**Oxidation & Reduction Reactions:**

**Oxidation** involves an atom or compound losing electrons

**Reduction** involves an atom or substance gaining electrons

Neither process can occur alone... that is, there must be an exchange of electrons in the process.

The substance that is **oxidized** is the *reducing agent*

The substance that is **reduced** is the *oxidizing agent*

\[ \text{Mg(s)} + 2\text{H}^+(aq) \rightarrow \text{Mg}^{2+}(aq) + \text{H}_2(g) \]

**Oxidation Numbers**

Chemists use *oxidation numbers* to account for the transfer of electrons in a RedOx reaction.

*Oxidation numbers* are the actual charge on an atom when combined in a compound.

1. The atoms of pure elements always have an oxidation number of zero.
2. If an atom is charged, then the charge is the oxidation number.
3. In a compound, fluorine always has an oxidation number of \(-1\).
4. Oxygen most often has an oxidation number of \(-2\).
   - When combined with fluorine, oxygen has a positive O.N.
   - In peroxide, the O.N. is \(-1\).
5. In compounds, Cl, Br & I are generally \(-1\) so long as F and O are not present.
6. In compounds, H is \(+1\), except as a hydride (H \(-2\)).
7. For neutral compounds, the sum of the O.N.’s equals zero. For a polyatomic ion, the sum equals the charge.

**Examples:**

- \(\text{Mg(s)}\) All have an oxidation number of zero (0)
- \(\text{Hg(l)}\)
- \(\text{I}_2(s)\)
- \(\text{O}_2(g)\)
**Oxidation Numbers**

2. If an atom is charged, then the charge is the oxidation numbers.

   **Examples:**
   
<table>
<thead>
<tr>
<th>Ion</th>
<th>Oxidation Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$(aq)</td>
<td>+2</td>
</tr>
<tr>
<td>Cl$^-$ (aq)</td>
<td>-1</td>
</tr>
<tr>
<td>Sn$^{4+}$(s)</td>
<td>+4</td>
</tr>
<tr>
<td>Hg$_2^{2+}$(aq)</td>
<td>+2/2 = +1 for each Hg atom</td>
</tr>
</tbody>
</table>

3. In a compound, fluorine always has an oxidation numbers of $-1$.
4. Oxygen most often has an oxidation numbers $-2$.
   *When combined with fluorine, oxygen has a positive O.N.
   *In peroxide, the O.N. is $-1$.
5. In compounds, Cl, Br & I are $-1$ (Except with F and O present)
6. In compounds, H is $+1$, except as a hydride (H$^-$: $-1$)

    **Examples:**
    
    | Compound      | Oxidation Numbers |
    |---------------|-------------------|
    | HF(g)         | H = +1 F = $-1$   |
    | H$_2$O(l)     | H = +1 O = $-2$   |
    | OF$_2$(g)     | O = +2 F = $-1$   |
    | Na$_2$O$_2$(s) | Na = +1 O = $-1$ |
    | HCl(g)        | H = +1 Cl = $-1$  |
    | NaH(l)        | Na = +1 H = $-1$  |

7. For neutral compounds, the sum of the O.N.’s equals zero.
   For a poly atomic ion, the sum equals the charge.

   **Examples:**
   
   $+2 + 2 \times (-1) = 0$
   $3 - 4 \times (+1) = 1$

**Most common oxidation numbers**

- H: +1
- Li+: +1
- Na+: +1
- K+: +1
- Mg$: +2$
- Al$: +3
- F$: -1$
- Cl$: -1
- Br$: -1$
- I$: -1
**Oxidation Numbers**

Determine the oxidation numbers of manganese in the following compound:

\[ +1 \ + \ ? \ + 4 \times (-2) = 0 \]

\[ \text{KMnO}_4 \]

Manganese must have an oxidation number of +7!

