

Physical constants, conversion factors, and useful equations

Physical Constants

$$\begin{aligned}
 R &= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \\
 &= 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \\
 &= 0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1} \\
 N_A &= 6.022 \times 10^{23} \text{ mol}^{-1} \\
 k_B &= 1.381 \times 10^{-23} \text{ J K}^{-1} \\
 h &= 6.626 \times 10^{-34} \text{ J s} \\
 F &= 96,500 \text{ C mol}^{-1} \\
 c &= 2.998 \times 10^8 \text{ m s}^{-1} \\
 g &= 9.81 \text{ m s}^{-2} \\
 B &= 0.51 \text{ mol}^{-1/2} \text{ dm}^{3/2} \text{ (in} \\
 &\text{H}_2\text{O, 25}^\circ\text{C)}
 \end{aligned}$$

Other Units

$$\begin{aligned}
 1 \text{ dm}^3 &= 1 \text{ L} \\
 1 \text{ dm}^3 &= 1000 \text{ cm}^3 \\
 1 \text{ J} &= 1 \text{ kg m}^2 \text{ s}^{-2} \\
 1 \text{ atm} &= 1.101325 \times 10^5 \text{ Pa} \\
 1 \text{ atm} &= 760 \text{ mmHg} \\
 1 \text{ Torr} &= 1 \text{ mmHg} \\
 1 \text{ Torr} &= 133.322 \text{ Pa} \\
 1 \text{ bar} &= 10^5 \text{ Pa} \\
 0 \text{ degree Celcius} &\text{ is} \\
 &273.15 \text{ Kelvin}
 \end{aligned}$$

Important Equations

$$\begin{aligned}
 E &= h\nu \\
 c &= \nu\lambda \\
 PV &= nRT \\
 \Delta G &= \Delta H - T\Delta S \\
 k &= A e^{-E_a/RT} \\
 k &= \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ/RT} \\
 E_a &= \Delta^\ddagger H^\circ - P\Delta^\ddagger V^\circ + RT \text{ (sol)} \\
 &= \Delta^\ddagger H^\circ - \sum \nu RT + RT \text{ (gas)} \\
 v &= \frac{V[S]}{K_m + [S]}; V = k_2[E]_0 \text{ and } K_m = \frac{k_{-1} + k_2}{k_1}
 \end{aligned}$$

Eyring equation:

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

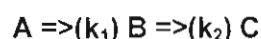
$$f = \exp(\Delta S^\ddagger / R) \times$$

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

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

$$\text{if } \theta \ll 1$$

Sequential reactions:



$$[B] = (k_1 / (k_2 - k_1)) \times$$

$$\times f(t)[A]_0$$

$$f(t) = \exp(-k_1 t) - \frac{\exp(-k_1 t) - \exp(-k_2 t)}{k_2 - k_1}$$

$$\log k = \log k_0 + 1.02 z_A z_B \sqrt{I}$$

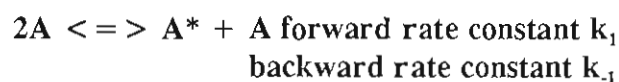
$$\log k = \log k_0 - \frac{\Delta^\ddagger V}{RT} P$$

$$pH = -\log [H^+]$$

$$\text{fluorescence lifetime } t_f = (k_r + k_q[Q])^{-1}$$

Q is the quencher

Lindemann mechanism:



backward rate constant k_{-1}



$$k_{\text{uni}} = k_1 k_2 [M] / (k_{-1} [M] + k_2)^{-1} \text{ where M can be another A molecule or an added inert buffer gas.}$$

Langmuir isotherm (P is pressure, theta is fractional occupation): $\theta = KP / (1 + KP)$, at T = const.

Michaelis-Menten kinetics:

$$\text{Rate} = k_2 [S][E]_0 / ([S] + K_m), \text{ where S is the reactant (substrate) and E the enzyme}$$

$$K_m = (k_{-1} + k_2) / k_1 \text{ maximum rate: } V = k_2 [E]_0$$

Note:

- Quantum yield = Φ = moles of product formed / moles of photons absorbed

CHEM 311 (132)

Second Major Exam

2 HOURS

Version 000

Sunday, April 27, 2014, 7:00-9:00 PM

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

Please give your section number below

STUDENT NAME: _____

STUDENT ID: _____

STUDENT SECTION NUMBER: _____

Number of Correct Answers	Your Score out of 100%

$$1) R = \frac{d[\text{CH}_3\text{Cl}]}{dt} = k_3 [\text{CH}_3^\cdot] [\text{Cl}_2]$$

