

Unit 5 study guide

Rxn Rate + (1) on other page
Rate laws

$$(2) \quad -\frac{1}{2} \frac{\Delta[\text{SO}_2]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{SO}_3]}{\Delta t}$$

$$(3) \text{ a) Rate} = k[\text{N}_2\text{O}_5] \quad k = 4.82 \cdot 10^{-3} \text{ s}^{-1}$$

$$\text{b) Rate} = (4.82 \cdot 10^{-3} \text{ s}^{-1})(.0240 \text{ M}) \\ = 1.16 \cdot 10^{-4} \text{ M/s}$$

c) when $[\text{N}_2\text{O}_5] \times 2$, the rate doubles
to $2.32 \cdot 10^{-4} \text{ M/s}$

(4) a) $[\text{A}] = 1.0 \text{ M}$ $[\text{B}] = 2.0 \text{ M}$ (or other similar answers)

b) $2 \times [\text{A}]$ $2 \times \text{Rate}$ \therefore 1st order $[\text{A}]$
 $3 \times [\text{B}]$ Rate unchanged \therefore 0 order in B
 $3 \times [\text{C}]$ $9 \times \text{Rate}$ $9 = 3^2$ \therefore 2nd order C

$$\text{Rate} = k[\text{A}]^1[\text{B}]^0[\text{C}]^2$$

$$\text{Rate} = k[\text{A}][\text{C}]^2$$

$$\left(\frac{1}{2}\right) \left(\frac{1}{2}\right)^2 = \frac{1}{8}$$

$$(5) \text{ a) Rate} = k[\text{OCI}^-][\text{I}^-]$$

$$\text{b) } 1.36 \cdot 10^{-4} \frac{\text{M}}{\text{s}} = k(1.5 \cdot 10^{-3} \text{ M})(1.5 \cdot 10^{-3} \text{ M}) \\ k = 6.0 \cdot 10^9 \frac{1}{\text{M} \cdot \text{s}}$$

$$\text{c) Rate} = (6.0 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1})(1.0 \cdot 10^{-3} \text{ M})(5.0 \cdot 10^{-4} \text{ M}) \\ = 3.0 \cdot 10^{-3} \frac{\text{M}}{\text{s}}$$

$$(6) \text{ a) Rate} = k[\text{ClO}_2]^2[\text{OH}^-]$$

$$\text{b) } .0248 \frac{\text{M}}{\text{s}} = k(.060 \text{ M})^2(.030 \text{ M}) \\ k = 230 \text{ M}^{-1} \text{ s}^{-1}$$

$$\text{c) Rate} = (230 \text{ M}^{-1} \text{ s}^{-1})(.010 \text{ M})^2(.015 \text{ M}) \\ = 3.4 \cdot 10^{-4} \frac{\text{M}}{\text{s}}$$

- ⑦ a) Rate = $k [BF_3] [NH_3]$
 b) 2nd order
 c) $.2130 \frac{M}{s} = k (1.250M)(1.250M)$
 $k = 3.41 M^{-1} s^{-1}$

Half-life ①

t	[A]	ln[A]	$\frac{1}{[A]}$
0.0	1.60	.470	.63
10.0	.40	-.916	2.5
20.0	.10	-2.30	10.

* Problem says 1st order (I just didn't read!)
 slope = $-k$
 slope = $-.13 \frac{1}{s}$

② $t_{1/2} = \frac{.693}{k} = \frac{.693}{.13} = 5.3 s$

③ $t_{1/2} = 225 s$ $k = \frac{.693}{t_{1/2}} = \frac{.693}{225 s} = .00308 \frac{1}{s}$

④ Rate = $k [NO_2]^2$ $\frac{1}{[NO_2]_t} - \frac{1}{[NO_2]_0} = kt$
 $k = .543 M^{-1} s^{-1}$
 $[NO_2]_0 = .260 M$ $\frac{1}{.100 M} - \frac{1}{.260 M} = (.543 M^{-1} s^{-1})(t)$
 $[NO_2]_t = .100 M$
 $t = ?$ $t = 18.3 s$

