, hours**	0	2.0	4.0	6.0
[HI], M	1.00	0.50	0.33	0.25

What are the order and rate constant (k, include units) of this reaction?

A) Second order and k = 2.0 $M^{-1}h^{-1}$

B) First order and k = 0.50 h^{-1} = ⑤ in O version

[✓ C)] Second order and k = 0.50 $M^{-1}h^{-1}$

D) Second order and k = 0.25 Mh^{-1}

E) First order and k = 0.25 h^{-1}

8. The adsorption of CO gas on charcoal at 273 K fit to the Langmuir isotherm,

$$\theta = \frac{Kp}{1+Kp} = \frac{V}{V_m}$$

Its linear plot of p/V vs. p of the CO gas variation introduced the following least square linear equation

$$p/V\ (\text{kPa/cm}^3) = 1.2\ \text{kPa/cm}^3 + 0.0100\ \text{cm}^{-3}\ p$$

Based on these results and given the surface area of a CO molecule 818 nm², the adsorption isotherm equilibrium constant (K) and the surface area of 1 g charcoal at 273 K and 1 atm, respectively, should be

A) 1.2e2 kPa^{-1} and 1.1 km²
B) 1.2e–2 kPa^{-1} and 2.2 km²
C) 1.2e–2 kPa^{-1} and 1.1 km²
D) 8.3e–3 kPa^{-1} and 1.1 km²
[✓ E)] 8.3e–3 kPa^{-1} and 2.2 km²

⑮ in Version 0

$V_m = 100\ cm^3$

$n = 4.467 \cdot 10^{-3}\ mol$, $A = 2.2\ km^2$

$K = 8.3 \cdot 10^{-3}\ \frac{1}{k\,Pa}$

9. Iodine and acetone react in acid solution according to the equation

$$I_2 + CH_3COCH_3 \longrightarrow CH_3COCH_2I + HI$$

The rate equation for the reaction is found to be

$$\text{rate} = k\,[CH_3COCH_3][H^+]$$

At the start of the experiment, the rate of reaction was found to be 2.00 × 10^{-5} mol dm^{-3} s^{-1} when the concentrations of the reactants were

Reactant	Concentration / mol dm^{-3}
CH_3COCH_3	1.50
I_2	2.00 × 10^{-4}

Use these data to calculate a value for the rate constant at pH = 2.0 and deduce its units.

A) 1.50e2 dm^6 mol^{-2} s^{-1}
[✓ B)] 1.33e–3 dm^3 mol^{-1} s^{-1}
C) 1.00e–2 dm^3 mol^{-1} s^{-1}
D) 1.33e–7 s^{-1}
E) 6.67e–2 dm^6 mol^{-2} s^{-1}

⑬ in Version 0

$pH = 2$, $[H^+] = 10^{-2}\ M$

$$k = \frac{2 \cdot 10^{-5}\ M/s}{1.5\,M \cdot 10^{-2}\,M}$$

$$= 1.33 \cdot 10^{-3}\ \frac{1}{M\,s}$$

10. The combustion of ethane (C_2H_6) is represented by the equation:

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$$

In this reaction:

A) the rate of consumption of oxygen equals the rate of consumption of water.
B) the rate of formation of CO_2 equals the rate of formation of water.
C) water is formed at a rate equal to two-thirds the rate of formation of CO_2.
[✓ D)] CO_2 is formed twice as fast as ethane is consumed.
E) the rate of consumption of ethane is seven times faster than the rate of consumption of oxygen.

same as ① 0 Version → (D)

11. A possible mechanism for the reaction,

$$2A + B \longrightarrow C + D,$$

is:

(1) $A + A \rightleftharpoons A_2$ fast, equilibrium
(2) $A_2 + A \longrightarrow A_3$ slow
(3) $A_3 + B \longrightarrow A + C + D$ fast

According to the mechanism, the rate law will be:

A) Rate = $k_{eff}[A]$
B) Rate = $k_{eff}[A][B]$
C) Rate = $k_{eff}[A]^3[B]$
[✓ D)] Rate = $k_{eff}[A]^3$
E) Rate = $k_{eff}[A]^2$

same as ⑦ in Version 0

12. The initial rate of the reaction between substances A and **B** is measured in a series of experiments as follows

Expt	Initial rate/mol dm^{-3} s^{-1}	Initial [**A**]/mol dm^{-3}	Initial [**B**]/mol dm^{-3}
1	1.5×10^{-2}	0.30	0.30
2	3.0×10^{-2}	X	0.60

Given the order with respect to each reactant is one, the X-value of the initial concentration of the reactant A in experiment 2 should be

A) 10.00
B) 3.33
[✓ C)] 0.30
D) 0.11
E) 0.54

= ② in Version 0

$$X = \frac{3\cdot10^{-2}\ M/s}{0{,}6\ M \cdot 0{,}1667\ \frac{1}{Ms}}$$

= 0,3 M

13. Given that an endothermic reaction has an activation energy of 25 kJ/mol, which of the following statements are **correct**?

I. The reverse reaction has an activation energy equal to 25 kJ/mol.
II. The reverse reaction has an activation energy less than 25 kJ/mol.
III. The reverse reaction has an activation energy greater than 25 kJ/mol.
IV. The change in internal energy is less than zero.
V. The change in internal energy is greater than zero.

A) II and IV
B) III and IV
C) I and IV
D) III and V
[✓ E)] II and V

Ⓒ in O version

II, V correct

14. The quenching of tryptophan fluorescence by dissolved oxygen gas was monitored by measuring emission lifetimes at 348 nm in aqueous solutions. Determine the fluorescence and quenching rate constants in for this process from the following data:

	①	②	③
$[O_2]/(10^{-2}$ mol dm$^{-3})$	0.0	2.3	8.0
$\tau/(10^{-9}$ s)	2.72	1.50	0.71

A) 1.1 x 10^8 and 2.8 x 10^8 dm^3 mol^{-1} s^{-1}
[✓ B)] 3.7 x 10^8 and 1.3 x 10^{10} dm^3 mol^{-1} s^{-1}
C) 8.1 x 10^8 and 1.3 x 10^{11} s^{-1}
D) 3.7 x 10^8 and 0.72 x 10^{10} dm^3 mol^{-1} s^{-1}
E) 1.1 x 10^8 and 0.72 x 10^{10} s^{-1}

⑯ in version 0

15. The decomposition of dimethylether at 504 °C is first order with a half-life of 1570 seconds. What fraction of an initial amount of dimethylether remains after 6280 seconds?