CH_3^\cdot is an intermediate, formed in (2) and consumed in (3), so it must be eliminated from a correct rate law

Steady State Approximation (SSA) is required:

$$\frac{d[\text{CH}_3^\cdot]}{dt} \underset{\substack{\uparrow \\ \text{SSA}}}{=} 0 = k_2 [\text{Cl}^\cdot] [\text{CH}_4] - k_3 [\text{CH}_3^\cdot] [\text{Cl}_2] \quad (\text{I})$$

$[\text{Cl}^\cdot]$ is also an intermediate, formed in (1) and (3) and consumed in (2) and (4) \Rightarrow SSA

$$\frac{d[\text{Cl}^\cdot]}{dt} \underset{\substack{\uparrow \\ \text{SSA}}}{=} 0 = -k_2 [\text{Cl}^\cdot] [\text{CH}_4] + k_3 [\text{CH}_3^\cdot] [\text{Cl}_2] - 2k_4 [\text{Cl}^\cdot]^2 + 2k_1 [\text{Cl}_2]$$

$$\Rightarrow \underbrace{k_2 [\text{Cl}^\cdot] [\text{CH}_4]}_{\text{into (I)}} = k_3 [\text{CH}_3^\cdot] [\text{Cl}_2] - 2k_4 [\text{Cl}^\cdot]^2 + 2k_1 [\text{Cl}_2]$$

$$0 = k_3 [\text{CH}_3^\cdot] [\text{Cl}_2] - 2k_4 [\text{Cl}^\cdot]^2 + 2k_1 [\text{Cl}_2] - k_3 [\text{CH}_3^\cdot] [\text{Cl}_2]$$

$$\Rightarrow 2k_4 [\text{Cl}^\cdot]^2 = 2k_1 [\text{Cl}_2]$$

$$\rightarrow [\text{Cl}^\cdot] = \sqrt{\frac{k_1}{k_4} [\text{Cl}_2]}$$

into (I):

$$k_3 [\text{CH}_3^\cdot] [\text{Cl}_2] = k_2 [\text{Cl}^\cdot] [\text{CH}_4] = k_2 \sqrt{\frac{k_1}{k_4} [\text{Cl}_2]} [\text{CH}_4]$$

$$\Rightarrow \frac{d[\text{CH}_3\text{Cl}]}{dt} = k_3 [\text{CH}_3^\cdot] [\text{Cl}_2]$$

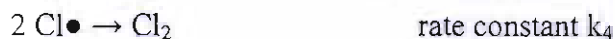
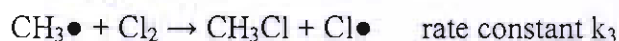
$$= k_2 \sqrt{\frac{k_1}{k_4} [\text{Cl}_2]} [\text{CH}_4]$$

$$= k_2 \sqrt{\frac{k_1}{k_4}} [\text{Cl}_2]^{1/2} [\text{CH}_4]$$

Overall order: $1 + \frac{1}{2} = 3/2$ intermediates are not in correct rate equations \rightarrow no order for $[\text{Cl}^\cdot]$ and $[\text{CH}_3^\cdot]$

1. The chlorination of methane (CH₄),
 $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g})$

follows the mechanism



Derive the correct rate law (using the steady state approximation) for the formation of CH₃Cl and find the overall order of this rate law as well as the orders of this rate law with respect to the chlorine (Cl•) and the methyl (CH₃•) radicals.

(A) overall order 3/2, intermediates do not show up in a correct rate law and thus have no order.

B) overall order 3/2, 1/2 order with respect to chlorine and methyl radicals.

C) overall order 5/2, first order with respect to chlorine and methyl radicals.

D) overall order 1/2, zero order with respect to chlorine and methyl radicals.

E) overall order 1, 1/2 order with respect to chlorine and methyl radicals.

