# DETERMINING THE RATE EXPONENT

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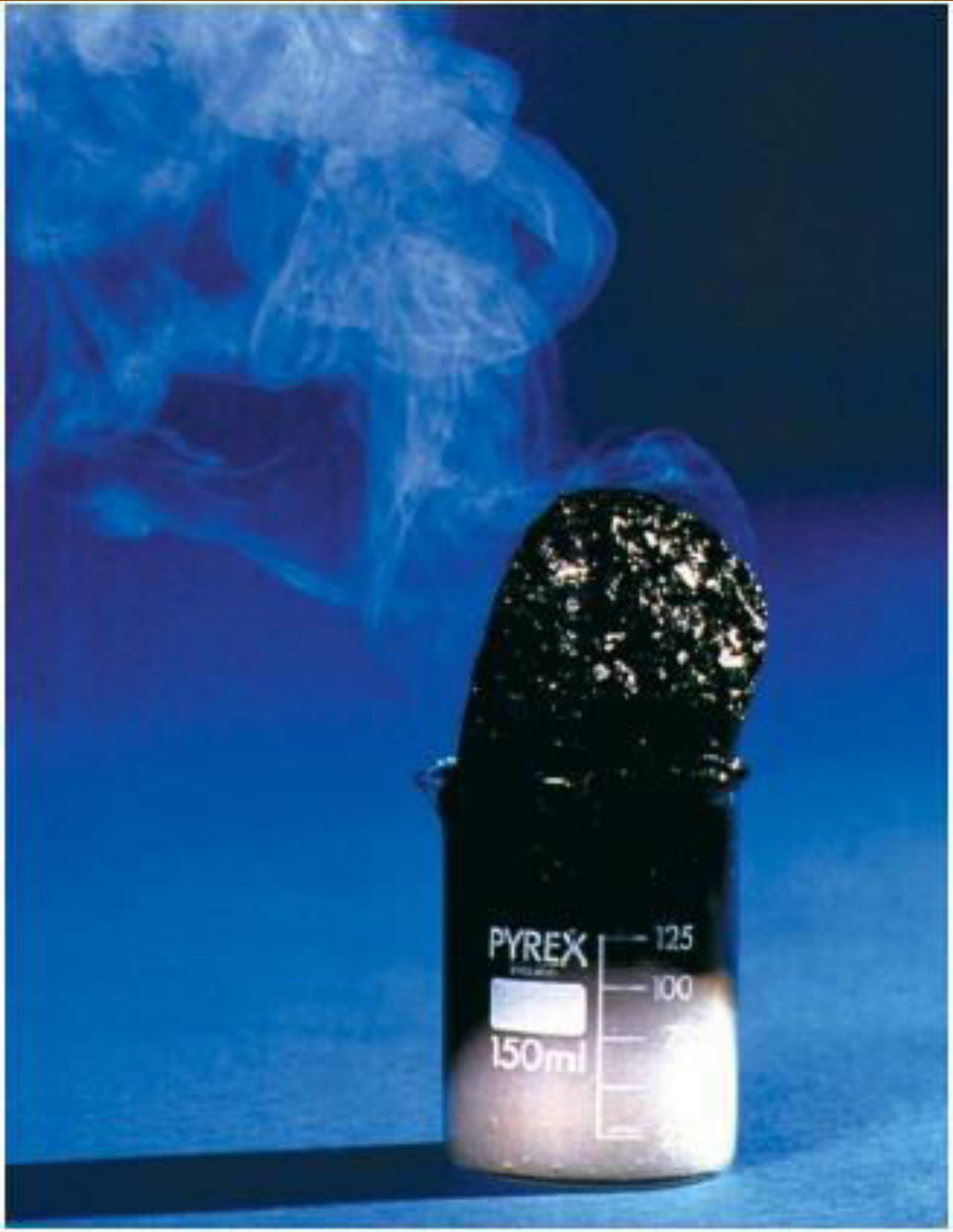
How would you set up an experiment to determine the rate exponent for the following reaction?

$C_6H_{12}O_{6(s)} + H_2SO_{4(aq)}$



# DETERMINING THE RATE EXPONENT

Exponents for a rate law expression must be determined experimentally (empirically).

Concentrations of each reactant must be changed one at a time to see how much the overall reaction rate does or doesn’t change.

Related to how the reaction takes place at the atomic level, which we cannot see.

# DETERMINING THE RATE EXPONENT

## HANDOUT - Table 1

| Concentration Factor Change | Reaction Rate Factor Change | Rate Law Exponent on the Concentration |
|---|---|---|
| 2x | no change | 0 |
| 3x | no change | 0 |
| 4x | no change | 0 |
| 2x | $2^1 = 2$ | 1 |
| 3x | $3^1 = 3$ | 1 |
| 4x | $4^1 = 4$ | 1 |

# DETERMINING THE RATE EXPONENT

## HANDOUT - Table 1

| Concentration Factor Change | Reaction Rate Factor Change | Rate Law Exponent on the Concentration |
|---|---|---|
| 2x | $2^2 = 4$ | 2 |
| 3x | $3^2 = 9$ | 2 |
| 4x | $4^2 = 16$ | 2 |
| 2x | $2^3 = 8$ | 3 |
| 3x | $3^3 = 27$ | 3 |
| 4x | $4^3 = 64$ | 3 |