⑤ Rate = $k [H_2O_2]$ $\ln [A]_t - \ln [A]_0 = -kt$
 $[H_2O_2]_0 = .600 M$ $\ln (.075 M) - \ln (.600 M) = -k (54 \text{ min})$
 $[H_2O_2]_t = .075 M$ $k = .039 \frac{1}{\text{min}}$
 $t = 54 \text{ min}$
 $t_{1/2} = ?$ $t_{1/2} = \frac{.693}{k} = \frac{.693}{.039} = 18 \text{ min}$

⑥ $t_{1/2} = 18\text{ s}$

$[A]_0 = .71\text{ M}$

$k = ?$

$[A]_t = \frac{1}{2} [A]_0 = .36\text{ M}$

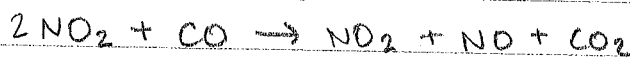
$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{.36\text{ M}} - \frac{1}{.71\text{ M}} = k(18\text{ s})$$

$$k = .13\text{ s}^{-1}\text{ M}^{-1}$$

Mechanism ①

Rate = $k[\text{NO}_2]^2$



Rate₂ = $k_2[\text{O}][\text{O}_3]$

O is intermediate

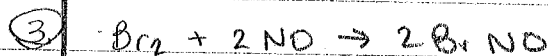
Rate₂ = $k_2 \left(\frac{k_1}{k_{-1}} \right) \frac{[\text{O}_3][\text{O}_3]}{[\text{O}_2]}$

Rate₂ = $k \frac{[\text{O}_3]^2}{[\text{O}_2]}$

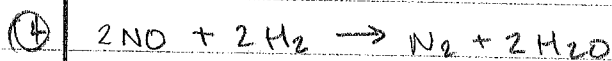
Rate₁ = Rate₋₁

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

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



rate = $k[\text{Br}_2][\text{NO}]$



Rate₂ = $k_2[\text{N}_2\text{O}_2][\text{H}_2]$

Rate₂ = $k_2 \left(\frac{k_1}{k_{-1}} \right) [\text{NO}]^2 [\text{H}_2]$

Rate₂ = $k [\text{NO}]^2 [\text{H}_2]$

Rate₁ = Rate₋₁

$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$

$\frac{k_1}{k_{-1}} [\text{NO}]^2 = [\text{N}_2\text{O}_2]$

MC

①

[H]

$1.0 \cdot 10^{-2}$
 $2.0 \cdot 10^{-2}$) $\times 2$

Rate

$4.0 \cdot 10^{-6}$

$1.6 \cdot 10^{-5} = 16 \cdot 10^{-6}$) $\times 4 = 2^2$

③

- ② A has low E_a
 B is endo
 C is endo w/ low E_a
 D is endo

- ④ a - \uparrow concentration \uparrow rate
 b \uparrow surface area \uparrow rate
 c partial pressure is similar to concentration
 d $\uparrow E_a$, decrease rate
 e $\uparrow T$ \uparrow rate

- ⑤ a - too specific. Does it really?
 b - changing $[A]$ doesn't change k
 c - similar to b
 d - k does change
 e - yes, a better answer

⑥ slow rxn step $\text{rate} = k[\text{NO}_2][\text{CF}_2]$ due to coefficient

⑦ $\text{Rate} = k[X][Y]^2$
 $8 \cdot 10^{-3} = k(0.2)(0.2^2)$
 $\frac{0.008}{\text{min}} = k \frac{(0.008)}{\text{M}^3}$ $k = 1.00 \frac{1}{\text{min} \cdot \text{M}^2}$

⑧ $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} = \frac{1}{\text{M} \cdot \text{s}}$

$\frac{\text{M}}{\text{s}} = \frac{1}{\text{M} \cdot \text{s}} \cdot \text{M} \cdot \text{M}$
 2nd mol cancel overall

(9) $t_{1/2} = 85s$ $1 \xrightarrow{85} \frac{1}{2} \xrightarrow{170} \frac{1}{4} \xrightarrow{255} \frac{1}{8}$