$1 \text{ ns} = 10^{-3} \mu\text{s}$

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

$$k_q = \text{slope} = \frac{(\frac{1}{\tau_f})_2 - (\frac{1}{\tau_f})_1}{[Q]_2 - [Q]_1} = \frac{(\frac{1}{145} - \frac{1}{203}) \cdot \frac{1}{10^{-3} \mu\text{s}}}{1.00 \cdot 10^{-9} \text{ M}}$$

2. For the fluorescence quenching of rhodamine B in solution with the quencher hexaiodocyclobutene, C₄I₆, the following data were obtained: at a concentration of 1.00 nM C₄I₆ the fluorescence lifetime τ_f was 203 ns, while at a C₄I₆ concentration of 2.0 nM the fluorescence lifetime was 145 ns. Determine the rate constants for fluorescence, k_f , and for quenching, k_q .

$$k_q = 1.9704434 \cdot 10^9 \frac{1}{\mu\text{s}} \quad k_f = (\frac{1}{\tau_f})_1 - k_q [Q]_1$$

$$k_f = \frac{1}{203} \frac{1}{10^{-3} \mu\text{s}} - 1.9704434 \cdot 10^9 \frac{1}{\mu\text{s}} \cdot 1 \cdot 10^{-9} \text{ M}$$

- (A) $k_f = 2.96 (\mu\text{s})^{-1}$, $k_q = 1.97 \times 10^9 \text{ M}^{-1}(\mu\text{s})^{-1}$
 B) $k_f = 2.96 \times 10^3 \text{ s}^{-1}$, $k_q = 1.97 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$
 C) $k_f = 2.96 \times 10^9 \text{ s}^{-1}$, $k_q = 1.97 \times 10^{12} \text{ M}^{-1}\text{s}^{-1}$
 D) $k_f = 2.96 \text{ s}^{-1}$, $k_q = 1.97 \text{ M}^{-1}\text{s}^{-1}$
 E) $k_f = 3.9 \times 10^6 (\text{ms})^{-1}$, $k_q = 9.9 \times 10^7 \text{ M}^{-1}(\text{ms})^{-1}$
- $= 2.96 \frac{1}{\mu\text{s}}$
(2.95566)

$$E_{\text{light}} = JSVA15153 = 11000 \text{ VAS} = 1453.5 \text{ J}$$

$$E_{\text{phot}} = h\nu = \frac{hc}{\lambda} = \frac{6.626 \cdot 10^{-34} \text{ J} \cdot 2.998 \cdot 10^8 \text{ m/s}}{290 \cdot 10^{-9} \text{ m}} = 6.84991 \cdot 10^{-19} \text{ J}$$

3. The reactant 1,3-butadiene can be photochemically converted to cyclobutene: in an experiment 3.5 mmol of 1,3-butadiene were converted to cyclobutene when irradiated with 95. W of 290 nm light for 15.3 s. All of the light was used for the conversion. What was the overall quantum yield for this process?

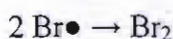
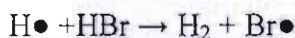
$$N_{\text{phot}} = \frac{1453.5 \text{ J}}{6.84991 \cdot 10^{-19} \text{ J}} = 2.1219 \cdot 10^{21}$$

- (A) 1 B) 2 C) 0.50 D) 1000 E) 10

$$n_{\text{phot}} = \frac{N_{\text{phot}}}{N_A} = \frac{2.1219 \cdot 10^{21}}{6.022 \cdot 10^{23} \text{ mol}^{-1}} = 3.5236 \text{ mmol}$$

$$\phi = \frac{3.5}{3.5236} = 0.993 = 1$$

4. The photochemical decomposition of HBr(g) follows the mechanism



What is the quantum yield for the decomposition of HBr, assuming that all photons are absorbed by HBr molecules and that the photon energy is large enough to break the H-Br bond?

- (A) 2 B) 1 C) 0 D) 3 E) 0.5

$$1 \text{ } h\nu \text{ decomposes } 2 \text{ HBr} \Rightarrow \phi = 2$$

5. Which one of the following processes is called Phosphorescence (S denotes a singlet state, T a triplet state)?

- (A) $T_1 \rightarrow S_0 + h\nu$ Phosphorescence
 B) $S_1 \rightarrow S_0 + h\nu$ Fluorescence
 C) $T_1 \rightarrow S_0$ intersystem crossing (T→S)
 D) $S_1 \rightarrow S_0$ Internal conversion (S→S)
 E) $S_1 \rightarrow T_1$ Inter system crossing (S→T)

(p. 984, Table 36.1)

6. In the unimolecular isomerization of cyclobutane to butylene, the following values for k_{uni} as a function of pressure were measured at 350K.