**Oxidation & Reduction Reactions:**

**Recognizing a Redox Reaction:**

In a Redox reaction, the species oxidized and the species reduced are identified by the changes in oxidation numbers:

\[ \begin{align*}
\text{Oxidation numbers:} & \quad +1 & 0 \\
2\text{Ag}^+ (aq) + \text{Cu}(s) & \rightarrow 2\text{Ag}(s) + \text{Cu}^{2+} (aq) \\
\text{Oxidation numbers:} & \quad 0 & +2
\end{align*} \]

Since silver goes from +1 to zero, it is reduced. Since copper goes from zero to +2, it is oxidized.

**Oxidation & Reduction Reactions:**

**Electron Transfer in a Redox Reaction:**

\[ 2\text{Ag}^+ (aq) + \text{Cu}(s) \rightarrow 2\text{Ag}(s) + \text{Cu}^{2+} (aq) \]

Two electrons leave copper. The silver ions accept them. The copper metal is oxidized to copper (II) ion. The silver ion is reduced to solid silver metal.
**Practice at home:**
Identify the species that is **Oxidized** and **Reduced** by assigning oxidation numbers in the following reaction.

\[ 3\text{CH}_4(g) + \text{Cr}_2\text{O}_7^{2-} (aq) + 8\text{H}^+ (aq) \rightarrow 3\text{CH}_3\text{OH}(l) + 2\text{Cr}^{3+} (aq) + 4\text{H}_2\text{O}(l) \]

**Answer:**
The carbon in methane (CH\(_4\)) is oxidized (−4 to −2)
Chromium in dichromate is reduced (+6 to +3)

---

**Electrochemical Cells**

If a RedOx reaction is spontaneous, the electron flow will have a positive potential which can be used to do work.

When the individual processes are separated by a salt bridge, the electron flow can be completed by a wire.

In the cell, oxidation (loss of electrons) occurs at the **Anode**
reduction (gain of electrons) occurs at the **cathode**

Electrons flow from the anode to the cathode.

---

**The Cu|Cu\(^{2+}\) and Ag|Ag\(^{+}\) Cell**

**CELL POTENTIAL, \(E_{cell}\)**

- For Zn/Cu cell, potential is +1.10 V at 25 °C and when [Zn\(^{2+}\)] and [Cu\(^{2+}\)] = 1.0 M.
- This is the **STANDARD CELL POTENTIAL, \(E^0\)**
- \(E_{cell}\) is a quantitative measure of the tendency of reactants to proceed to products when all are in their standard states at 25 °C.

Not reaction: Cu(s) + 2 Ag\(^{+}\)(aq) \rightarrow Cu\(^{2+}\)(aq) + 2 Ag(s)
CELL POTENTIALS, $E^\circ$

Individual ½ reaction cell potentials ($E^\circ$) can’t be measured directly. They are measured relative to a STANDARD HYDROGEN CELL, “SHE”.

$$2 \text{H}^+(aq, 1 \text{ M}) + 2e^- \rightarrow \text{H}_2(g, 1 \text{ atm})$$

$E^\circ = 0.0 \text{ V}$

Standard Redox Potentials, $E^\circ$

<table>
<thead>
<tr>
<th>CATHODE</th>
<th>Chemical Reaction</th>
<th>$E^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$ + 2e$^-\rightarrow$ Cu</td>
<td>+0.34</td>
<td></td>
</tr>
<tr>
<td>2 H$^+$ + 2e$^-\rightarrow$ H$_2$</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Zn$^{2+}$ + 2e$^-\rightarrow$ Zn</td>
<td>-0.76 ANODE</td>
<td></td>
</tr>
</tbody>
</table>

Northwest-southeast rule:
- reducing agent at southeast corner = ANODE
- oxidizing agent at northwest corner = CATHODE

$E^\circ_{\text{net}}$ = “distance” from “top” half-reaction (cathode) to “bottom” half-reaction (anode)

$E^\circ_{\text{net}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

$E^\circ_{\text{cathode}} = +0.799 \text{ V}$ and $E^\circ_{\text{anode}} = +0.337 \text{ V}$.

