

Kinetics Worksheet #4



The following data about the reaction shown above were obtained from three experiments:

Trial	[A]	[B]	Rate of Formation of C (M min ⁻¹)
1	0.60	0.15	6.3×10^{-3}
2	0.20	0.60	2.8×10^{-3}
3	0.20	0.15	7.0×10^{-4}

(a) What is the rate law for this reaction?

$$\text{RATE} = k[A]^2[B]$$

(b) What is the numerical value of the rate constant k ? What are the units for k ?

$$6.3 \times 10^{-3} = k[.60]^2[.15]$$

$$k = .12$$

$$\frac{M}{\text{min}} = k M^2 \cdot M$$

$$k = .12 M^{-2} \text{min}^{-1}$$



For the reaction above, carried out in a solution at 30°C, the following kinetic data were obtained:

Trial	[A]	[B]	Rate of Reaction (M/hr)
1	0.240	0.480	8.00
2	0.240	0.120	2.00
3	0.360	0.240	9.00
4	0.120	0.120	0.500
5	0.240	0.0600	1.00
6	0.0140	1.35	?

(a) Write the rate law expression for this reaction.

$$\text{RATE} = k[A]^2[B]$$

(b) Calculate the value of the specific rate constant k at 30°C and specify its units.

$$8.00 = k[.240]^2[.480]$$

$$k = 289$$

$$\frac{M}{\text{hr}} = k M^2 M$$

$$k = 289 M^{-2} \text{hr}^{-1}$$

(c) Calculate the initial rate of this reaction at 30°C for Trial #6.

$$\text{RATE} = 289[.0140]^2[1.35]$$

$$\text{RATE} = .0765 M \text{hr}^{-1}$$

1987B



Trial	Initial [A]	Initial [B]	Initial Rate of Formation of C (M min ⁻¹)
1	0.0836	0.202	5.2×10^{-5}
2	0.0836	0.404	2.08×10^{-4}
3	0.0418	0.404	1.06×10^{-4}
4	0.0316	?	1.27×10^{-4}

(a) According to the data shown, what is the rate law for the reaction above?

$$\text{RATE} = k[A][B]^2$$

(b) On the basis of the rate law from part (a), calculate the specific rate constant. Specify the units.

$$5.2 \times 10^{-5} = k[.0836][.202]^2$$

$$\frac{M}{\text{min}} = k M M^2$$

$$k = .0152$$

$$k = .0152 \text{ M}^{-2} \text{ min}^{-1}$$

(c) What is the numerical value for the initial rate of disappearance of B for Trial #1?

TRICKY PROBLEM: FROM BALANCED EQUATION, WE SEE THAT
C FORMS $\times 2$ 'S AS FAST AS B DISAPPEARS.

$$2.6 \times 10^{-5} \text{ M min}^{-1}$$

(d) Calculate the initial concentration of B for Trial #4.

$$1.27 \times 10^{-4} = .0152 [0.0316][B]^2$$

$$.264 = [B]^2$$

$$[B] = .514 \text{ M}$$

1991 B



The following results were obtained when the reaction represented above was studied at 25°C.

Trial	Initial $[\text{ClO}_2]$	Initial $[\text{F}_2]$	Initial Rate of Increase of ClO_2F (M min^{-1})
1	0.010	0.10	2.4×10^{-3}
2	0.010	0.40	9.6×10^{-3}
3	0.020	0.20	9.6×10^{-3}

(a) Write the rate law expression for the reaction above.

$$\text{RATE} = k [\text{ClO}_2] [\text{F}_2]$$

* compare trials 1 + 2 to know 1st order w/ respect to F_2

* compare trials 2 + 3 to see "offsetting" changes to concentrations have no effect on rate

(b) Calculate the numerical value for the rate constant and specify the units.

$$2.4 \times 10^{-3} = k [0.010] [0.10]$$

$$k = 2.4$$

$$\frac{\text{M}}{\text{min}} = k \text{ M} \cdot \text{M}$$

$$k = 2.4 \text{ M}^{-1} \text{ min}^{-1}$$

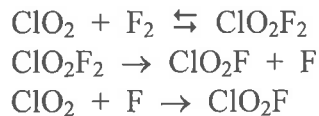
(c) In trial #2, what is the initial rate of decrease of $[\text{F}_2]$?