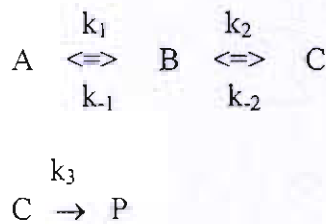
[M] (mM)	5.04	34.8
k_{uni} (s^{-1})	9.58	11.1

Assuming that the Lindemann mechanism accurately describes this reaction, what are k_f and k_{-1}/k_2 (M is an added ideal buffer gas and serves as collision partner to activate A).

- (A) $k_f = 1.19 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-1}/k_2 = 1.04 \times 10^3 \text{ M}^{-1}$
 B) $k_f = 3.49 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-1}/k_2 = 1.05 \times 10^2 \text{ M}^{-1}$
 C) $k_f = 2.19 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-1}/k_2 = 2.08 \times 10^4 \text{ M}^{-1}$
 D) $k_f = 5.12 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-1}/k_2 = 1.85 \times 10^4 \text{ M}^{-1}$
 E) $k_f = 6.59 \times 10^4 \text{ M} \text{ s}^{-1}$ and $k_{-1}/k_2 = 1.05 \times 10^2 \text{ M}^{-1}$

next page

7. Consider the following reaction mechanism that describes the formation of product P.



$$\begin{aligned}
 [B] &= K_1 [A] = [C] / K_2 \\
 \frac{dP}{dt} &= k_3 [C] = k_3 K_1 K_2 [A] \\
 [C] &= K_1 K_2 [A]
 \end{aligned}$$

If only the species A is present at $t=0$, what is the expression for the concentration of P as a function of time? (Apply the pre-equilibrium approximation)

- (A) $d[P]/dt = k_3 K_1 K_2 [A]$
 B) $d[P]/dt = k_2 K_1^{-1} K_2 [A]$
 C) $d[P]/dt = k_3 K_1 K_2^{-1} [A]$
 D) $d[P]/dt = k_1 (K_1 K_2)^{-1} [A]$
 E) $d[P]/dt = (k_1 K_1 K_2)^{-1} [A]$

$$6) \frac{1}{k_{uni}} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1} [M]$$

$$\text{slope} = \frac{(\frac{1}{k_{uni}})_2 - (\frac{1}{k_{uni}})_1}{([\text{M}]_2 - [\text{M}]_1)}$$

$$\frac{1}{[\text{M}]_1} = 198.41 \text{ M}^{-1} \quad \frac{1}{[\text{M}]_2} = 28.74 \text{ M}^{-1}$$

$$\left(\frac{1}{k_{uni}}\right)_2 = \frac{1}{11.1 \text{ s}^{-1}} = 0.09009 \text{ s}$$

$$\left(\frac{1}{k_{uni}}\right)_1 = \frac{1}{9.58 \text{ s}^{-1}} = 0.10438 \text{ s}$$

$$\text{slope} = \frac{0.09009 - 0.10438}{28.74 - 198.41} \frac{\text{s}}{\text{M}^{-1}}$$

$$= 8.4222 \cdot 10^{-5} \text{ Ms}$$

$$k_1 = \frac{1}{\text{slope}} = 1.18734 \cdot 10^4 \frac{1}{\text{Ms}} \quad \text{bimolecular: } 2A \rightleftharpoons$$

$$= 1.19 \cdot 10^4 \frac{1}{\text{Ms}}$$

$$\text{intercept} = \left(\frac{1}{k_{uni}}\right)_1 - \frac{1}{k_1} [M]_1$$

$$= 0.10438 \text{ s} - 8.4222 \cdot 10^{-5} \text{ Ms} \cdot 198.41 \frac{1}{\text{M}}$$

$$= 0.08767 \text{ s}$$

$$\frac{k_{-1}}{k_2} = k_1 \cdot \text{intercept} = 0.08767 \text{ s} \cdot 1.18733 \cdot 10^4 \frac{1}{\text{Ms}}$$

$$= 1.041 \cdot 10^3 \frac{1}{\text{M}}$$

$$\left[\frac{k_{-1}}{k_2}\right] = \frac{1/\text{Ms}}{1/\text{Ms}} = \frac{1}{\text{M}}$$

V_m : monolayer coverage

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

8. The adsorption of ethyl chloride (C_2H_5Cl) on a sample of charcoal at $0^\circ C$ measured at several different pressures is as follows;

P of C_2H_5Cl (Torr)	50	100
V_{ads} (mL)	3.8	4.3

$$\frac{1}{R_0} = \frac{1}{V} + \frac{K_m}{V} \frac{1}{[S]}$$

maximum rate $V = R_m$

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

Using the Langmuir isotherm, determine the fractional coverage at 100 Torr.