$E^\circ_{\text{net}}$ for Cu/Ag$^+$ reaction = +0.46 V
Cell Notation

oxidized | reduced form | oxidized | reduced form

“||” represents a phase boundary
“|” represents a salt bridge

What is the correct cell notation for an electrolytic cell based on the reaction below?

\[ \text{Ag}^+(aq) + \text{Sn}(s) \rightarrow \text{Ag}(s) + \text{Sn}^{2+}(aq) \]

\( \text{Ag}^+\text{(aq)} \) is reduced to \( \text{Ag}(s) \) **Cathode**

\( \text{Sn}(s) \) is oxidized to \( \text{Sn}^{2+}(aq) \) **Anode**

\( \text{Sn}(s) \mid \text{Sn}^{2+}(aq) || \text{Ag}^+(aq) \mid \text{Ag}(s) \)

---

**E\text{cell} at Nonstandard Conditions**

\[ E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0257 \, \text{V}}{n} \ln Q \]

**The NERNST EQUATION**

- \( E_{\text{cell}} \) = potential under nonstandard conditions
- \( n = \#. \) of electrons exchanged
- \( \ln = \) “natural log”
- If \( [P] \) and \( [R] \) = 1 mol/L, then \( E = E^\circ \)
- If \( [R] > [P] \), then \( E \) is **lower** than \( E^\circ \)
- If \( [R] < [P] \), then \( E \) is **higher** than \( E^\circ \)

---

Calculate \( E_{\text{cell}} \) for the following electrochemical cell at 25 °C

\( \text{Ag(s)} \mid \text{AgCl(s)} \mid \text{Cl}^-(aq, 0.20 \, \text{M}) || \text{Fe}^{3+}(aq, \text{0.25 M}), \text{Fe}^{2+}(aq, \text{0.25 M}) \mid \text{Pt(s)} \)

given the following standard reduction potentials.

\( \text{AgCl(s)} + \text{e}^- \rightarrow \text{Ag(s)} + \text{Cl}^-(aq) \quad E^\circ = +0.222 \, \text{V} \)

\( \text{Fe}^{3+}(aq) + \text{e}^- \rightarrow \text{Fe}^{2+}(aq) \quad E^\circ = +0.771 \, \text{V} \)

**runs in reverse**

\[ E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \]

\[ E_{\text{cell}} = 0.771 \, \text{V} - 0.222 \, \text{V} = 0.549 \, \text{V} \]
**THE EQUILIBRIUM CONSTANT**

For any type of chemical equilibrium of the type

\[ a \, A + b \, B \rightarrow c \, C + d \, D \]

the following is a CONSTANT (at a given T)

\[
K = \frac{[C]^c [D]^d}{[A]^a [B]^b}
\]

Write the expression for \( K \) for the reaction of ammonium ion with hydroxide ion.

\[ \text{NH}_4^+(aq) + \text{OH}^-(aq) \rightleftharpoons \text{NH}_3(aq) + \text{H}_2\text{O}(l) \]

\[ (a) \, K = \frac{[\text{NH}_3]}{[\text{NH}_4^+][\text{OH}^-]} \]

\[ (b) \, K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \]

\[ (c) \, K = \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \]

\[ (d) \, K = \frac{[\text{NH}_3][\text{H}_2\text{O}]}{[\text{NH}_4^+][\text{OH}^-]} \]

\[ (e) \, K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]} \]

The Reaction Quotient, \( Q \)

In general, ALL reacting chemical systems are characterized by their REACTION QUOTIENT, \( Q \).

\[ a \, A + b \, B \rightarrow c \, C + d \, D \]

**Under Any Reaction Conditions**

\[
\text{Reaction quotient} = Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}
\]

If \( Q < K \), then system will shift to the right, reactants convert to products.
If \( Q > K \), then system will shift to the left, products convert to reactants.
If \( Q = K \), then system is at equilibrium.
The pH Scale: 0 to 14

The pH of a solution provides a way to express the *acidity*, or the concentration of H⁺ in solution:

- low pH = high [H⁺] *acidic solution*
- high pH = low [H⁺] *basic solution*

A pH of 7 indicates that the solution is *neutral*.