A) 0.02
B) 0.05
C) 0.333333
D) 0.2
[✓ E)] 0.0625

④ in 0 version with 4710 s instead of 6280s

$$e^{-kt} = 0.0625$$

	①	②	③
$[O_2]/M$	0	$2.3 \cdot 10^{-2}$	$8.0 \cdot 10^{-2}$
τ_f (ns)	2.72	1.50	0.71
$\frac{1}{\tau_f}$ (ns^{-1}) =	0.3676	0.6667	1.4085

$$\text{slope}_{12} = \frac{(\cancel{0.3676}\ 0.6667 - 0.3676)\ \text{ns}^{-1}}{2.3 \cdot 10^{-2}\ M}$$

$$= 13.004 \frac{1}{M\,\text{ns}}$$

$$\text{slope}_{23} = \frac{(1.4085 - 0.667)\ \text{ns}^{-1}}{(8 - 2.3) \cdot 10^{-2}\ M}$$

$$= 13.0140 \frac{1}{M\,\text{ns}}$$ ✓ next page

16. For the consecutive reactions;

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

the rate of concentration changes of the intermediate I is given by,

$$\frac{d[I]}{dt} = k_1[A] - k_2[I].$$

The maximum intermediate concentration is reached when d[I]/dt = 0.
Given

$$[A]=[A]_0 e^{-k_1 t} \quad \text{and}$$

$$[I]=\frac{k_1}{k_2-k_1}\left(e^{-k_1 t}-e^{-k_2 t}\right)[A]_0$$

the time, t_{max}, at which [I] is at a maximum should be given by

A) $t_{max} = k_1/(k_1-k_2)$

B) $t_{max} = k_1/(k_2-k_1)$

C) $t_{max} = (k_1/(k_1-k_2)) \ln (k_1/k_2)$

[✓ D)] $t_{max} = (1/(k_1-k_2)) \ln (k_1/k_2)$ = ⑩ in O Version

E) $t_{max} = (k_2/(k_1-k_2)) \ln (k_1/k_2)$

from Q 15, page before:

$$= 1{,}30 \cdot 10^{10} \frac{1}{Ms} = k_q$$

$$k_f = \frac{1}{\tau_f} - k_q [O_2] = 0{,}3676\ ns^{-1} - 1{,}3 \cdot 10^{10} \frac{1}{Ms} \times$$

$$= 0{,}37\ (10^{-9} s)^{-1} = 0{,}37 \cdot 10^{+9} \frac{1}{s}$$

$$\cancel{= 0{,}3}\ 3{,}7 \cdot 10^{+8} \frac{1}{s}$$

CHEM 311 (152)

Second Major Exam

Thursday, April 14, 2016, 7:30-9:30 PM

2 HOURS

STUDENT NAME: ....

STUDENT ID NUMBER: ....

Test Code (002)

(16 Questions)

Dr. M. Wazeer	Section 1
Dr. M. Morsy	Section 2
Dr. W. Foerner	Section 3
Dr. H. Badawi	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)

Parallel reactions:

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

Yield of the reaction:

$\Phi_i = k_i/S$

Where S is the sum of all rate constants of the parallel 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:

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

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

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

Sequential reactions:

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

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

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

Important Equations

$E = h\upsilon$

$c = \upsilon\lambda$

$PV = nRT$

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

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

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

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

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

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

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

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

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

$dP/dt = k\theta$

$\theta = KP/(1 + KP)$, 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

1. The quenching of tryptophan fluorescence by dissolved oxygen gas was monitored by measuring emission lifetimes at 348 nm in aqueous solutions. Determine the fluorescence and quenching rate constants in for this process from the following data:

$[O_2]/(10^{-2}\ \text{mol dm}^{-3})$	0.0	2.3	8.0
$\tau/(10^{-9}\ \text{s})$	2.72	1.50	0.71

A) 3.7×10^8 and $0.72 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$
B) 1.1×10^8 and $2.8 \times 10^8\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$
[✓ C)] 3.7×10^8 and $1.3 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$
D) 1.1×10^8 and $0.72 \times 10^{10}\ \text{s}^{-1}$
E) 8.1×10^8 and $1.3 \times 10^{11}\ \text{s}^{-1}$

16
Same as ~~[illegible]~~ in
Version 0

2. If reaction A has an activation energy of 275 kJ and reaction B has an activation energy of 125 kJ, which of the following statements **must** be correct?

[✓ A)] At the same temperature the rate of reaction B is greater than the rate of reaction A.
B) If reaction A is exothermic and reaction B is endothermic then reaction A is favored kinetically.
C) The energy of reaction A must be greater than the energy of reaction B.
D) The energy of reaction B must be greater than the energy of reaction A.
E) The rate of reaction A at 25 °C equals the rate of reaction B at 100 °C.

(14) in Version 0

3. The adsorption of CO gas on charcoal at 273 K fit to the Langmuir isotherm,

$$\theta = \frac{Kp}{1+Kp} = \frac{V}{V_m}$$

Its linear plot of p/V vs. p of the CO gas variation introduced the following least square linear equation

$$p/V\ (\text{kPa/cm}^3) = 1.2\ \text{kPa/cm}^3 + 0.0010\ \text{cm}^{-3}\ p$$

Based on these results and given the surface area of a CO molecule 818 nm^2, the adsorption isotherm equilibrium constant (K) and the surface area of 1 g charcoal at 273 K and 1 atm, respectively, should be

A) 8.3e–4 kPa^{-1} and 11.0 km^2
B) 1.2e3 kPa^{-1} and 11.0 km^2
[✓ C)] 8.3e–4 kPa^{-1} and 22.0 km^2
D) 1.2e–3 kPa^{-1} and 11.0 km^2
E) 1.2e–3 kPa^{-1} and 22.0 km^2

Same as (15) in Version B

V_m = 1000 cm^3

n = 4.467 · 10^{-2} mol

$K = 8.3 \cdot 10^{-4} \frac{1}{kPa}$

A = 22 km^2

4. The oxidation of HSO_3^- by O_2 in aqueous solution is a reaction of importance to processes of acid rain formation, which is reported to be

$$2HSO_3^- + O_2 \xrightarrow{k} 2\ SO_4^{-2} + 2\ H^+$$

The rate law of this process is found to be

$$\text{Rate} = k\,[HSO_3^-]^2[H^+]^2$$

Given pH = 5 and an oxygen molar concentration of 2.4 × 10^{-4} mol dm^{-3} (both presumed constant), an initial HSO_3^- molar concentration 5 × 10^{-5} mol dm^{-3}, and rate constant of 3.6 × 10^{6} dm^{9} mol^{-3} s^{-1}, how long would it take for HSO_3^- to reach half its initial concentration?

