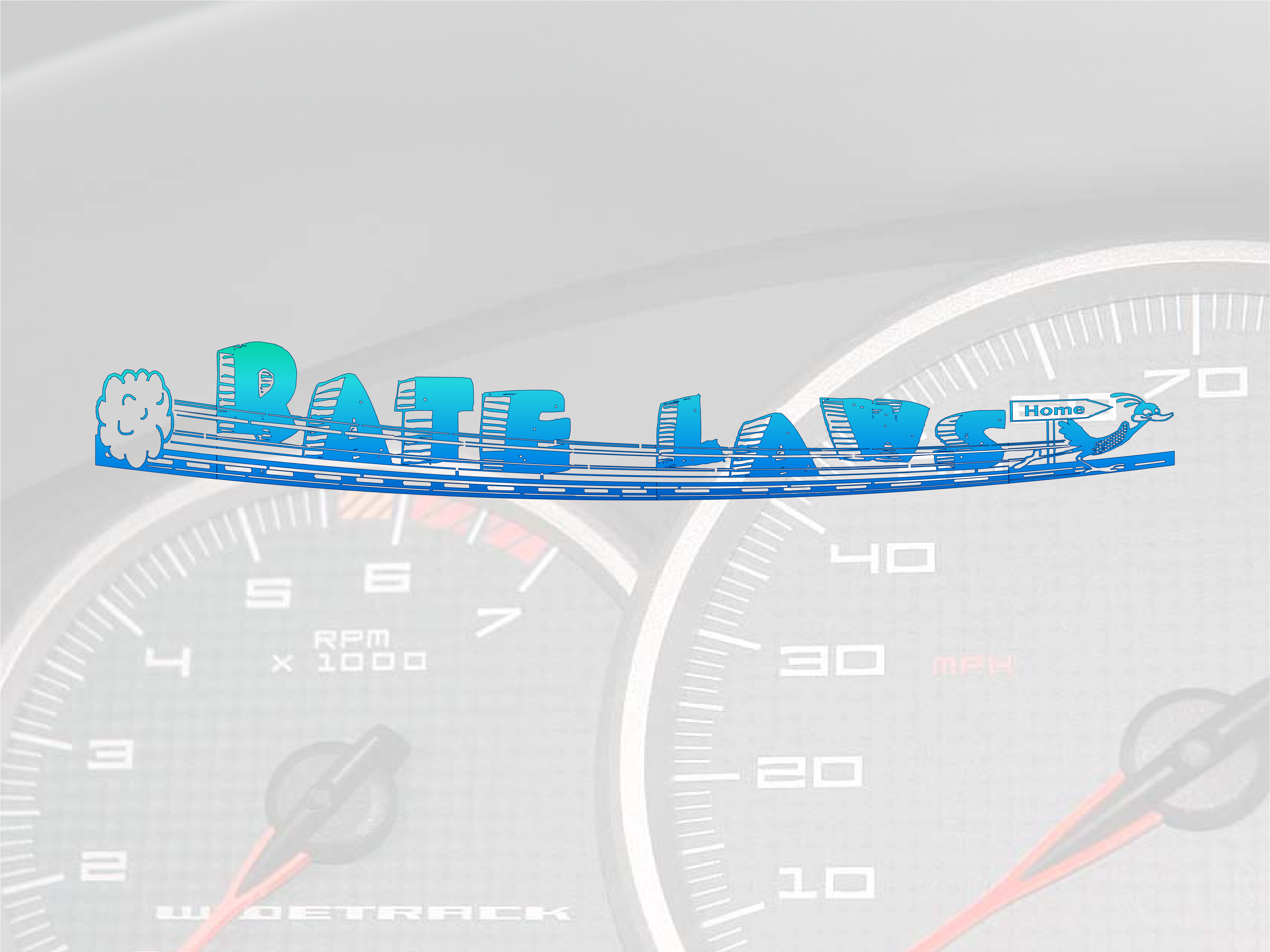
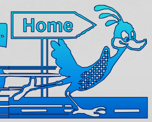


RATE LAWS

REACTION RATES



WRITE DOWN

- Reaction rates are defined as the change in concentration of a reactant *or* product per unit of time.
- Chemical reactions are reversible.
  - When reactants are first placed in the reaction vessel, initially the forward reaction is the dominant reaction.
  - As the concentration of products increases, the reverse reaction becomes important.
  - $(\Delta_{\text{REACTANTS}} = \text{Rate}_{\text{FORWARD}} - \text{Rate}_{\text{REVERSE}})$
- If conditions permit the reverse reaction to be neglected, the reaction rate depends on only the concentration of the reactants.

THE NATURE OF RATE LAWS

Home

- The expression showing how the rate of the reaction depends on the concentration of the reactants is called a **rate law.**

WRITE DOWN

- For the reaction A + B → C,
  - The concentration of A, [A], can be held constant while the concentration of B, [B] is changed, and the rate measured,

    and
  - The concentration of B, [B], can be held constant while the concentration of A, [A] is changed, and the rate measured.
- This is how rate laws are determined.