Example: A student is given a solution that is labeled pH = 4.72, what is the molarity of H⁺ in this solution?

\[ [H^+] = 10^{-pH} \]

Plugging in $10^{-4.72}$ into you calculators yields: $1.90546 \times 10^{-5}$

But wait... how many sig. figs. are allowed?

\[ 10^{-4.72} = 10^{0.28-5} = 10^{0.28} \times 10^{-5} \]

\[ 10^{0.28} = 1.9 \]

*2 sig. figs.!!*

Therefore the concentration should be reported as: $1.9 \times 10^{-5} \text{ M}[H^+]$

Reactions in Aqueous Solutions

Aqueous Solutions: *Water as the solvent*

Solution = *solute* + *solvent*

That which is dissolved (lesser amount)

That which is dissolves (greater amount)

There are three types of aqueous solutions:

Those with *Strong Electrolytes*  Those with *Weak Electrolytes*

& those with *non-Electrolytes*

Species in Solution, *Electrolytes*:

*Strong electrolytes:* Characterized by *ions only* (cations & anions) in solution (water).

*Weak electrolytes:* Characterized by *ions* (cations & anions) & *molecules* in solution.

*Non-electrolytes:* Characterized by *molecules* in solution.

- Conduct electricity well
- Conduct electricity poorly
- Do not conduct electricity
Reactions of Acids & Bases: Acid-Base Neutralization

Acid + Base → Salt + Water (usually)

\[ \text{HA (aq)} + \text{MOH(aq)} \rightarrow \text{MA(aq)} + \text{HOH(l)} \]

Strong acid - Strong base neutralization: \[ \text{HBr(aq)}/\text{KOH(aq)} \]

Molecular Equation:

\[ \text{HBr(aq)} + \text{KOH(aq)} \rightarrow \text{KBr (aq)} + \text{H}_2\text{O(l)} \]

Total Ionic Equation:

\[ \text{H}^+(aq) + \text{Br}^-(aq) + \text{K}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}^+(aq) + \text{Br}^-(aq) + \text{H}_2\text{O(l)} \]

Net Ionic equation:

\[ \text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O(l)} \]

Solution Stoichiometry

Prior to now, we have discussed reactions in solution from a qualitative aspect.

Reactants → Products

With the addition of molarity to our tools of chemistry, we now can perform quantitative calculations for reactions in aqueous solutions.

volume → moles → moles → grams

grams → moles → moles → volume

Example:

How many grams of calcium carbonate can be consumed by 35.5mL of 0.125 M H\(_2\)SO\(_4\) (aq) ?

Solution: We know that acids react with carbonate salts to produce CO\(_2\)(g)

\[
\text{H}_2\text{SO}_4(aq) + \text{CaCO}_3(s) \rightarrow \text{H}_2\text{O(l)} + \text{CO}_2(g) + \text{CaSO}_4(s)
\]

\[
\text{mL H}_2\text{SO}_4 \rightarrow \text{mol H}_2\text{SO}_4 \rightarrow \text{mol CaCO}_3 \rightarrow \text{g CaCO}_3
\]

\[
35.5\text{mL} \times \frac{1\text{L}}{10^3\text{mL}} \times 0.125 \text{mol H}_2\text{SO}_4 \times \frac{1\text{mol CaCO}_3}{1\text{mol H}_2\text{SO}_4} \times \frac{100.1\text{g CaCO}_3}{1\text{mol CaCO}_3} = 0.444\text{g CaCO}_3
\]

Recall: Strong acid + strong base

Yields: \[ \text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O(l)} \]

Solution:

1. Compute mols H\(^+\) and mols OH\(^-\)
2. Determine limiting reactant and excess of the other.
3. Compute conc. of excess from mols left over and new total volume.
If 50.0 ml of 0.200 M HCl(aq) is added to 50.0 ml of 0.150 M Ba(OH)$_2$ (aq), what is the remaining H$^+$ or OH$^-$ concentration depending on the limiting reactant?