[✓ A)] 8.8e–1 yr
B) 4.0e5 s
C) 8.8e–1 days
D) 1.0e–5 days
E) 3.2e2 yr

Same as (9) in Version O

$t_{1/2}$ = 0.88 y

5. Iodine and acetone react in acid solution according to the equation

$$I_2 + CH_3COCH_3 \longrightarrow CH_3COCH_2I + HI$$

The rate equation for the reaction is found to be

$$\text{rate} = k\,[CH_3COCH_3][H^+]$$

At the start of the experiment, the rate of reaction was found to be 2.00×10^{-5} mol $\mathrm{dm^{-3}\,s^{-1}}$ when the concentrations of the reactants were

Reactant	Concentration / mol $\mathrm{dm^{-3}}$
CH_3COCH_3	1.50
I_2	2.00×10^{-4}

Use these data to calculate a value for the rate constant at pH = 1.2 and deduce its units.

A) 8.41e–7 $\mathrm{s^{-1}}$
B) 1.00e–2 $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$
C) 6.67e–2 $\mathrm{dm^6\,mol^{-2}\,s^{-1}}$
[✓ D)] 2.11e–4 $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$
E) 2.38e1 $\mathrm{dm^6\,mol^{-2}\,s^{-1}}$

⑬ in Version O

pH = 1,2 , $[H^+] = 0{,}0631\,(M)$

$$k = \frac{2\cdot 10^{-5}\,M/s}{1{,}5\,M \cdot 0{,}0631\,M} = 2{,}11\cdot 10^{-4}\,\frac{1}{Ms}$$

6. For the consecutive reactions;

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

the rate of concentration changes of the intermediate I is given by,

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

The maximum intermediate concentration is reached when d[I]/dt = 0. Given

$$[A] = [A]_0 e^{-k_1 t} \quad \text{and}$$

$$[I] = \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)[A]_0$$

the time, t_{max}, at which [I] is at a maximum should be given by

A) $t_{max} = (k_2/(k_1-k_2)) \ln (k_1/k_2)$
B) $t_{max} = k_1/(k_1-k_2)$
C) $t_{max} = k_1/(k_2-k_1)$
D) $t_{max} = (k_1/(k_1-k_2)) \ln (k_1/k_2)$
[✓ E)] $t_{max} = (1/(k_1-k_2)) \ln (k_1/k_2)$

⑩ in Version O

7. The thermal decomposition of phosphine (PH_3) into phosphorous and molecular hydrogen is a first order process.

$$2PH_3\ (g) \longrightarrow 2P\ (s) + 3H_2\ (g)$$

At 680° C the rate constant for this reaction is 0.0198 s^{-1}. You would expect the half-life of phosphine at room temperature (25° C) to be _____ than that at 680° C.

A) Not enough information given. Must know E_a to answer this.
B) the same
C) shorter
D) Not enough information given. Must know ΔH to answer this.
[✓ E) longer]

⑫ in Version 0

8. The initial rate of the reaction between substances **A** and **B** is measured in a series of experiments as follows

Expt	Initial rate/mol dm^{-3} s^{-1}	Initial [A]/mol dm^{-3}	Initial [**B**]/mol dm^{-3}
1	1.5×10^{-2}	0.30	0.30
2	3.0×10^{-2}	X	0.60

Given the order with respect to each reactant is one, the X-value of the initial concentration of the reactant A in experiment 2 should be

A) 3.33
[✓ B) 0.30]
C) 0.11
D) 0.54
E) 10.00

② in Version 0

X = 0,3 M

9. Given that an endothermic reaction has an activation energy of 25 kJ/mol, which of the following statements are **correct**?

I. The reverse reaction has an activation energy equal to 25 kJ/mol.
II. The reverse reaction has an activation energy less than 25 kJ/mol.
III. The reverse reaction has an activation energy greater than 25 kJ/mol.
IV. The change in internal energy is less than zero.
V. The change in internal energy is greater than zero.

[✓ A) II and V]
B) III and V
C) III and IV
D) II and IV
E) I and IV

⑥ in Version 0

II, V correct

10. For the reaction A + B $\longrightarrow$ C, the rate constant at 215 °C is 5.0×10^{-3} s^{-1} and the rate constant at 452° C is 5.5×10^{-1} s^{-1}. What is the rate constant at 100° C.

[✓ A)] 5.94e–5 s^{-1}
B) 2.59e3 s^{-1}
C) 7.02e3 s^{-1}
D) 4.88e–9 s^{-1}
E) 1.99e–2 s^{-1}

③ in Version 0

$$\ln \frac{k_1}{k_2} = \cancel{\ln}\frac{5 \cdot 10^{-3}}{0{,}55} = -4{,}7005$$

$$E_a = \cancel{112{,}367}\ \underset{58{,}370}{} \frac{kJ}{mol}\ ,\ A = \cancel{0{,}4617}\ 8812\ \frac{1}{s}$$

$$k(100°C) = 5{,}94 \cdot 10^{-5}\ \frac{1}{s}$$

11. An enzyme-substrate system obeys the simple Michaelis-Menten mechanism:

$$S + E \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [SE]$$

$$[SE] \xrightarrow{k_2} E + \text{Products}$$

The rate of product formation at large substrate concentration has a maximum rate value 0.02 mol sec^{-1}. The rate is half of this value at a substrate concentration of 120 mg L^{-1}. Find the equilibrium constant (K_1) of the [SE]-complex formation assuming that $k_2 \ll k_{-1}$.