FORMAT OF RATE LAWS

Home

- If
    - doubling the concentration of A causes the reaction rate to double,
    - while doubling the concentration of B causes it to quadruple,
    - and doubling them both causes the reaction rate to increase eightfold,
    - the rate law is Rate = $k[A][B]^2$.
- The general form of rate laws is: Rate = $k[A]^m[B]^n$
- The value of *m* and *n* can only be determined experimentally.

WRITE DOWN

PATTERNS OF RATE LAWS

Home

WRITE DOWN

- The form of the rate law depends on the reaction mechanisms.
- Experimental data verifying the rate law confirms the reaction mechanism.
- In multiple step reactions, the rate law is based on the rate determining step.

SINGLE STEP RATE LAWS

Home

WRITE DOWN

Single Step Reactions

Concentrations of reactants are raised to their stoichiometric coefficients based on collision theory.

- For A + B → 2C, where one particle of A collides with one of B to form two particles of C,
  - o R = $k[A][B]$
- For 2C → A + B, where two particles of C collide to form one of A and one of B,
  - o R = $k[C]^2$

MULTIPLE STEP RATE LAWS

Home

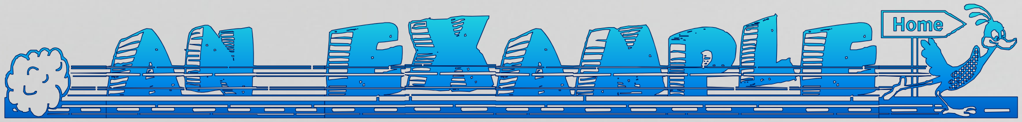
WRITE DOWN

Multiple Step Reactions

For the reaction: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

- The mechanism is believed to consist of two steps.
  - Step 1: $NO_2\ (g) + NO_2(g) \rightarrow NO_3\ (g) + NO(g)$ slow
  - Step 2: $NO_3\ (g) + CO\ (g) \rightarrow NO_2(g) + CO_2(g)$ fast
  - Net $NO_2\ (g) + CO\ (g) \rightarrow NO(g) + CO_2(g)$
- The rate law is determined from the rate determining step.
  - $R = k[NO_2]^2$
- Experimental measurement of the rate law confirms the mechanism.

AN EXAMPLE



- Consider the reaction: $NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(\ell)$
- If it is a single step reaction, the rate law should be $R = k[NH_4^+][NO_2^-]$
- Below is some sample data:

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate (mol/L•s)
1	0.100 *M*	0.0050 *M*	1.35×10^{-7}
2	0.100 *M*	0.010 *M*	2.70×10^{-7}
3	0.200 *M*	0.010 *M*	5.40×10^{-7}

- Analysis of the data:

Experiment 1:

$$\text{Rate 1} = 1.35\times10^{-7}\,mol/L\cdot s = k(0.100mol/L)^n(0.0050mol/L)^m$$

Experiment 2:

$$\text{Rate 2} = 2.70\times10^{-7}\,mol/L\cdot s = k(0.100mol/L)^n(0.010mol/L)^m$$

Comparison:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{2.70\times10^{-7}\,mol/L\cdot s}{1.35\times10^{-7}\,mol/L\cdot s} = \frac{k(0.100mol/L)^n(0.010mol/L)^m}{k(0.100mol/L)^n(0.0050mol/L)^m}$$

$$\frac{\text{Rate 2}}{\text{Rate 1}} = 2.00 = (2.00)^m$$

$m = 1$

Experiment 2:

$$\text{Rate 2} = 2.70\times10^{-7}\,mol/L\cdot s = k(0.100mol/L)^n(0.010mol/L)^m$$

Experiment 3:

$$\text{Rate 1} = 5.40\times10^{-7}\,mol/L\cdot s = k(0.200mol/L)^n(0.010mol/L)^m$$

Comparison:

$$\frac{\text{Rate 3}}{\text{Rate 2}} = \frac{5.40\times10^{-7}\,mol/L\cdot s}{2.70\times10^{-7}\,mol/L\cdot s} = \frac{k(0.200mol/L)^n(0.010mol/L)^m}{k(0.100mol/L)^n(0.010mol/L)^m}$$

$$\frac{\text{Rate 3}}{\text{Rate 2}} = 2.00 = (2.00)^n$$

$n = 1$

SAMPLE PROBLEMS

WRITE DOWN

- A single step reaction occurs as follows:
  $X + 2Y \rightarrow C$
  - Write the rate law. **$R = k[X][Y]^2$**
  - What effect does cutting the concentration of Y in half have on the reaction rate? **It cuts the rate to one fourth.**
- A multistep reaction occurs as follows:

$2X \rightarrow Y + A$	*slow*
$\underline{2Y + A \rightarrow X + C}$	*fast*
$X + Y \rightarrow C$	*net*

  - Write the rate law. **$R = k[X]^2$**
  - What effect does doubling the concentration of X have on the reaction rate? **It quadruples the rate.**