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12.3 Initial Rates from Three Experiments for the Reaction

$$\text{NH}_4^+(\text{aq}) + \text{NO}_2^-(\text{aq}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$$

| Experiment | Exp. | Initial Concentration of $\text{NH}_4^+$ | Initial Concentration of $\text{NO}_2^-$ | Initial Rate ( $\text{mol/L} \cdot \text{s}$ ) |
|------------|------|------------------------------------------|------------------------------------------|------------------------------------------------|
| 1          | 1    | 0.100 M                                  | 0.0050 M                                 | $1.35 \times 10^{-7}$                          |
| 2          | 2    | 0.100 M                                  | 0.010 M                                  | $2.70 \times 10^{-7}$                          |
| 3          | 3    | 0.200 M                                  | 0.010 M                                  | $5.40 \times 10^{-7}$                          |

a) what is the rate law?  
The overall reaction order?

b) what is the rate constant?  
rate law =  $k [\text{NH}_4^+]^m [\text{NO}_2^-]^n$

Exp # 1 & 2  $[\text{NH}_4^+]$  is constant  
double  $[\text{NO}_2^-]$ , double rate

$$2^n = 2$$

$$\text{so } n = 1$$

Exp #2 & 3  $[NO_2^-]$  is  
constant

double  $[NH_4^+]$ , double  
rate

$$2^n = 2, \text{ so } n = 1$$

overall order is 2  
 $m + n$

using exp #1 data

$$1.35 \times 10^{-7} \frac{M}{s} = k(0.100 M)(0.0050 M)$$

solve for  $k$ , =

$$2.7 \times 10^{-4} M^{-1} s^{-1}$$

$$\text{rate} = 2.7 \times 10^{-4} M^{-1} s^{-1} [NH_4^+][NO_2^-]$$

Table 12.5 The Results from Four Experiments to Study the Reaction  
 $\text{BrO}_3^-(\text{aq}) + 5\text{Br}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\text{l}) + 3\text{H}_2\text{O}(\text{l})$

| Experiment | Initial Concentration of $\text{BrO}_3^-$ (mol/L) | Initial Concentration of $\text{Br}^-$ (mol/L) | Initial Concentration of $\text{H}^+$ (mol/L) | Measured Initial Rate (mol/L · s) |
|------------|---------------------------------------------------|------------------------------------------------|-----------------------------------------------|-----------------------------------|
| 1          | 0.10                                              | 0.10                                           | 0.10                                          | $8.0 \times 10^{-4}$              |
| 2          | 0.20                                              | 0.10                                           | 0.10                                          | $1.6 \times 10^{-3}$              |
| 3          | 0.20                                              | 0.20                                           | 0.10                                          | $3.2 \times 10^{-3}$              |
| 4          | 0.10                                              | 0.10                                           | 0.20                                          | $3.2 \times 10^{-3}$              |

$\text{BrO}_3^-$  initial rate  
 $8.0 \times 10^{-4}$   
 $1.6 \times 10^{-3}$   
 $3.2 \times 10^{-3}$   
 $3.2 \times 10^{-3}$

1) What is the rate law and rate constant?

(K) rate =  $8.0 \text{ M}^{-3} \text{ s}^{-1}$   
 constant

rate =  $8.0 \text{ M}^{-3} \text{ s}^{-1} [\text{BrO}_3^-]^1 [\text{Br}^-]^1 [\text{H}^+]^2$

Exp 1 & 2  $[\text{Br}^-]$  and  $[\text{H}^+]$  are constant  
 $[\text{BrO}_3^-]$  doubles, rate doubles  
 so 1st order

Exp # 2 & 3  $[\text{BrO}_3^-]$  and  $[\text{H}^+]$  are constant  
 $[\text{Br}^-]$  doubles, rate doubles  
 so 1st order

Exp #1 & 4  $[\text{BrO}_3^-]$  and  $[\text{Br}^-]$

are constant

$[\text{H}^+]$  doubles, rate  $\times 4$

so order is 2

overall rxn order is 4