A) 10 L mg^{-1}
B) 4.2e1 L mg^{-1}
C) 5.0e2 L mg^{-1}
[✓ D)] 8.3e–3 L mg^{-1}
E) 1.2e2 L mg^{-1}

⑨ in Version 0

$$K_m = 120\ \frac{mg}{L}$$

$$\frac{k_1}{k_{-1}} = \frac{1}{K_m} = 8{,}3 \cdot 10^{-3}\ \frac{L}{mg}$$

12. The following free radical mechanism has been proposed for the thermal decomposition of acetaldehyde (ethanal):

$$CH_3CHO \xrightarrow{k_1} \bullet CH_3 + CHO$$

$$\bullet CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + \bullet CH_2CHO$$

$$\bullet CH_2CHO \xrightarrow{k_3} \bullet CH_3 + CO$$

$$\bullet CH_3 + \bullet CH_3 \xrightarrow{k_4} CH_3CH_3$$

Based on the proposed mechanism, the apparent rate constant expression and the order of the formation of ethane (CH_3CH_3), respectively, should be

A) k_1k_2/k_3 and second order
B) $(k_1/k_4)^{1/2}$ and half order
[✓ C)] $k_1/2$ and first order
D) k_1/k_4 and half order
E) k_1 and zero order

⑪ in Version O

13. The decomposition of dimethylether at 504 °C is first order with a half-life of 1570 seconds. What fraction of an initial amount of dimethylether remains after 3140 seconds?

[✓ A)] 0.25
B) 0.2
C) 0.05
D) 0.02
E) 0.333333

④ in O version but
there 4710 s
here $e^{-kt} = 0.25$

14. The gas phase decomposition data of hydrogen iodide are

***t*, hours**	0	2.0	4.0	6.0
[HI], M	1.00	0.50	0.33	0.25

What are the order and rate constant (k, include units) of this reaction?

[✓ A)] Second order and k = 0.50 $M^{-1}h^{-1}$ ⑤ in 0 version
B) Second order and k = 0.25 Mh^{-1}
C) First order and k = 0.50 h^{-1}
D) First order and k = 0.25 h^{-1}
E) Second order and k = 2.0 $M^{-1}h^{-1}$

15. A possible mechanism for the reaction,

$$2A + B \longrightarrow C + D,$$

is:

(1) $A + A \rightleftharpoons A_2$ fast, equilibrium
(2) $A_2 + A \longrightarrow A_3$ slow
(3) $A_3 + B \longrightarrow A + C + D$ fast

According to the mechanism, the rate law will be:

A) Rate = $k_{eff}[A]^3[B]$ same as ⑦ in Version 0
B) Rate = $k_{eff}[A]$
[✓ C)] Rate = $k_{eff}[A]^3$
D) Rate = $k_{eff}[A]^2$
E) Rate = $k_{eff}[A][B]$

16. The combustion of ethane (C_2H_6) is represented by the equation:

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$$

In this reaction:

A) water is formed at a rate equal to two-thirds the rate of formation of CO_2.
B) the rate of consumption of ethane is seven times faster than the rate of consumption of oxygen.
C) the rate of formation of CO_2 equals the rate of formation of water.
D) the rate of consumption of oxygen equals the rate of consumption of water.
[✓ E)] CO_2 is formed twice as fast as ethane is consumed. Same as ① in Version 0

CHEM 311 (152) **Second Major Exam** 2 HOURS
Thursday, April 14, 2016, 7:30-9:30 PM

STUDENT NAME: ....

STUDENT ID NUMBER: ....

Q 10 rounding problems
8,44 is not 8,41!

Test Code (003)

(16 Questions)

Dr. M. Wazeer	Section 1
Dr. M. Morsy	Section 2
Dr. W. Foerner	Section 3
Dr. H. Badawi	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)

Parallel reactions:

A -k$_1$-> B
A -k$_2$-> C

Yield of the reaction:

$\Phi_i = k_i/S$

Where S is the sum of all rate constants of the parallel 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:

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

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

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

Sequential reactions:

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

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

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

Important Equations

$E = h\upsilon$

$c = \upsilon\lambda$

$PV = nRT$

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

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

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

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

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

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

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

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

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

$dP/dt = k\theta$

$\theta = KP/(1+KP)$, 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

1. For the reaction $A + B \longrightarrow C$, the rate constant at 215 °C is $5.0 \times 10^{-3}\ s^{-1}$ and the rate constant at 452° C is $2.0 \times 10^{-1}\ s^{-1}$. What is the rate constant at 100° C.
   A) 2.17e3 s^{-1}
   B) 4.49e–8 s^{-1}
   C) 1.70e–2 s^{-1}
   D) 5.51e3 s^{-1}
   [✓ E)] 1.54e–4 s^{-1}

③ in O Version

$$\ln \frac{k_1}{k_2} = -3{,}6889$$

$$E_a = 45.809\ \frac{kJ}{mol} \qquad A = 399\ \frac{1}{s}$$

$$k(100^\circ C) = 1{,}54 \cdot 10^{-4}\ \frac{1}{s}$$

2. The following free radical mechanism has been proposed for the thermal decomposition of acetaldehyde (ethanal):

$$CH_3CHO \xrightarrow{k_1} \bullet CH_3 + CHO$$

$$\bullet CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + \bullet CH_2CHO$$

$$\bullet CH_2CHO \xrightarrow{k_3} \bullet CH_3 + CO$$

$$\bullet CH_3 + \bullet CH_3 \xrightarrow{k_4} CH_3CH_3$$

Based on the proposed mechanism, the apparent rate constant expression and the order of the formation of ethane (CH_3CH_3), respectively, should be
   A) k_1/k_4 and half order
   [✓ B)] $k_1/2$ and first order
   C) k_1k_2/k_3 and second order
   D) k_1 and zero order
   E) $(k_1/k_4)^{1/2}$ and half order

⑪ in Version O

3. The oxidation of HSO_3^- by O_2 in aqueous solution is a reaction of importance to processes of acid rain formation, which is reported to be

$$2HSO_3^- + O_2 \xrightarrow{k} 2\,SO_4^{-2} + 2\,H^+$$

The rate law of this process is found to be

$$\text{Rate} = k\,[HSO_3^-]^2[H^+]^2$$

Given pH = 5.4 and an oxygen molar concentration of 2.4×10^{-4} mol dm^{-3} (both presumed constant), an initial HSO_3^- molar concentration 5×10^{-5} mol dm^{-3}, and rate constant of 3.6×10^6 dm^9 mol^{-3} s^{-1}, how long would it take for HSO_3^- to reach half its initial concentration?

