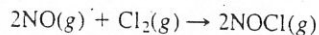


2

**AP Chemistry CHEMICAL KINETICS CHAPTER 12**

**Rate Laws from Experimental Data: Initial Rates Method**

17. The reaction



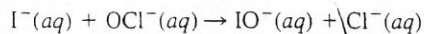
was studied at  $-10^\circ\text{C}$ . The following results were obtained where

$$\text{Rate} = -\frac{\Delta[\text{Cl}_2]}{\Delta t}$$

	$[\text{NO}]_0$ (mol/L)	$[\text{Cl}_2]_0$ (mol/L)	Initial Rate (mol/L · min)
1.	0.10	0.10	0.18
2.	0.10	0.20	0.35
3.	0.20	0.20	1.45

- What is the rate law?
- What is the value of the rate constant?

19. The reaction

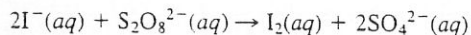


was studied and the following data were obtained:

	$[\text{I}^-]_0$ (mol/L)	$[\text{OCl}^-]_0$ (mol/L)	Initial Rate (mol/L · s)
1.	0.12	0.18	$7.91 \times 10^{-2}$
2.	0.060	0.18	$3.95 \times 10^{-2}$
3.	0.030	0.090	$9.88 \times 10^{-3}$
4.	0.24	0.090	$7.91 \times 10^{-2}$

- What is the rate law?
- Calculate the rate constant.

18. The reaction



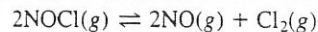
was studied at  $25^\circ\text{C}$ . The following results were obtained where

$$\text{Rate} = -\frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t}$$

	$[\text{I}^-]_0$ (mol/L)	$[\text{S}_2\text{O}_8^{2-}]_0$ (mol/L)	Initial Rate (mol/L · s)
1.	0.080	0.040	$12.50 \times 10^{-6}$
2.	0.040	0.040	$6.250 \times 10^{-6}$
3.	0.080	0.020	$5.560 \times 10^{-6}$
4.	0.032	0.040	$4.350 \times 10^{-6}$
5.	0.060	0.030	$6.410 \times 10^{-6}$

- Determine the rate law.
- Calculate a value for the rate constant for each experiment and an average value for the rate constant.

20. The decomposition of nitrosyl chloride was studied:



The following data were obtained where

$$\text{Rate} = -\frac{\Delta[\text{NOCl}]}{\Delta t}$$

	$[\text{NOCl}]_0$ (molecules/cm <sup>3</sup> )	Initial Rate (molecules/cm <sup>3</sup> · s)
1.	$3.0 \times 10^{16}$	$5.98 \times 10^4$
2.	$2.0 \times 10^{16}$	$2.66 \times 10^4$
3.	$1.0 \times 10^{16}$	$6.64 \times 10^3$
4.	$4.0 \times 10^{16}$	$1.06 \times 10^5$

- What is the rate law?
- Calculate the rate constant.
- Calculate the rate constant for the concentrations given in moles per liter.

17.  $R = k [\text{NO}]^x [\text{Cl}_2]^y$

	NO	Cl <sub>2</sub>	mol L <sup>-1</sup> min <sup>-1</sup>
1.	.1	.1	.18
2.	.1	.2	.36
3.	.2	.2	1.45

(Arrows in original image indicate: from exp 1 to 2, NO is constant, Cl<sub>2</sub> doubles, rate doubles (2x); from exp 1 to 3, both double, rate increases 8x (2<sup>3</sup>)).

a)  $R = k [\text{NO}]^2 [\text{Cl}_2]^1$

b)  $k = \frac{R}{[\text{NO}]^2 [\text{Cl}_2]^1}$

$$= \frac{0.18 \text{ mol L}^{-1} \text{ min}^{-1}}{(.1 \text{ mol L}^{-1})^2 (.1 \text{ mol L}^{-1})} \quad \text{exp \#1}$$

$$= \frac{0.18 \text{ mol L}^{-1} \text{ min}^{-1}}{0.001 \text{ mol}^3 \text{ L}^{-3}}$$


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$$= 180 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

$$k = 1.80 \times 10^2 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

18.  $R = k [\text{I}^-]^x [\text{S}_2\text{O}_8^{2-}]^y$

	[I <sup>-</sup> ]	[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ]	R mol L <sup>-1</sup> s <sup>-1</sup>
1.	.08	.04	12.50 × 10 <sup>-6</sup>
2.	.04	.04	6.25 × 10 <sup>-6</sup>
3.	.08	.02	5.56 × 10 <sup>-6</sup>

(Arrows in original image indicate: from exp 1 to 2, [I<sup>-</sup>] halves, [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] constant, rate halves (1/2 x); from exp 1 to 3, [I<sup>-</sup>] constant, [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] halves, rate halves (1/2 x)).