A) 0.868

B) 0.595

C) 0.952

D) 0.754

E) 0.126

$$1 + \frac{1}{K P} = \frac{V_m}{V_{ads}} \quad (= \text{B})$$

$$(1) \quad 1 + \frac{1}{50 \text{ Torr} \cdot K} = \frac{V_m}{3.8 \text{ mL}}$$

$$(2) \quad 1 + \frac{1}{100 \text{ Torr} \cdot K} = \frac{V_m}{4.3 \text{ mL}}$$

$$\frac{1}{2} \times (1) - (2) \quad \frac{1}{2} - 1 = V_m \left(\frac{1}{2 \times 3.8} - \frac{1}{4.3} \right) \frac{1}{\text{mL}}$$

$$-0.5 = -V_m \cdot 0.10098 \frac{1}{\text{mL}}$$

$$V_m = 4.9515 \text{ mL}$$

$$\theta(100 \text{ Torr}) = \frac{V_{ads}}{V_m} = \frac{4.3}{4.9515} = 0.868$$

9. The cleavage of N-acetyl-tyrosylamide (NAT) by chymotrypsin was studied and the following reaction rates versus substrate concentration were measured;

[NAT] (mM)	4.00	8.00
R_0 (mM s ⁻¹)	0.016	0.028

$$\frac{1}{R} = \frac{1}{R_m} + \frac{K_m}{R_m} \frac{1}{[NAT]} \quad R_m = k_2 [E]_0$$

What are the Michaelis constant and the limiting rate of this reaction?

A) $K_m = 24.0 \text{ mM}$; $R_{max} = 0.112 \text{ mM s}^{-1}$

B) $K_m = 24.4 \text{ mM}$; $R_{max} = 0.137 \text{ mM s}^{-1}$

C) $K_m = 57.3 \text{ mM}$; $R_{max} = 0.298 \text{ mM s}^{-1}$

D) $K_m = 73.3 \text{ mM}$; $R_{max} = 0.137 \text{ mM s}^{-1}$

E) $K_m = 98 \text{ mM}$; $R_{max} = 0.193 \text{ mM s}^{-1}$

$$\text{slope} = \frac{K_m}{R_m} = \frac{(\frac{1}{R})_2 - (\frac{1}{R})_1}{(\frac{1}{[NAT]_2}) - (\frac{1}{[NAT]_1})}$$

$$= \frac{(\frac{1}{0.028} - \frac{1}{0.016}) \frac{s}{\text{mM}}}{(\frac{1}{8} - \frac{1}{4}) \frac{1}{\text{mM}}}$$

$$= \frac{-26.7857}{-0.125} s = 214.2856 s$$

$$\frac{1}{R_m} = \left(\frac{1}{R}\right)_2 - \frac{K_m}{R_m} \frac{1}{[NAT]_2} = \frac{1}{0.028 \text{ mM}} - 214.2856 s \cdot \frac{1}{8} \text{ mM}^{-1}$$

$$= 8.9286 \frac{s}{\text{mM}} \quad R_m = 0.112 \frac{\text{mM}}{s} \quad (0.1119996)$$

$$K_m = R_m \cdot \text{slope} = 0.1119996 \frac{\text{mM}}{s} \cdot 214.2856 s = 24.0 \text{ mM} \quad (23.99990)$$

10. For a system obeying the Langmuir isotherm, the slope of the plot of $\ln(\theta/P)$ versus θ for very small coverage ($\theta \ll 1$) is,

A) -1

B) +1

C) +2

D) -2

E) +3

$$\theta = \frac{KP}{1+KP} \Rightarrow \theta = KP \frac{1}{1+KP}$$

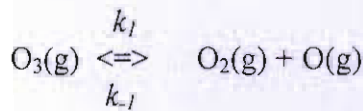
$$\Rightarrow 1 - \theta = \frac{1}{1+KP} = KP(1-\theta)$$

$$\ln \frac{\theta}{P} = \ln K(1-\theta) = \ln K + \ln(1-\theta)$$

$$\theta \ll 1 \Rightarrow \ln \frac{\theta}{P} = \ln K - \theta$$

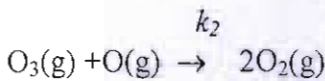
$$\Rightarrow \text{slope} = -1 \text{ if } \theta \ll 1$$