A) 4.0e5 s
B) 2.0e3 yr
[✓ C)] 5.6e0 yr
D) 5.6e0 days
E) 4.0e–6 days

⑨ in Version 0

$[H^+] = 10^{-5.4}\ M = 3.981 \cdot 10^{-6}\ M$

$k_{eff} = 5.705 \cdot 10^{-5}\ \frac{1}{Ms}$

$t_{1/2} = 1.75 \cdot 10^{8}\ s = 5.6\ y$

4. The initial rate of the reaction between substances **A** and **B** is measured in a series of experiments as follows

Expt	Initial rate/mol dm^{-3} s^{-1}	Initial [A]/mol dm^{-3}	Initial [B]/mol dm^{-3}
1	1.5×10^{-2}	0.30	0.30
2	5.0×10^{-2}	X	0.60

Given the order with respect to each reactant is one, the X-value of the initial concentration of the reactant A in experiment 2 should be

A) 0.11
B) 0.90
C) 16.67
D) 5.56
[✓ E)] 0.50

② in version 0

$$X = \frac{5 \cdot 10^{-2}\ M/s}{0.6\ M \cdot 0.1667\ \frac{1}{Ms}}$$

$= 0.50\ M$

5. For the consecutive reactions;

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

the rate of concentration changes of the intermediate I is given by,

$$\frac{d[I]}{dt} = k_1[A] - k_2[I].$$

The maximum intermediate concentration is reached when d[I]/dt = 0. Given

$$[A]=[A]_0 e^{-k_1 t} \quad \text{and}$$

$$[I]=\frac{k_1}{k_2-k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)[A]_0$$

the time, t_{max}, at which [I] is at a maximum should be given by

[✓ A)] $t_{max} = (1/(k_1-k_2)) \ln (k_1/k_2)$
B) $t_{max} = (k_1/(k_1-k_2)) \ln (k_1/k_2)$
C) $t_{max} = k_1/(k_1-k_2)$
D) $t_{max} = (k_2/(k_1-k_2)) \ln (k_1/k_2)$
E) $t_{max} = k_1/(k_2-k_1)$

⑩ in version 0

6. If reaction A has an activation energy of 300 kJ and reaction B has an activation energy of 200 kJ, which of the following statements **must** be correct?

A) The energy of reaction B must be greater than the energy of reaction A.
B) The energy of reaction A must be greater than the energy of reaction B.
[✓ C)] At the same temperature the rate of reaction B is greater than the rate of reaction A.
D) The rate of reaction A at 25 °C equals the rate of reaction B at 100 °C.
E) If reaction A is exothermic and reaction B is endothermic then reaction A is favored kinetically.

⑭ in Version 0

7. The gas phase decomposition data of hydrogen iodide are

***t*, hours**	0	2.0	4.0	6.0
[HI], M	1.00	0.50	0.33	0.25

What are the order and rate constant (k, include units) of this reaction?

A) First order and k = 0.50 h^{-1}

B) Second order and k = 2.0 $M^{-1}h^{-1}$

C) First order and k = 0.25 h^{-1}

D) Second order and k = 0.25 Mh^{-1}

[✓ E)] Second order and k = 0.50 $M^{-1}h^{-1}$

⑤ in Version D

8. The combustion of ethane (C_2H_6) is represented by the equation:

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$$

In this reaction:

A) the rate of formation of CO_2 equals the rate of formation of water.

B) the rate of consumption of oxygen equals the rate of consumption of water.

[✓ C)] CO_2 is formed twice as fast as ethane is consumed.

D) water is formed at a rate equal to two-thirds the rate of formation of CO_2.

E) the rate of consumption of ethane is seven times faster than the rate of consumption of oxygen.

① in Version D

9. An enzyme-substrate system obeys the simple Michaelis-Menten mechanism:

$$\mathrm{S + E} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{[SE]}$$

$$\mathrm{[SE]} \xrightarrow{k_2} \mathrm{E + Products}$$

The rate of product formation at large substrate concentration has a maximum rate value 0.02 mol sec^{-1}. The rate is half of this value at a substrate concentration of 140 mg L^{-1}. Find the equilibrium constant (K_1) of the [SE]-complex formation assuming that $k_2 << k_{-1}$.

A) 3.6e1 L mg^{-1}
B) 5.0e2 L mg^{-1}
[✓ C) 7.1e–3 L mg^{-1}]
D) 1.4e2 L mg^{-1}
E) 10 L mg^{-1}

⑧ in Version O

$$K_m = 50 \cdot 0.02 \cdot 140 \frac{mg}{L} = 140 \frac{mg}{L}$$

$$K_1 = \frac{k_1}{k_{-1}} = \frac{1}{K_m} = 7.1 \cdot 10^{-3} \frac{L}{mg}$$

10. Iodine and acetone react in acid solution according to the equation

$$I_2 + CH_3COCH_3 \longrightarrow CH_3COCH_2I + HI$$

The rate equation for the reaction is found to be

$$\text{rate} = k\,[CH_3COCH_3][H^+]$$

At the start of the experiment, the rate of reaction was found to be 2.00×10^{-5} mol dm^{-3} s^{-1} when the concentrations of the reactants were

Reactant	Concentration / mol dm^{-3}
CH_3COCH_3	1.50
I_2	2.00×10^{-4}

Use these data to calculate a value for the rate constant at pH = 1.8 and deduce its units.