$R = k [\text{I}^-]^1 [\text{S}_2\text{O}_8^{2-}]^1$

$k = \frac{R}{[\text{I}^-]^1 [\text{S}_2\text{O}_8^{2-}]^1}$

$$k = \frac{6.250 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}}{(0.04 \text{ mol L}^{-1})(0.04 \text{ mol L}^{-1})} \quad \text{exp \#2}$$

$$k = 3.9 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$$

(19)

$$R = [I^-]^x [OCI^-]^y$$

	$[I^-]$	$[OCI^-]$	$R \text{ (mol L}^{-1} \text{ s}^{-1})$
* 1	0.12	0.18	$7.91 \times 10^{-2}$
2	0.060	0.18	$3.95 \times 10^{-2}$
3	0.030	0.090	$9.88 \times 10^{-3}$
4	0.24	0.090	$7.91 \times 10^{-2}$

$$R = k [I^-] [OCI^-]^y$$

$[I^-]$  is not held constant  $\therefore$

$$\frac{R_3}{R_2} = \frac{k [I^-]^1 [OCI^-]^y}{k [I^-]^1 [OCI^-]^y}$$

$$\frac{9.88 \times 10^{-3}}{3.95 \times 10^{-2}} = \frac{(0.03)^1 (0.09)^y}{(0.06)^1 (0.18)^y}$$

$$.25 = (.5) .5^y$$

$$.25 = .25^y$$

$$y = 1 \quad [OCI^-]^1 \quad \text{1st order}$$

$$R = k [I^-]^1 [OCI^-]^1 \quad k = \frac{R}{[I^-]^1 [OCI^-]^1}$$

$$k = \frac{7.91 \times 10^{-2} \text{ M s}^{-1}}{(0.24 \text{ M})^1 (0.09 \text{ M})^1} = 3.66 \text{ M}^{-1} \text{ s}^{-1}$$
$$3.66 \text{ L mol}^{-1} \text{ s}^{-1}$$

from exp 4

20

$$R = k [\text{NOCl}]^x$$

	[NOCl]	R
1	$3.0 \times 10^{16}$	$5.98 \times 10^4$
2	$2.0 \times 10^{16}$	$2.66 \times 10^4$
3	$1.0 \times 10^{16}$	$6.64 \times 10^3$
4	$4.0 \times 10^{16}$	$1.06 \times 10^5$

$\left. \begin{matrix} 2 \times \\ 4 \times \end{matrix} \right\}$

molecules  $(\text{cm}^3)^{-1}$       molecules  $(\text{cm}^3)^{-1} \text{ s}^{-1}$

$$R = k [\text{NOCl}]^2$$

$$k = \frac{R}{[\text{NOCl}]^2}$$

$$k = \frac{5.98 \times 10^4 \text{ molecules}(\text{cm}^3)^{-1} \text{ s}^{-1}}{\left[ 3.00 \times 10^{16} \text{ molecules}(\text{cm}^3)^{-1} \right]^2}$$

$3.0 \times 10^{16}$ molecules	1 mol	1000 $\text{cm}^3$
1 $\text{cm}^3$	$6.02 \times 10^{23}$ molecules	1 L

$$[\text{NOCl}] = 4.98 \times 10^{-5} \text{ M}$$

$5.98 \times 10^4$ molecules	1 mol	1000 $\text{cm}^3$
1 $\text{cm}^3$	$6.02 \times 10^{23}$ molecules	1 L

$$R = 9.9 \times 10^{-17} \text{ M s}^{-1}$$

$$R = \frac{9.9 \times 10^{-17} \text{ M s}^{-1}}{(4.98 \times 10^{-5} \text{ M})^2} = 4 \times 10^{-13} \text{ M s}^{-1}$$