11. Consider the following mechanism for ozone thermal decomposition.



$$K = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]}$$

$$[\text{O}] = K \frac{[\text{O}_3]}{[\text{O}_2]} = \frac{k_1}{k_{-1}} \frac{[\text{O}_3]}{[\text{O}_2]}$$



$$\frac{d[\text{O}_3]}{dt} = -k_1[\text{O}_3] + k_{-1}[\text{O}_2][\text{O}] - k_2[\text{O}_3][\text{O}]$$

What is the rate law expression for the loss of $\text{O}_3(\text{g})$ (use the pre-equilibrium approximation)?

A) Rate = $2k_1k_2[\text{O}_3]^2/(k_{-1}[\text{O}_2])$

B) Rate = $k_1k_2[\text{O}_3]^2/(k_{-1}[\text{O}_2])$

C) Rate = $k_{-1}k_2[\text{O}_3]^2/(k_1[\text{O}_2])$

D) Rate = $2k_{-1}k_2[\text{O}_2]^2/(k_1[\text{O}_3])$

E) Rate = $k_1k_2[\text{O}_2]/(k_{-1}[\text{O}_3])$

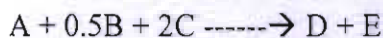
$$= -k_1[\text{O}_3] + k_{-1} \frac{k_1}{k_{-1}} \frac{[\text{O}_3]}{[\text{O}_2]} - k_2 K \frac{[\text{O}_3]}{[\text{O}_2]}$$

$$= -k_2 K \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

loss of $\text{O}_3 = \text{rate of consumption of } \text{O}_3$

$$\Rightarrow -\frac{d[\text{O}_3]}{dt} = k_2 k_1 [\text{O}_3]^2 / (k_{-1} [\text{O}_2])$$

12. Which statement is true regarding the following reaction



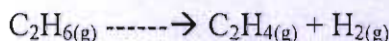
- (A) The rate of change of C is 4 times the rate of change of B
- B. The rate of change of B is 4 times the rate of change of C
- C. The rate of change of A is 4 times the rate of change of C
- D. The rate of change of C is 4 times the rate of change of A
- E. The rate of change of B is 4 times the rate of change of D

$$\frac{1}{0.5} \frac{d[C]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$$

$$\frac{d[C]}{dt} = 4 \frac{d[B]}{dt}$$

$$P = P_{C_2H_6}$$

13. Consider the first order decomposition of ethane to ethene:



$$-\frac{d[C_2H_6]}{dt} = k[C_2H_6]$$

$$= \frac{k}{RT} P$$

How long it will take for the partial pressure of ethane to change by 30% of its initial value when the rate constant for decomposition is $3.52 \times 10^{-3} \text{ s}^{-1}$.

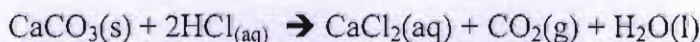
$$-\frac{1}{RT} \frac{dP}{dt} = \frac{k}{RT} P$$

- (A) 101.3s
- B. 110.0s
- C. 342s
- D. 27.5s
- E. $3.20 \times 10^3 \text{ s}$

$$\int_{P_0}^P \frac{dP}{P} = -kt$$

$$\ln \frac{P}{P_0} = -kt, \quad P = 0.7 P_0, \quad t = \frac{1}{k} \ln \frac{1}{0.7}$$

14. The rate of the following reaction is the rate of formation of CO_2 .



The rate of reaction will be the largest at:

$$[CaCO_3(s)] = \frac{d}{dt} = \text{const.}$$

M molar mass

- (A) The beginning of the reaction because $[HCl]$ is largest.
- B. The beginning of the reaction because $[CaCO_3(s)]$ is largest.
- C. The end of the reaction because $[HCl]$ is smallest.
- D. The end of the reaction because $[CaCO_3(s)]$ is smallest.
- E. In the middle of reaction time because then $[HCl]$ is not too large.

$$\frac{d[CO_2]}{dt} = k [HCl]^2$$

$$t = \frac{1}{3.52 \times 10^{-3} \text{ s}^{-1}} \ln \frac{1}{0.7} = 284.0909 \text{ s} \cdot 0.3567 = 101.3 (3) \text{ s}$$

15. The following tabulated data were obtained for the reaction: $\text{SO}_2 + \text{O}_3 \rightarrow \text{SO}_3 + \text{O}_2$ at 298 K.

