AP Chemistry CHEMICAL KINETICS CHAPTER 12

Rate Laws from Experimental Data: Initial Rates Method

17. The reaction

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

was studied at −10°C. The following results were obtained where

$$\text{Rate} = -\frac{\Delta[Cl_2]}{\Delta t}$$

	$[NO]_0$ (mol/L)	$[Cl_2]_0$ (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

a. What is the rate law?
b. What is the value of the rate constant?

18. The reaction

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

was studied at 25°C. The following results were obtained where

$$\text{Rate} = -\frac{\Delta[S_2O_8^{2-}]}{\Delta t}$$

	$[I^-]_0$ (mol/L)	$[S_2O_8^{2-}]_0$ (mol/L)	Initial Rate (mol/L · s)
1.	0.080	0.040	12.50×10^{-6}
2.	0.040	0.040	6.250×10^{-6}
3.	0.080	0.020	5.560×10^{-6}
4.	0.032	0.040	4.350×10^{-6}
5.	0.060	0.030	6.410×10^{-6}

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

19. The reaction

$$I^-(aq) + OCl^-(aq) \rightarrow IO^-(aq) + Cl^-(aq)$$

was studied and the following data were obtained:

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

a. What is the rate law?
b. Calculate the rate constant.

20. The decomposition of nitrosyl chloride was studied:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

The following data were obtained where

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

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

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

(17.) $R = k[NO]^x[Cl_2]^y$

	NO	Cl_2	$mol\ L^{-1}\ min^{-1}$
1.	.1	.1	.18
2.	.1	.2 (2x)	.36 (2x)
3.	.2 (2x)	.2	1.45 (4x)

a) $R = k[NO]^2[Cl_2]^1$

b) $k = \dfrac{R}{[NO_2]^2[Cl_2]^1}$

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

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

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

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

(18) $R = k[I^-]^x[S_2O_8^{-2}]^y$

	$[I^-]$	$[S_2O_8^{-2}]$	R $mol\ L^{-1}s^{-1}$
1	.08 (½x)	.04	12.50×10^{-6} (½x)
2	.04	.04 (½x)	6.25×10^{-6} (½x)
3.	.08	.02	5.56×10^{-6}

$R = k[I^-]^1[S_2O_8]^1$

$R = \dfrac{R}{[I^-]^1[S_2O_8^{-2}]}$

$R = \dfrac{6.250 \times 10^{-6}\ mol\ L^{-1}\ s^{-1}}{(0.04\ mol\ L^{-1})(0.04\ mol\ L^{-1})}$ exp #2

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

(19) $R = [I^-]^x [OCl^-]^y$

	$[I^-]$	$[OCl^-]$	$R\ (mol\ L^{-1} s^{-1})$
1	0.12	0.18	7.91×10^{-2}
* 2	0.060 (½)	0.18	3.95×10^{-2} (½x)
3	0.030	0.090	9.88×10^{-3}
4	0.24	0.090	7.91×10^{-2}

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

$[I^-]$ is not held constant ∴

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

$$\frac{9.88 \times 10^{-3}}{3.95 \times 10^{-2}} = \frac{(.03)^1 (.09)^y}{(.06)^1 (.18)^y}$$

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

$$.25 = .25^y$$

$y = 1$ $[OCl^-]^1$ 1st order

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

$$k = \frac{7.91 \times 10^{-2}\ M\ s^{-1}}{(.24\ M)^1 (.09\ M)^1} = 3.66\ M^{-1} s^{-1}$$

$3.66\ L\ mol^{-1} s^{-1}$

from exp # 4

(20) $R = k[NOCl]^x$

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

2x 4x

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

$$R = k[NOCl]^2$$

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

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

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

1 $[NOCl] = 4.98 \times 10^{-5}$ M

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

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

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

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