# DETERMINING THE RATE EXPONENT

## HANDOUT - Example 1

| Initial Concentration (mol / L) | | Initial Rate of Formation of Products (mol/L•s) |
|---|---|---|
| [A] | [B] | |
| 0.10 | 0.10 | 0.20 |
| 0.20 | 0.10 | 0.40 |
| 0.30 | 0.10 | 0.60 |
| 0.30 | 0.20 | 2.40 |
| 0.30 | 0.30 | 5.40 |

Order for [A]: 1

Order for [B]: 2

Order of overall rxn: 3

k = $2.0 \times 10^2\ L^2\ mol^{-2}\ s^{-1}$

$r=k[A][B]^2$

# DETERMINING THE RATE EXPONENT

## HANDOUT - Example 2

| Initial Concentration (mol/L) | Initial Rate of Formation of Products (mol/L•s) |
|---|---|
| $[SO_2Cl_2]$ | |
| 0.100 | $2.2 \times 10^{-6}$ |
| 0.200 | $4.4 \times 10^{-6}$ |
| 0.300 | $6.6 \times 10^{-6}$ |

Order for $[SO_2Cl_2]$: 1

Order of overall rxn: 1

$k =$ $2.2 \times 10^{-5}\ s^{-1}$

$r=k[SO_2Cl_2]$

# DETERMINING THE RATE EXPONENT

## HANDOUT - Example 3

| Initial Concentration (mol/L) | | Initial Rate of Formation of Products (mol/L•s) |
|---|---|---|
| [A] | [B] | |
| 0.40 | 0.30 | $1.0 \times 10^{-4}$ |
| 0.80 | 0.30 | $4.0 \times 10^{-4}$ |
| 0.80 | 0.60 | $1.6 \times 10^{-3}$ |

Order for [A]: 2

Order for [B]: 2

Order of overall rxn: 4

$k = 6.9 \times 10^{-3}\ L^3\ mol^{-3}\ s^{-1}$

$r=k[A]^2[B]^2$

# DETERMINING THE RATE EXPONENT

## HANDOUT - Example 4

| Initial Concentration (mol/L) | | Initial Rate of Formation of Products (mol/L•s) |
|---|---|---|
| [NO] | $[H_2]$ | |
| 0.10 | 0.10 | $1.23 \times 10^{-3}$ |
| 0.10 | 0.20 | $2.46 \times 10^{-3}$ |
| 0.20 | 0.10 | $4.92 \times 10^{-3}$ |

Order for [NO]: 2

Order for $[H_2]$: 1

Order of overall rxn: 3

k = 1.2 $L^2\ mol^{-2}\ s^{-1}$

$r = k[NO]^2[H_2]$

# DETERMINING THE RATE EXPONENT

**Ex. 1** The decomposition of $N_2O_5$ is:

$$2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$$

This is a first order rxn with respect to $N_2O_5$. Given initial rate of $2.1 \times 10^{-4}$ mol/L•s and initial $[N_2O_5]$ = 0.40 mol / L, predict the rate when $[N_2O_5]$ = 0.80 M.

$$r = k\,[N_2O_5]$$

$$2.1 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1} = k\,[0.40\text{mol/L}]$$

$$\frac{2.1 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}}{0.40\text{mol/L}} = k$$

$$0.000525\ \text{s}^{-1} = k$$

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$$r = k\,[N_2O_5]$$
$$= 0.000525\ s^{-1}\ [0.80 mol/L]$$
$$= 4.2 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$$

Notice how this is a first order reaction, so doubling the concentration DOUBLES the rate of reaction

Therefore the rate is $4.2 \times 10^{-4}$ mol $L^{-1}$ $s^{-1}$

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**Ex. 2** Given $2C_4H_6 \rightarrow C_8H_{12}$ where $r = k[C_4H_6]^2$.

If the initial rate was 32 mmol $C_4H_6$/L•min at a certain $[C_4H_6]$, what would be the initial rate if the concentration were doubled?

Since this is a second order reaction, doubling the concentration quadruples the rate.

$$2 \times [\;] = r \times 4$$

Therefore the rate of reaction is $1.3 \times 10^2$ mmol/L•min

# DETERMINING THE RATE EXPONENT

**half-life** - the time required for *half* the concentration of a reactant to be used up in a rxn

**Ex. 3** If the mass of an antibiotic is 2.464 g, what mass will remain after 6.0 h, if the half-life is 2.0 h, and no more antibiotic is added.

$$m_{final} = m_{initial}\,(0.5)^n \qquad \text{n=\# of half lives}$$

$$m_{final} = 2.464\text{g}\,(0.5)^{6.0/2.0}$$

$$= 2.464\text{g}\,(0.5)^3$$

$$= 0.308\text{g}$$

$$= 0.31\text{g}$$

Therefore 0.31g of antibiotic remains

# DETERMINING THE RATE EXPONENT

## Equation relating half-life and the rate constant:

$$\boxed{kt_{\frac{1}{2}} = 0.693}$$

Can ONLY be applied to a FIRST ORDER reaction

The radioisotope lead-212 has half-life of 10.6 h. What is the rate constant for this isotope?

$$r = k[\text{Pb-212}]^1$$

and $kt_{\frac{1}{2}} = 0.693$

$$k = \frac{0.693}{t_{\frac{1}{2}}}$$

$$k = \frac{0.693}{10.6\text{h}}$$

$$k = 0.0654\text{h}^{-1}$$

.: the rate constant is $0.0654\text{h}^{-1}$