$[\text{SO}_2]$, mol/L	$[\text{O}_3]$, mol/L	Initial Rate, mol/(L · s)
0.25	0.60	0.284
0.25	0.40	0.189
0.75	0.40	0.567

$$R = k [\text{SO}_2]^\alpha [\text{O}_3]^\beta$$

$$\frac{R_1}{R_2} = \frac{0.284}{0.189} = \left(\frac{0.6}{0.4}\right)^\beta$$

$$1.50 = (1.50)^\beta$$

$$\Rightarrow \beta = 1$$

The following describes best the rate parameters:

A. rate = $2.36 \text{ (M}^{-1} \text{ s}^{-1}) [\text{SO}_2]^2$

B. rate = $1.27 \text{ (M}^{-1} \text{ s}^{-1}) [\text{O}_3]^2$

C. rate = $0.56 \text{ (M}^{-1} \text{ s}^{-1}) [\text{O}_3]^2$

D. rate = $1.89 \text{ (M}^{-1} \text{ s}^{-1}) [\text{SO}_2][\text{O}_3]$

E. rate = $0.29 \text{ (M}^{-1} \text{ s}^{-1}) [\text{O}_3]^2$

$$\frac{R_2}{R_3} = \frac{0.189}{0.567} = \frac{1}{3} = \left(\frac{0.25}{0.75}\right)^\alpha$$

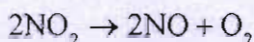
$$\frac{1}{3} = \left(\frac{1}{3}\right)^\alpha \Rightarrow \alpha = 1$$

line 1

$$0.284 \frac{\text{M}}{\text{s}} = k \cdot 0.25 \text{ M} \cdot 0.60 \text{ M}$$

$$k = \frac{0.284}{0.25 \cdot 0.60} \frac{1}{\text{M s}} = 1.89 \frac{1}{\text{M s}} \quad (1.89 \bar{3})$$

16. Nitrogen dioxide decomposes to nitric oxide and oxygen according to:



At 300 °C, NO_2 drops from 0.0100 M by 50% M in 1.50 min. The rate of appearance of O_2 for this period in M/s is:

A. 2.78×10^{-5}

B. 1.94×10^{-5}

C. 2.67×10^{-5}

D. 1.74×10^{-5}

E. 4.33×10^{-5}

$$\frac{d[\text{O}_2]}{dt} = k [\text{NO}_2]^2$$

$$\left. \frac{d[\text{NO}_2]}{dt} \right|_{1.5 \text{ min}} = - \frac{0.005 \text{ M}}{1.50 \text{ min}} = - \frac{1}{3} \cdot 10^{-2} \frac{\text{M}}{\text{min}} \quad (3.33333 \cdot 10^{-3})$$

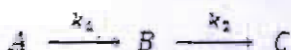
$$-\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt} = \frac{1}{2} \cdot \frac{1}{3} \cdot 10^{-2} \frac{\text{M}}{\text{min}}$$

$$= \frac{0.5 \cdot (1/3) \cdot 10^{-2}}{60} \frac{\text{M}}{\text{s}}$$

$$= 2.78 \cdot 10^{-5} \frac{\text{M}}{\text{s}}$$

$$(2.77777 \dots) \cdot 10^{-5}$$

17. For the sequential reaction:



$$-\frac{d(A)}{dt} = k_1(A)$$

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

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

the rate constants are $k_1 = 2.0 \times 10^{12} \text{ s}^{-1}$ and $k_2 = 3.3 \times 10^{10} \text{ s}^{-1}$. At what time does the maximum concentration of the intermediate B occur?

$$\left. \frac{d(B)}{dt} \right|_{t_m} = 0 = -k_1 e^{-k_1 t_m} + k_2 e^{-k_2 t_m}$$

(A) $2.09 \times 10^{-12} \text{ s}$

B) $1.08 \times 10^{-12} \text{ s}$

C) $3.09 \times 10^{-11} \text{ s}$

D) $4.11 \times 10^{-10} \text{ s}$

E) $1.28 \times 10^{-12} \text{ s}$

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

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

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

$$t_m = \frac{\ln(2 \cdot 10^{12} / 3.3 \cdot 10^{10})}{(2 \cdot 10^{12} - 3.3 \cdot 10^{10}) \text{ s}^{-1}} = \frac{(2.0866)}{(2 \cdot 10^{12} - 3.3 \cdot 10^{10}) \text{ s}^{-1}} = 2.09 \cdot 10^{-12} \text{ s}$$

18. The rate constant and activation energy for the reaction of hydrogen and iodine to produce gaseous hydrogen iodide are $2.45 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 302°C and $1.5 \times 10^5 \text{ J mol}^{-1}$, respectively. At what temperature the rate constant will be 100 times the rate constant at 302°C (assume constant pre-exponential factor A)?