**mols OH$^-$ needed to react with mols H$^+$ available:**

$$
\begin{align*}
50.0 \text{ ml} \times \frac{1 \text{ L}}{1000 \text{ ml}} \times \frac{0.200 \text{ mol HCl}}{1 \text{ L}} \times \frac{1 \text{ mol H}^+}{1 \text{ mol HCl}} \times \frac{1 \text{ mol OH}^-}{1 \text{ mol H}^+} &= 1.00 \times 10^{-2} \text{ mol OH}^- \\
&= \text{ needed to consume all of the H}^+
\end{align*}
$$

**mols OH$^-$ left after reaction with H$^+$:**

$$
\text{mols OH}^- \text{ in excess} = \text{mols OH}^- \text{ available} - \text{mols OH}^- \text{ needed} \\
= 1.50 \times 10^{-2} - 1.00 \times 10^{-2} \\
= 5.0 \times 10^{-3}
$$

$$
[\text{OH}^-] = \frac{5.0 \times 10^{-3} \text{ mol OH}^-}{(50.0 \text{ ml} + 50.0 \text{ ml}) \times \frac{1 \text{ L}}{1000 \text{ ml}}} = 0.050 \text{ M OH}^-
$$

If 50.0 ml of 0.200 M HCl(aq) is added to 50.0 ml of 0.150 M Ba(OH)$_2$ (aq), what is the remaining H$^+$ or OH$^-$ concentration depending on the limiting reactant?

**mols OH$^-$ needed to consume all of the moles of H$^+$**

$$
1.00 \times 10^{-2} \text{ mols OH}^- \text{ needed to consume all of the moles of H}^+
$$

**mols OH$^-$ available:**

$$
\begin{align*}
50.0 \text{ ml} \times \frac{1 \text{ L}}{1000 \text{ ml}} \times \frac{0.150 \text{ mol Ba(OH)$_2$}}{1 \text{ L}} \times \frac{2 \text{ mol OH}^-}{1 \text{ mol Ba(OH)$_2$}} &= 1.50 \times 10^{-2} \text{ mol OH}^- \text{ available} \\
\text{mols OH}^- \text{ available} > \text{mols OH}^- \text{ needed}, \text{ H}^+ \text{ limits!!!}
\end{align*}
$$

**COLLIGATIVE PROPERTIES OF SOLUTIONS**

Colligative solution properties are properties that depend directly on the concentration of solute particles in the solution.

Experiments demonstrate that the vapor pressure of water (solvent) above a solution is lower than the vapor pressure of pure water at a given temperature.

When a solute is added to a solvent, the boiling point increases and the freezing point decreases.

Also, when a pure solvent is separated from a solution by a semi-permeable membrane, solvent molecules flow across the membrane towards the solvent side. This phenomenon is known as osmosis.
**Boiling Point Elevation:**

The *boiling point* of a solution is always higher than the boiling point of the pure solvent of the solution.

\[ t_b (\text{solution}) > t_b (\text{solvent}) \]

The difference in boiling point between pure solvent and solution depends on the concentration of solute particles, and is calculated using the following equation:

\[ \Delta t_b = nK_bM \]

\[ \Delta t_b = t_b(\text{solution}) - t_b(\text{solvent}) \]

- \( K_b \) = bp constant (depends on the substance)
- \( M \) = the molarity of the solution
- \( n \) = total number of particles in solution
  - \( n = 1 \) for molecular compounds
  - \( n = 2 \) for NaCl (Na\(^+\) and Cl\(^-\))

Calculate the freezing point of a solution made up by adding and completely dissolving 4.52g sodium phosphate to 100.0 mL of water.

\[ \Delta t_f = nK_fM \]

\[ K_f = -1.86^\circ C \frac{M}{mol} \]

**Step 1:** Calculate the molarity of the solution

\[ \text{Na}_3\text{PO}_4(\text{aq}) \rightarrow 3\text{Na}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \]