A) 1.00e–2 dm^{3} mol^{-1} s^{-1}
[✓ B) 8.41e–4 dm^{3} mol^{-1} s^{-1}]
C) 9.46e1 dm^{6} mol^{-2} s^{-1}
D) 6.67e–2 dm^{6} mol^{-2} s^{-1}
E) 2.11e–7 s^{-1}

⑬ in Version O

$pH = 1.8$, $[H^+] = 0.0158\,M$

$$k = \frac{2 \cdot 10^{-5}\ M/s}{1.5M \cdot 0.0158M} = 8.44 \cdot 10^{-4} \frac{1}{Ms}$$

11. The decomposition of dimethylether at 504 °C is first order with a half-life of 1570 seconds. What fraction of an initial amount of dimethylether remains after 7850 seconds?

4
~~46~~ in Version O

A) 0.2
B) 0.333333
C) 0.02
[✓ D)] 0.03125
E) 0.05

$e^{-kt} = 0.03125$

12. The adsorption of CO gas on charcoal at 273 K fit to the Langmuir isotherm,

$$\theta = \frac{Kp}{1+Kp} = \frac{V}{V_m}$$

Its linear plot of p/V vs. p of the CO gas variation introduced the following least square linear equation

$$p/V\ (\text{kPa/cm}^3) = 1.2\ \text{kPa/cm}^3 + 0.0010\ \text{cm}^{-3}\ p$$

Based on these results and given the surface area of a CO molecule 818 nm², the adsorption isotherm equilibrium constant (K) and the surface area of 1 g charcoal at 273 K and 1 atm, respectively, should be

(15) in Version O

[✓ A)] 8.3e–4 kPa^{-1} and 22.0 km^2
B) 1.2e–3 kPa^{-1} and 11.0 km^2
C) 1.2e3 kPa^{-1} and 11.0 km^2
D) 1.2e–3 kPa^{-1} and 22.0 km^2
E) 8.3e–4 kPa^{-1} and 11.0 km^2

13. A possible mechanism for the reaction,

$$2A + B \longrightarrow C + D,$$

is:

(1) $A + A \rightleftharpoons A_2$ fast, equilibrium
(2) $A_2 + A \longrightarrow A_3$ slow
(3) $A_3 + B \longrightarrow A + C + D$ fast

According to the mechanism, the rate law will be:

(7) in Version O

A) Rate = k_{eff} [A]
B) Rate = k_{eff} [A][B]
C) Rate = $k_{eff}\,[A]^3[B]$
[✓ D)] Rate = $k_{eff}\,[A]^3$
E) Rate = $k_{eff}\,[A]^2$

14. Given that an endothermic reaction has an activation energy of 25 kJ/mol, which of the following statements are **correct**?
    I. The reverse reaction has an activation energy equal to 25 kJ/mol.
    II. The reverse reaction has an activation energy less than 25 kJ/mol.
    III. The reverse reaction has an activation energy greater than 25 kJ/mol.
    IV. The change in internal energy is less than zero.
    V. The change in internal energy is greater than zero.
    A) II and IV
    [✓ B)] II and V
    C) I and IV
    D) III and IV
    E) III and V

⑥ in Version O

15. The quenching of tryptophan fluorescence by dissolved oxygen gas was monitored by measuring emission lifetimes at 348 nm in aqueous solutions. Determine the fluorescence and quenching rate constants in for this process from the following data:

$[O_2]/(10^{-2}\ \text{mol dm}^{-3})$	0.0	2.3	8.0
$\tau/(10^{-9}\ \text{s})$	2.72	1.50	0.71

⑯ in Version O

    A) 8.1×10^8 and $1.3 \times 10^{11}\ \text{s}^{-1}$
    B) 3.7×10^8 and $0.72 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$
    C) 1.1×10^8 and $0.72 \times 10^{10}\ \text{s}^{-1}$
    D) 1.1×10^8 and $2.8 \times 10^8\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$
    [✓ E)] 3.7×10^8 and $1.3 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$

16. The thermal decomposition of phosphine (PH_3) into phosphorous and molecular hydrogen is a first order process.

$$2PH_3\ (g) \longrightarrow 2P\ (s) + 3H_2\ (g)$$

At 680° C the rate constant for this reaction is $0.0198\ \text{s}^{-1}$. You would expect the half-life of phosphine at room temperature (25° C) to be _____ than that at 680° C.
    A) Not enough information given. Must know ΔH to answer this.
    [✓ B)] longer
    C) the same
    D) shorter
    E) Not enough information given. Must know E_a to answer this.

⑫ in Version O

CHEM 311 (152)

Second Major Exam

Thursday, April 14, 2016, 7:30-9:30 PM

2 HOURS

STUDENT NAME: ....

STUDENT ID NUMBER: ....

Q 8 rounding problems

$5.40\ km^2$ is not $5.5\ km^2$

Test Code (004)

(16 Questions)

Dr. M. Wazeer	Section 1
Dr. M. Morsy	Section 2
Dr. W. Foerner	Section 3
Dr. H. Badawi	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$mol^{-1/2}$$dm^{3/2}$
(in H_2O, 25°C)

Parallel reactions:

A -k₁-> B
A -k₂-> C

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

Yield of the reaction:

$\Phi_i = k_i/S$

Where S is the sum of all rate constants of the parallel 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:

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

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

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

Sequential reactions:

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

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

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

Important Equations

$E = h\upsilon$

$c = \upsilon\lambda$

$PV = nRT$

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

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

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

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

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

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

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

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

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

$dP/dt = k\theta$

$\theta = KP/(1 + KP)$, 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

1. For the consecutive reactions;

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

the rate of concentration changes of the intermediate I is given by,

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

The maximum intermediate concentration is reached when d[I]/dt = 0. Given

$$[A] = [A]_0 e^{-k_1 t} \quad \text{and}$$

$$[I] = \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)[A]_0$$

the time, t_{max}, at which [I] is at a maximum should be given by

A) $t_{max} = k_1/(k_2-k_1)$

B) $t_{max} = (k_2/(k_1-k_2)) \ln (k_1/k_2)$ ⑩ in Version O

[✓ C)] $t_{max} = (1/(k_1-k_2)) \ln (k_1/k_2)$

D) $t_{max} = k_1/(k_1-k_2)$

E) $t_{max} = (k_1/(k_1-k_2)) \ln (k_1/k_2)$

2. The oxidation of HSO_3^- by O_2 in aqueous solution is a reaction of importance to processes of acid rain formation, which is reported to be

$$2HSO_3^- + O_2 \xrightarrow{k} 2\, SO_4^{-2} + 2\, H^+$$

The rate law of this process is found to be

$$\text{Rate} = k\, [HSO_3^-]^2[H^+]^2$$

Given pH = 6 and an oxygen molar concentration of 2.4×10^{-4} mol dm^{-3} (both presumed constant), an initial HSO_3^- molar concentration 5×10^{-5} mol dm^{-3}, and rate constant of 3.6×10^6 dm^9 mol^{-3} s^{-1}, how long would it take for HSO_3^- to reach half its initial concentration?