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

(A) 401°C

B) 350°C

C) 250°C

D) 675°C

E) 525°C

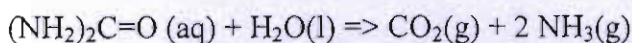
$$\frac{k_2}{k_1} = \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}} = e^{-\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

$$-\frac{R}{E_a} \ln \frac{k_2}{k_1} = \frac{1}{T_2} - \frac{1}{T_1}, \quad \frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{E_a} \ln 100$$

$$\frac{1}{T_2} = \frac{1}{575.15 \text{ K}} - \frac{8.314}{1.5 \cdot 10^5} \text{ K} \ln 100$$

$$= 1.7387 \cdot 10^{-3} \text{ K}^{-1} - 2.5525 \cdot 10^{-4} \text{ K}^{-1} = 1.4835 \cdot 10^{-3} \text{ K}^{-1}$$

19. The rate constants of the gas decomposition of urea in aqueous solution, $T_2 = 674.0 \text{ K}$



$$= 401^\circ \text{C} \quad (400, 954)$$

at two different temperatures, 60.0°C and 71.5°C , are found to be $1.2 \times 10^{-7} \text{ s}^{-1}$ and $4.4 \times 10^{-7} \text{ s}^{-1}$, respectively. Use these parameters to estimate the enthalpy of activation (ΔH^\ddagger) of this reaction at 25°C as described by the Eyring equation.

(A) 105 kJ mol^{-1}

B) 115 kJ mol^{-1}

C) 106 kJ mol^{-1}

D) 123 kJ mol^{-1}

E) 101 kJ mol^{-1}

$$\text{Eyring: } k = \frac{k_B T}{h c^\ddagger} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

$$\frac{k_1}{k_2} = \frac{T_1}{T_2} e^{-\frac{\Delta H^\ddagger}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)}$$

$$T_1 = 60.0^\circ \text{C} = 333.15 \text{ K}$$

$$T_2 = 71.5^\circ \text{C} = 344.65 \text{ K}$$

$$\frac{\Delta H^\ddagger}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \ln \left(\frac{k_1}{k_2} \frac{T_2}{T_1} \right)$$

$$\ln \left(\frac{k_1}{k_2} \frac{T_2}{T_1} \right) = \ln \left(\frac{1.2 \cdot 10^{-7}}{4.4 \cdot 10^{-7}} \cdot \frac{344.65}{333.15} \right) = \ln 0.28259$$

20. Consider the data for several systems for the conversion of reactants to products at the same temperature:

System	Activation energy, E_a (kJ)	Enthalpy of reaction ΔH (kJ)
1	40	-25
2	60	30
3	15	10
4	90	-55

- A) Systems 1 and 4 are ^{exo} endothermic while 2 and 3 are ^{endo} exothermic reactions.
- B) System 1 is the fastest ^{exo} endothermic reaction.
- C) System 2 is the slowest ^{endo} exothermic reaction.
- D) System 3 is the fastest endothermic reaction. *smallest E_a , $\Delta H > 0$*
- E) Systems 1 and 2 are faster than 3 and 4 reactions. *no*

19) continued

$$\Delta \ln k^\ddagger = \frac{1}{T_2} - \frac{1}{T_1} = \left(\frac{1}{344.65} - \frac{1}{333.15} \right) \frac{1}{K} = -1.00157 \cdot 10^{-4} \frac{1}{K}$$

$$\Delta H^\ddagger = R \frac{\ln \left(\frac{k_2 T_2}{k_1 T_1} \right)}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{-1.26535}{-1.00157 \cdot 10^{-4}} \text{ K} \cdot 8.314 \frac{\text{J}}{\text{K mol}}$$

$$= 105.04 \text{ kJ/mol} \quad (105036)$$

$$= 105 \text{ kJ/mol}$$