(11) $(2[A])^n = 8$ $n = 3$

(12) $\frac{1}{[A]}$ vs t

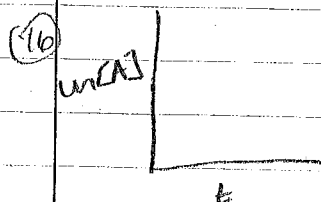
(13) a - depends on E_a

b - T

c - true, some rxns may only have 30% yield

d - true, lower E_a means more molec have enough E

e - T - usually



(14) a - Adding catalyst decreases E_a

c - see a

b is best answer

(19) slow 1st step means rate law has same molecularity
 $Rate = k [NO] [NO] = Rate = k [NO]^2$

(21) $Rate = k [CH_2]^{(1)} [NO]^{(2)}$ $1+2 = 3$

(22) $Rate = k [CH_2] [NO]^2$
 $(3[NO])^2 = 9$

23 Mechanism I

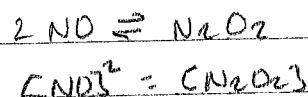
$$\text{Rate} = k[\text{H}_2][\text{NO}]$$

Mechanism II

$$\text{Rate} = k[\text{H}_2][\text{NO}]^2$$

Mechanism III

$$\begin{aligned}\text{Rate} &= k[\text{N}_2\text{O}_2][\text{H}_2] \\ &= k[\text{NO}]^2[\text{H}_2]\end{aligned}$$



FRQ 1

a) $\begin{matrix} [\text{OH}^-] & [\text{ClO}_2] & \text{Rate} \\ \begin{bmatrix} .030 \\ .060 \\ .030 \end{bmatrix} \times 2 & 2 \times \begin{bmatrix} .020 \\ -.020 \\ .040 \end{bmatrix} & 4 \times \begin{bmatrix} .166 \\ .331 \\ .661 \end{bmatrix} \times 2 \end{matrix}$ 1st order OH^-
2nd order ClO_2

- i) 1st order w/ respect to OH^- : If $[\text{OH}^-]$ is doubled while $[\text{ClO}_2]$ is held constant, the rate doubles, indicating 1st order
2nd order w/ respect to ClO_2 : If $[\text{ClO}_2]$ is doubled while $[\text{OH}^-]$ is constant, the rate increases by factor of 4, indicating 2nd order

ii) $\text{Rate} = k[\text{OH}^-][\text{ClO}_2]^2$

b) $.166 \frac{\text{M}}{\text{min}} = k(.030\text{M})(.020\text{M})^2$
 $k = 1.4 \cdot 10^4 \text{ M}^{-2} \text{ min}^{-1}$

c) $\frac{\Delta[\text{ClO}_2^-]}{\Delta t} = .166 \frac{\text{M}}{\text{min}}$ $\frac{\Delta[\text{ClO}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{ClO}_2^-]}{\Delta t}$

initial rate disappearance of $\text{ClO}_2 = 2 \cdot .166 \frac{\text{M}}{\text{min}} = .332 \frac{\text{M}}{\text{min}}$

d) step 2

FRQ 1

e) i) step 2:

Rate determining step

$$\text{Rate} = k_2 [\text{Cl}_2\text{O}_4] [\text{OH}^-]$$

↑ intermediate



Rate₁ = Rate₋₁ at equilib

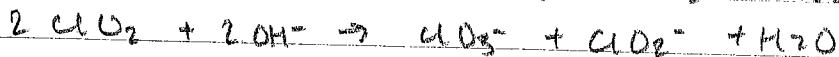
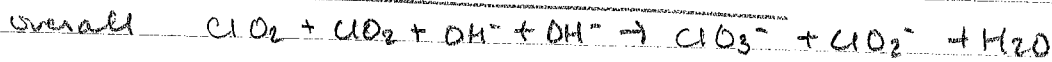
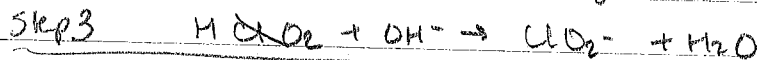
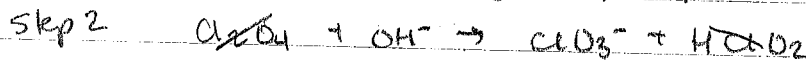
$$k_1 [\text{ClO}_2]^2 = k_{-1} [\text{Cl}_2\text{O}_4]$$