- \( n = 3 + 1 = 4 \)

**Step 2:** Recognize that \( n = 4 \)

**Step 3:** Enter the values into the equation

\[ \Delta t_f = 4 \times \left( -1.86^\circ C \frac{mol}{L} \right) \times 4.52 \text{g Na}_3\text{PO}_4 \times \frac{1 \text{mol Na}_3\text{PO}_4}{163.94 \text{g}} \times \frac{1}{100.0 \text{mL}} \times 10^3 \text{mL} \]

\[ \Delta t_f = -2.05^\circ C \]

\[ t_f = 0.00^\circ C + \Delta t_f = 0.00^\circ C - 2.05^\circ C = -2.05^\circ C \]

**For the general reaction:**

\[ aA + bB \rightarrow cC + dD \]

\[ \text{Rate} = k [A]^x [B]^y \]

Each concentration is expressed with an order (exponent).

The rate constant converts the concentration expression into the correct units of rate (Ms\(^{-1}\)).

- \( x \) and \( y \) are the reactant orders determined from experiment.
- \( x \) and \( y \) are **NOT** the stoichiometric coefficients.
Reaction Orders:
A reaction order can be zero, or positive integer and fractional number.

<table>
<thead>
<tr>
<th>Order</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>zeroth</td>
</tr>
<tr>
<td>1</td>
<td>first</td>
</tr>
<tr>
<td>2</td>
<td>second</td>
</tr>
<tr>
<td>0.5</td>
<td>one-half</td>
</tr>
<tr>
<td>1.5</td>
<td>three-half</td>
</tr>
<tr>
<td>0.667</td>
<td>two-thirds</td>
</tr>
</tbody>
</table>

Rate law Expression:
Rate law Expression: \( \text{Rate} = k [A]^x [B]^y \)

If the rate doubles when \([A]\) doubles and \([B]\) stays constant, the order for \([A]\) is?  
one... 1

If the rate remains constant as \([B]\) doubles and \([A]\) is held constant, the order for \([A]\) is?  
zero... 0

If the rate triples \([B]\) doubles and \([A]\) reduced by \(\frac{1}{2}\), the order for \([A]\) & \([B]\) are?  
Heck if I know... you need to know at least one of 'em to answer this! Ha Ha!

The Overall Order of a reaction is the sum of the individual orders:

\[ \text{Rate (Ms}^{-1}) = k[A][B]^{\frac{1}{2}}[C]^2 \]

Overall order: \(1 + \frac{1}{2} + 2 = 3.5 = \frac{7}{2} \)

or seven–halves order

note: when the order of a reaction is 1 (first order) no exponent is written.

EXAMPLE: The reaction,

\[ 2 \text{NO (g)} + 2 \text{H}_2 (g) \rightarrow \text{N}_2 (g) + 2 \text{H}_2\text{O (g)} \]

is experimentally found to be first order in \(\text{H}_2\) and third order in \(\text{NO}\)

a) Write the rate law.  
the "1" in first order is omitted

\[ \text{Rate(Ms}^{-1}) = k [\text{H}_2]^{1}[\text{NO}]^3 \]

b) What is the overall order of the reaction?

Overall order = \(1 + 3 = 4 \)

"4th order"

c) What are the units of the rate constant?

\[ \text{Rate} = \frac{M}{\text{Ms}} = k \times \text{M} \times \text{M}^3 = k \times \text{M}^4 \]

\[ k = \frac{M}{\text{s} \times \text{M}^4} = \text{M}^{-3} \text{s}^{-1} \]
Determining Reaction Order: The Method of Initial Rates

The reaction of nitric oxide with hydrogen at 1280°C is:

\[ 2\text{NO}(g) + 2\text{H}_2(g) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g) \]

From the following experimental data, determine the rate law and rate constant.