⑨ in Version O

A) 8.8e1 days

B) 1.0e–6 days

C) 3.2e4 yr

[✓ D)] 8.8e1 yr

E) 4.0e5 s

$pH = 6 \; ; \; [H^+] = 10^{-6}\ M$

$k_{eff} = 3.6 \cdot 10^{-6}$ [illegible]

$$t_{1/2} = \frac{1}{2 \cdot 3.6 \cdot 10^{-6} \cdot 5 \cdot 10^{-5}\ M}$$

$\overset{1/Ms}{\wedge}$

$= 2.79 \cdot 10^{9}\ s = 88\ y$

3. The thermal decomposition of phosphine (PH_3) into phosphorous and molecular hydrogen is a first order process.

$$2PH_3\ (g) \longrightarrow 2P\ (s) + 3H_2\ (g)$$

At 680° C the rate constant for this reaction is 0.0198 s^{-1}. You would expect the half-life of phosphine at room temperature (25° C) to be _____ than that at 680° C.

A) the same
B) Not enough information given. Must know ΔH to answer this.
C) Not enough information given. Must know E_a to answer this.
[✓ D) longer]
E) .shorter

⑫ in Version O

4. The gas phase decomposition data of hydrogen iodide are

***t*, hours**	0	2.0	4.0	6.0
[HI], M	1.00	0.50	0.33	0.25

What are the order and rate constant (k, include units) of this reaction?

A) Second order and k = 2.0 $M^{-1}h^{-1}$
B) First order and k = 0.25 h^{-1}
C) Second order and k = 0.25 Mh^{-1}
[✓ D) Second order and k = 0.50 $M^{-1}h^{-1}$]
E) First order and k = 0.50 h^{-1}

⑤ in Version O

5. The following free radical mechanism has been proposed for the thermal decomposition of acetaldehyde (ethanal):

$$
\begin{aligned}
CH_3CHO &\xrightarrow{k_1} \bullet CH_3 + CHO \\
\bullet CH_3 + CH_3CHO &\xrightarrow{k_2} CH_4 + \bullet CH_2CHO \\
\bullet CH_2CHO &\xrightarrow{k_3} \bullet CH_3 + CO \\
\bullet CH_3 + \bullet CH_3 &\xrightarrow{k_4} CH_3CH_3
\end{aligned}
$$

Based on the proposed mechanism, the apparent rate constant expression and the order of the formation of ethane (CH_3CH_3), respectively, should be

A) k_1 and zero order

B) k_1k_2/k_3 and second order

C) k_1/ k_4 and half order

D) $(k_1/ k_4)^{1/2}$ and half order

[✓ E)] $k_1/2$ and first order

⑪ in Version 0

6. The decomposition of dimethylether at 504 °C is first order with a half-life of 1570 seconds. What fraction of an initial amount of dimethylether remains after 6280 seconds?

A) 0.333333

[✓ B)] 0.0625

C) 0.05

D) 0.02

E) 0.2

④ in Version 0

$e^{-kt} = 0.0625$

7. Iodine and acetone react in acid solution according to the equation

$$I_2 + CH_3COCH_3 \longrightarrow CH_3COCH_2I + HI$$

The rate equation for the reaction is found to be

$$\text{rate} = k\,[CH_3COCH_3][H^+]$$

At the start of the experiment, the rate of reaction was found to be 2.00×10^{-5} mol $dm^{-3}\,s^{-1}$ when the concentrations of the reactants were

Reactant	Concentration / mol dm^{-3}
CH_3COCH_3	1.50
I_2	2.00×10^{-4}

Use these data to calculate a value for the rate constant at pH = 1.0 and deduce its units.

[✓ A)] 1.33e–4 $dm^3\,mol^{-1}\,s^{-1}$
B) 6.67e–2 $dm^6\,mol^{-2}\,s^{-1}$
C) 1.00e–2 $dm^3\,mol^{-1}\,s^{-1}$
D) 1.33e–6 s^{-1}
E) 1.50e1 $dm^6\,mol^{-2}\,s^{-1}$

⑬ in Version O

$pH = 1 \quad [H^+] = 10^{-1}\,M$

$$k = \frac{2\cdot10^{-5}\,M/s}{1{,}5M\cdot10^{-1}\,M} = 1{,}33\cdot10^{-4}\,\frac{1}{Ms}$$

8. The adsorption of CO gas on charcoal at 273 K fit to the Langmuir isotherm,

$$\theta = \frac{Kp}{1+Kp} = \frac{V}{V_m}$$

Its linear plot of p/V vs. p of the CO gas variation introduced the following least square linear equation

$$p/V\,(\text{kPa/cm}^3) = 1.2\ \text{kPa/cm}^3 + 0.0040\ \text{cm}^{-3}\ p$$

Based on these results and given the surface area of a CO molecule 818 nm^2, the adsorption isotherm equilibrium constant (K) and the surface area of 1 g charcoal at 273 K and 1 atm, respectively, should be

A) 3.0e2 kPa^{-1} and 2.7 km^2
B) 3.3e–3 kPa^{-1} and 2.7 km^2
C) 4.8e–3 kPa^{-1} and 5.5 km^2
D) 4.8e–3 kPa^{-1} and 2.7 km^2
[✓ E)] 3.3e–3 kPa^{-1} and 5.5 km^2

