CHEM 101B Kinetics – Initial Rates Method for determining Rate Law

29. The reaction

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

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 ×2	0.36 ×2
3)	0.20 ×2	0.20	1.45 ×4

1st order in $[Cl_2]$

2nd order in [NO]

$\boxed{rate = k[NO]^2[Cl_2]}$

a. What is the rate law?

b. What is the value of the rate constant?

~~exp 1 & exp 2~~

$\frac{exp\,2}{exp\,1}$ $\quad [Cl_2] \quad$ rate

$$\left(\frac{.20}{.10}\right)^n = \left(\frac{.36}{.18}\right)$$

$$2^n = 2 \qquad \log_2 2 = n$$

$$n = 1 \qquad 1 = n$$

$\frac{exp\,1}{exp\,3}$ $\quad$ [NO]

$$\left(\frac{.10}{.20}\right)^n = \frac{.18}{1.45}$$

$$.5^n = 0.124 \qquad \log_{.5}(.124) = n$$

$$\frac{\log(.124)}{\log(.5)} = n$$

$$3.01 = n$$

$$n = 3 \quad (2+1)$$

$$\frac{rate}{[NO]^2[Cl_2]} = \frac{k\cancel{[NO]^2}\cancel{[Cl_2]}}{\cancel{[NO]^2}\cancel{[Cl_2]}}$$

1) $k = \frac{rate}{[NO]^2[Cl_2]} = \frac{.18}{(.10)^2(.10)} = 180$

2) $\frac{.36}{(.10)^2(.20)} = 180$

3) $\frac{1.45}{(.20)^2(.20)} = 181$

$$\boxed{k = 180 \quad (\text{value})}$$

k (unit)

$$k = \frac{rate}{[NO]^2[Cl_2]} = \frac{\frac{\cancel{mol}}{\cancel{L}\cdot min}}{\left(\frac{mol}{L}\right)^2\left(\frac{\cancel{mol}}{\cancel{L}}\right)} = \frac{\frac{1}{min}}{\frac{mol^2}{L^2}} = \frac{L^2}{mol^2\cdot min}$$

$$= \frac{\frac{\cancel{M}}{min}}{M^2\cdot\cancel{M}} = \frac{\frac{1}{min}}{M^2} = \frac{1}{M^2\cdot min}$$

30. The reaction

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

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	12.5×10^{-6}
2	0.040	0.040	6.25×10^{-6}
3	0.080	0.020	6.25×10^{-6}
4	0.032	0.040	5.00×10^{-6}
5	0.060	0.030	7.00×10^{-6}

$\frac{1}{2}[I^-]$

$\left(\frac{.080}{.040}\right)^n = \frac{12.5 \times \cancel{10^{-6}}}{6.25 \times \cancel{10^{-6}}}$

$2^n = 2 \quad n = 1$

$\frac{1}{3}[S_2O_8^{2-}]$

$\left(\frac{.040}{.020}\right)^n = \frac{12.5 \times \cancel{10^{-6}}}{6.25 \times \cancel{10^{-6}}}$

$2^n = 2 \quad n = 1$

a. Determine the rate law. $rate = k[I^-][S_2O_8^{2-}]$

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

$$k = \frac{rate}{([I^-][S_2O_8^{2-}])} =$$

1) 3.9×10^{-3}
2) 3.9×10^{-3}
3) 3.9×10^{-3}
4) 3.9×10^{-3}
5) 3.9×10^{-3}

Avg $k = 3.9 \times 10^{-3}$

34. The reaction

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

was studied, and the following data were obtained where

$$\text{Rate} = -\frac{\Delta[O_2]}{\Delta t}$$

	$[NO]_0$ (molecules/cm^3)	$[O_2]_0$ (molecules/cm^3)	Initial Rate (molecules/cm$^3 \cdot$ s)
1)	1.00×10^{18}	1.00×10^{18}	2.00×10^{16}
2)	3.00×10^{18}	1.00×10^{18}	1.80×10^{17}
3)	2.50×10^{18}	2.50×10^{18}	3.13×10^{17}

What would be the initial rate for an experiment where $[NO]_0 = 6.21 \times 10^{18}$ molecules/cm^3 and $[O_2]_0 = 7.36 \times 10^{18}$ molecules/cm^3?

$\frac{\text{exp 3}}{\text{exp 1}}$ [NO] $\left(\frac{3.00\times10^{18}}{1.00\times10^{18}}\right)^n = \frac{1.80\times10^{17}}{2.00\times10^{16}}$

$3.00^n = 9.00$

$n = 2$

$\log_3 9 = n$

$\frac{\log 9}{\log 3} = n$

$2 = n$

$\frac{\text{exp 3}}{\text{exp 2}}$ [NO]'

$\left(\frac{2.50\times10^{18}}{3.00\times10^{18}}\right)^2 \left(\frac{2.50\times10^{18}}{1.00\times10^{18}}\right)^n = \frac{3.13\times10^{17}}{1.80\times10^{17}}$

$0.694\,(2.50)^n = 1.74$

$2.50^n = 2.504$

$n = 1$

$\text{rate} = k[NO]^2[O_2]$

1) $k = \frac{\text{rate}}{[NO]^2[O_2]} = 2.00\times10^{-38}$

2) $= 2.00\times10^{-38}$

3) $= 2.00\times10^{-38}$

$\text{rate} = (2.00\times10^{-38})(6.21\times10^{18})^2(7.36\times10^{18})$

$= \boxed{5.69\times10^{18}\ \frac{\text{molecules}}{\text{cm}^3\cdot\text{s}}}$

35. The rate of the reaction between hemoglobin (Hb) and carbon monoxide (CO) was studied at 20°C. The following data were collected with all concentration units in μmol/L. (A hemoglobin concentration of 2.21 μmol/L is equal to 2.21×10^{-6} mol/L.)

$[Hb]_0$ (μmol/L)	$[CO]_0$ (μmol/L)	Initial Rate (μmol/L · s)
2.21	1.00	0.619
4.42	1.00	1.24
4.42	3.00	3.71

a. Determine the orders of this reaction with respect to Hb and CO.

1st in both

b. Determine the rate law.

rate $= k[Hb]_0[CO]$

c. Calculate the value of the rate constant.

.280
.281
.280

.280

d. What would be the initial rate for an experiment with $[Hb]_0 = 3.36$ μmol/L and $[CO]_0 = 2.40$ μmol/L?

rate $= .280(3.36)(2.40)$

$\approx \boxed{2.26\ \mu mol/L \cdot s}$