<table>
<thead>
<tr>
<th>Run</th>
<th>[NO] (_o) (M)</th>
<th>[H(_2)] (_o) (M)</th>
<th>Initial Rate (M/min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0100</td>
<td>0.0100</td>
<td>0.00600</td>
</tr>
<tr>
<td>2</td>
<td>0.0200</td>
<td>0.0300</td>
<td>0.144</td>
</tr>
<tr>
<td>3</td>
<td>0.0100</td>
<td>0.0200</td>
<td>0.0120</td>
</tr>
</tbody>
</table>

\[
\frac{0.0120 \text{M/min}}{0.00600 \text{M/min}} \times \frac{[0.0200]^y}{[0.0100]^y} = \frac{[0.0200]}{[0.0100]} = 2.00
\]

Taking the ratio of the rates of runs 3 and 1 one finds:

\[
\frac{\text{Rate (run 3)}}{\text{Rate (run 1)}} = \frac{k [\text{NO}]^x [\text{H}_2]^y}{k [\text{NO}]^x [\text{H}_2]^y}
\]

Plugging in the values from the data:

\[
\frac{0.0120 \text{M/min}}{0.00600 \text{M/min}} \times \frac{[0.0200]^y}{[0.0100]^y} = \frac{[0.0200]^y}{[0.0100]^y}
\]

log(2.00) = \log\left(\frac{0.0200}{0.0100}\right)

\[
\log(2.00) = \log\left(\frac{0.0200}{0.0100}\right)
\]

\[
\log(2.00) = y \times \log\left(\frac{0.0200}{0.0100}\right) = y \times \log(2.00)
\]

\[
y = \frac{\log(2.00)}{\log(2.00)} = 1
\]

Now that “y” is known, we may solve for x in a similar manner:

\[
\text{Rate (M/min)} = k [\text{NO}]^x [\text{H}_2]^y
\]
**Similarly for x:**

The Rate Law expression is:

\[
\text{Rate(M/min)} = k \left[\text{NO}\right]^{3} \left[\text{H}_2\right]
\]

The order for NO was 3

The order for H\(_2\) was 1

The over all order is 3 + 1 = 4

---

**The Rate Law is:**

\[
\text{Rate(M/min)} = k \left[\text{NO}\right]^{3} \left[\text{H}_2\right]
\]

rate law expression

To find the rate constant, choose one set of data and solve:

\[
0.0120 \text{ M} \text{ min}^{-1} = k \left(0.0100 \text{ M}\right)^3 \left(0.0200 \text{ M}\right)
\]

\[
k = \frac{0.0120 \text{ M} \text{ min}^{-1}}{\left(0.0100 \text{ M}\right)^3 \left(0.0200 \text{ M}\right)} = 6.00 \times 10^4 \text{ M}^{-3} \text{ min}^{-1}
\]

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**Homogeneous and Heterogeneous Catalysts**

A *homogeneous catalyst* exists in the same phase as that of the reactants.

In the presence of the bromide ion, the decomposition of hydrogen peroxide occurs rapidly:

\[
2\text{H}_2\text{O}_2(aq) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)
\]

**Step 1:**

\[
2\text{Br}^- (aq) + \text{H}_2\text{O}_2(aq) + 2\text{H}^+(aq) \rightarrow \text{Br}_2 (aq) + 2\text{H}_2\text{O}(l).
\]

**Step 2:**

\[
\text{Br}_2 (aq) + \text{H}_2\text{O}_2(aq) \rightarrow 2\text{Br}^- (aq) + 2\text{H}^+(aq) + \text{O}_2(g).
\]

**Net:**

\[
2\text{H}_2\text{O}_2(aq) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)
\]

Br\(^-\) acts as a catalyst since it regenerates at the end of the reaction.
The $E_a$ for the catalyzed pathway is lower. The reaction takes a “shortcut”, therefore the rate increases!

Consider $\text{H}_2$ bond energy = 218 kJ/mol

On the surface of the metal, there are full orbitals that stick out into space:

When the $\text{H}_2$ sits on the surface, the electrons from the metal can fill the anti-bonding orbital

The bond order becomes zero! Dissociation!

Since the energy of activation is lowered, the reaction proceeds with a faster rate!