⑮ in Version O

$V_m = 250\ cm^3$

K ~~n~~ $=$ ~~$3{,}33\cdot10^{-3}$ mol~~ $3{,}3\cdot10^{-3}\,\frac{1}{kPa}$

$n = 11{,}17\cdot10^{-3}$ mol

$A = 5{,}40\ km^2$

9. The initial rate of the reaction between substances A and B is measured in a series of experiments as follows

Expt	Initial rate/mol dm^{-3} s^{-1}	Initial [A]/mol dm^{-3}	Initial [B]/mol dm^{-3}
1	1.5×10^{-2}	0.30	0.30
2	2.0×10^{-2}	X	0.60

Given the order with respect to each reactant is one, the X-value of the initial concentration of the reactant A in experiment 2 should be

A) 6.67
[✓ B)] 0.20
C) 0.36
D) 0.11
E) 2.22

② in Version O

$$X = \frac{2\cdot10^{-2}\ M/s}{0.6\ M \cdot 0.1667\ \frac{1}{Ms}} = 0.20\ M$$

10. Given that an endothermic reaction has an activation energy of 40 kJ/mol, which of the following statements are **correct**?
I. The reverse reaction has an activation energy equal to 40 kJ/mol.
II. The reverse reaction has an activation energy less than 40 kJ/mol.
III. The reverse reaction has an activation energy greater than 40 kJ/mol.
IV. The change in internal energy is less than zero.
V. The change in internal energy is greater than zero.

A) III and V
B) I and IV
C) II and IV
[✓ D)] II and V
E) III and IV

⑥ in O Version

II, V

11. The quenching of tryptophan fluorescence by dissolved oxygen gas was monitored by measuring emission lifetimes at 348 nm in aqueous solutions. Determine the fluorescence and quenching rate constants in for this process from the following data:

$[O_2]/(10^{-2}\ \text{mol dm}^{-3})$	0.0	2.3	8.0
$\tau/(10^{-9}\ \text{s})$	2.72	1.50	0.71

A) 3.7×10^8 and $0.72 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$
B) 1.1×10^8 and $2.8 \times 10^8\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$
[✓ C)] 3.7×10^8 and $1.3 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$
D) 1.1×10^8 and $0.72 \times 10^{10}\ \text{s}^{-1}$
E) 8.1×10^8 and $1.3 \times 10^{11}\ \text{s}^{-1}$

~~Same~~ ⑯ in Version O

12. An enzyme-substrate system obeys the simple Michaelis-Menten mechanism:

$$S + E \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [SE]$$

$$[SE] \xrightarrow{k_2} E + \text{Products}$$

The rate of product formation at large substrate concentration has a maximum rate value 0.02 mol sec^{-1}. The rate is half of this value at a substrate concentration of 100 mg L^{-1}. Find the equilibrium constant (K_1) of the [SE]-complex formation assuming that $k_2 << k_{-1}$.

⑧ in Version O

A) 5.0e2 L mg^{-1}
B) 1.0e2 L mg^{-1}
C) 10 L mg^{-1}
[✓ D)] 10.0e–3 L mg^{-1}
E) 5.0e1 L mg^{-1}

$$K_m = 50 \cdot 0.02 \cdot 100\ \frac{mg}{L} = 100\ \frac{mg}{L}$$

$$K_1 = \frac{k_1}{k_{-1}} \approx \frac{1}{K_m} = 10^{-2}\ \frac{L}{mg} = 10 \cdot 10^{-3}\ \frac{L}{mg}$$

13. If reaction A has an activation energy of 300 kJ and reaction B has an activation energy of 175 kJ, which of the following statements **must** be correct?

A) The energy of reaction A must be greater than the energy of reaction B.
B) If reaction A is exothermic and reaction B is endothermic then reaction A is favored kinetically.
C) The rate of reaction A at 25 °C equals the rate of reaction B at 100 °C.
D) The energy of reaction B must be greater than the energy of reaction A.
[✓ E)] At the same temperature the rate of reaction B is greater than the rate of reaction A.

⑭ in Version 0

14. A possible mechanism for the reaction,

$$2A + B \longrightarrow C + D,$$

is:

$$(1)\ A + A \rightleftharpoons A_2 \qquad \text{fast, equilibrium}$$
$$(2)\ A_2 + A \longrightarrow A_3 \qquad \text{slow}$$
$$(3)\ A_3 + B \longrightarrow A + C + D \qquad \text{fast}$$

According to the mechanism, the rate law will be:

A) Rate = $k_{eff}[A]^2$
[✓ B)] Rate = $k_{eff}[A]^3$
C) Rate = $k_{eff}[A]$
D) Rate = $k_{eff}[A]^3[B]$
E) Rate = $k_{eff}[A][B]$

⑦ in Version 0

15. For the reaction A + B $\longrightarrow$ C, the rate constant at 215 °C is $5.0 \times 10^{-3}\ s^{-1}$ and the rate constant at 452° C is $7.0 \times 10^{-1}\ s^{-1}$. What is the rate constant at 100° C.

A) 2.88e–9 s^{-1}
[✓ B)] 4.73e–5 s^{-1}
C) 2.69e3 s^{-1}
D) 2.06e–2 s^{-1}
E) 7.38e3 s^{-1}

③ in Version 0

$$\ln\frac{k_1}{k_2} = \ln\frac{5\cdot10^{-3}}{0.7} = -4{,}9416$$

$$E_a = 61{,}\cancel{424}\ \cancel{365}\ 365\ \frac{kJ}{mol}$$

$A = ~~0,00786\ 510~~ ~~18,120~~ ~~18\ 0,06786~~$ $\frac{1}{s}$ 18432

$$\cancel{A}\ k = 4{,}73\cdot10^{-5}\ \frac{1}{s}$$

16. The combustion of ethane (C_2H_6) is represented by the equation:

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$$

In this reaction:

A) water is formed at a rate equal to two-thirds the rate of formation of CO_2.
B) the rate of formation of CO_2 equals the rate of formation of water.
C) the rate of consumption of oxygen equals the rate of consumption of water.
D) the rate of consumption of ethane is seven times faster than the rate of consumption of oxygen.
[✓ E)] CO_2 is formed twice as fast as ethane is consumed.

① in Version O