F_2 decreases at half the rate ClO_2F appears so

$$\frac{9.6 \times 10^{-3}}{2} = 4.8 \times 10^{-3} \text{ M min}^{-1}$$

(d) Which of the two proposed reaction mechanisms shown below is consistent with the rate law developed in part (a)? Justify your choice.

Mech #1:



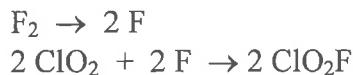
fast
slow
fast

$\text{RATE} = k [\text{ClO}_2\text{F}_2]$
can't have intermediate in final answer

$$k_f [\text{ClO}_2] [\text{F}_2] = k_{\text{rev}} [\text{ClO}_2\text{F}_2]$$

$$\text{RATE} = k [\text{ClO}_2] [\text{F}_2]$$

Mech #2:



slow
fast

$$\text{RATE} = k [\text{F}_2]$$

Mechanism #1, when all intermediates are removed, matches the rate law observed in the data shown above. Therefore, mechanism #1 is consistent.

1997 B



The following results were obtained when the reaction represented above was studied at 25°C.

Experiment	Initial [A]	Initial [B]	Initial Rate of Formation of C (M min ⁻¹)
1	0.25	0.75	4.3 x 10 ⁻⁴
2	0.75	0.75	1.3 x 10 ⁻³
3	1.50	1.50	5.3 x 10 ⁻³
4	1.75	?	8.0 x 10 ⁻³

(a) Determine the order of the reaction with respect to A and to B.

RATE IS 1ST ORDER WITH RESPECT TO A (compared trials 1 + 2)
 RATE IS 1ST ORDER WITH RESPECT TO B (compared trials 2 + 3)

(b) Write the rate law for the reaction. Calculate the value of the rate constant, specifying units.

$$\text{RATE} = k[A][B]$$

$$4.3 \times 10^{-4} = k[0.25][0.75]$$

$$k = .0023$$

$$\frac{M}{\text{min}} = k[M][M]$$

$$k = .0023 \text{ M}^{-1} \text{ min}^{-1}$$

(c) Determine the initial rate of change of [A] in Experiment #3. (Interesting curveball says Bracken!)

BASED ON BALANCED EQUATION, A DISAPPEARS 2x'S FASTER THAN C APPEARS.

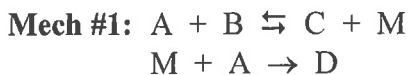
$$5.3 \times 10^{-3} \times 2 = 1.06 \times 10^{-2} \text{ M min}^{-1}$$

(d) Determine the initial concentration of B in Experiment #4.

$$8.0 \times 10^{-3} = .0023 [1.75][B]$$

$$B = 1.99 \text{ M}$$

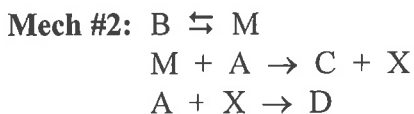
(e) Identify which of the reaction mechanisms represented below is consistent with the rate law developed in part (b). Justify your choice.



Fast equilibrium
 Slow
 $k_f[A][B] = k_{rev}[C][M]$
 $k_{rev}[C]$

$$\text{RATE} = k[M][A]$$

$$\text{RATE} = \frac{k[A]^2[B]}{[C]}$$



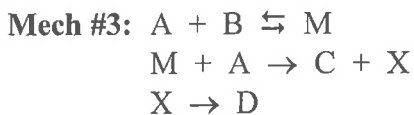
$$k_f[B] = k_{rev}[M]$$

Fast equilibrium
 Slow
 Fast

$$\text{RATE} = k[M][A]$$

$$\text{RATE} = k[A][B]$$

consistent with data above



$$k_f[A][B] = k_{rev}[M]$$

Fast equilibrium
 Slow
 Fast

$$\text{RATE} = k[M][A]$$

$$\text{RATE} = k[A]^2[B]$$