$$\frac{k_1}{k_{-1}} [\text{ClO}_2]^2 = [\text{Cl}_2\text{O}_4]$$

$$\text{Rate} = k_2 \left(\frac{k_1}{k_{-1}} \right) [\text{ClO}_2]^2 [\text{OH}^-]$$

$$\text{Rate} = k [\text{ClO}_2]^2 [\text{OH}^-]$$

ii) intermediates cancel out in mechanism steps



FRQ 2

a) $[\text{S}_2\text{O}_8^{2-}]$

$[\text{I}^-]$

initial rate

$$2 \times \begin{pmatrix} .08 \\ .10 \\ .16 \end{pmatrix}$$

$$\begin{pmatrix} .034 \\ .017 \\ .017 \end{pmatrix} \times 2$$

$$2 \times \begin{pmatrix} 2.2 \cdot 10^{-4} \\ 1.1 \cdot 10^{-4} \\ 2.2 \cdot 10^{-4} \end{pmatrix} \times 2$$

1st order
I⁻

1st order
S₂O₈²⁻

$$\text{Rate} = k [\text{S}_2\text{O}_8^{2-}] [\text{I}^-]$$

b) $2.2 \cdot 10^{-4} \frac{\text{M}}{\text{s}} = k (.08 \text{M}) (.034 \text{M})$

$$k = 8.1 \cdot 10^{-2} \text{M}^{-1} \text{s}^{-1}$$

c) $\text{Rate} = k [\text{S}_2\text{O}_8^{2-}] [\text{I}^-]$

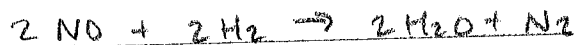
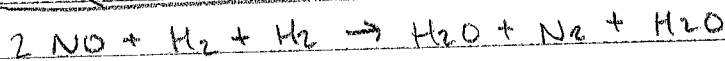
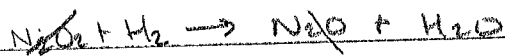
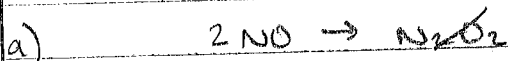
$$5.7 \cdot 10^{-4} \text{M s}^{-1} = (8.1 \cdot 10^{-2} \text{M}^{-1} \text{s}^{-1}) (.280 \text{M}) [\text{I}^-]$$

$$[\text{I}^-] = 2.5 \cdot 10^{-2} \text{M}$$

d) overall order = 2nd

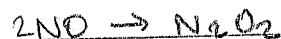
e) slow step of mechanism is bimolecular

FRQ 3



b) $\text{Rate}_2 = k_2 [\text{N}_2\text{O}_2] [\text{H}_2]$

(intermediate, substitute



$\text{Rate} = k_1 [\text{NO}]^2 [\text{H}_2]$

c) step 3 $\text{Rate} = k [\text{N}_2\text{O}_2] [\text{H}_2]$

$\text{Rate} = k [\text{N}_2\text{O}_2] [\text{H}_2] [\text{H}_2]$ from step 2

$\text{Rate} = k [\text{NO}]^2 [\text{H}_2] [\text{H}_2] = k [\text{NO}]^2 [\text{H}_2]^2$

d) 2nd order in NO

0 order in H₂

FRQ 4

a) $\text{Rate} = k [\text{C}_2\text{H}_4] [\text{HCl}]$

b) intermediate: C_2H_5^+ + Cl^-

c) 1st step is rate determining, \therefore it has highest E_a

Rxn is $-\Delta H$ \therefore exothermic

d) see graph

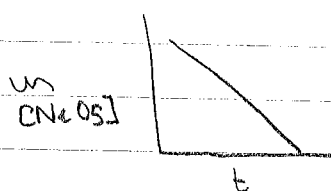
FRQ 5

a) on graph

b) i) on graph

ii) rate at time t = slope of tangent line

iii) graph $\ln[\text{N}_2\text{O}_5]$ vs time



slope of line = $-k$

iv) $[\text{N}_2\text{O}_5]$ does not affect k

k is constant for a reaction at a given T

c) i) $\text{Rate} = k[\text{A}]^1$

rxn is first order, shown by plot of $\ln[\text{A}]$ vs t is linear

ii) determine slope of line for $\ln[\text{A}]$ vs t
slope = $-k$

