# Equilibrium electrochemistry

An **electrochemical cell** consists of two **electrodes**, or metallic conductors, in contact with an **electrolyte** (an ionic conductor: solution, a liquid, or a solid). An electrode and its electrolyte constitute an **electrode compartment**. If the electrolytes are different, the two compartments may be joined by a **salt bridge**, (tube containing a concentrated electrolyte solution) that completes the electrical circuit. The types of cells are:

A **galvanic cell** is an electrochemical cell that produces electricity as a result of the spontaneous reaction occurring inside it.

An **electrolytic cell** is an electrochemical cell in which a non-spontaneous reaction is driven by an external source of current.
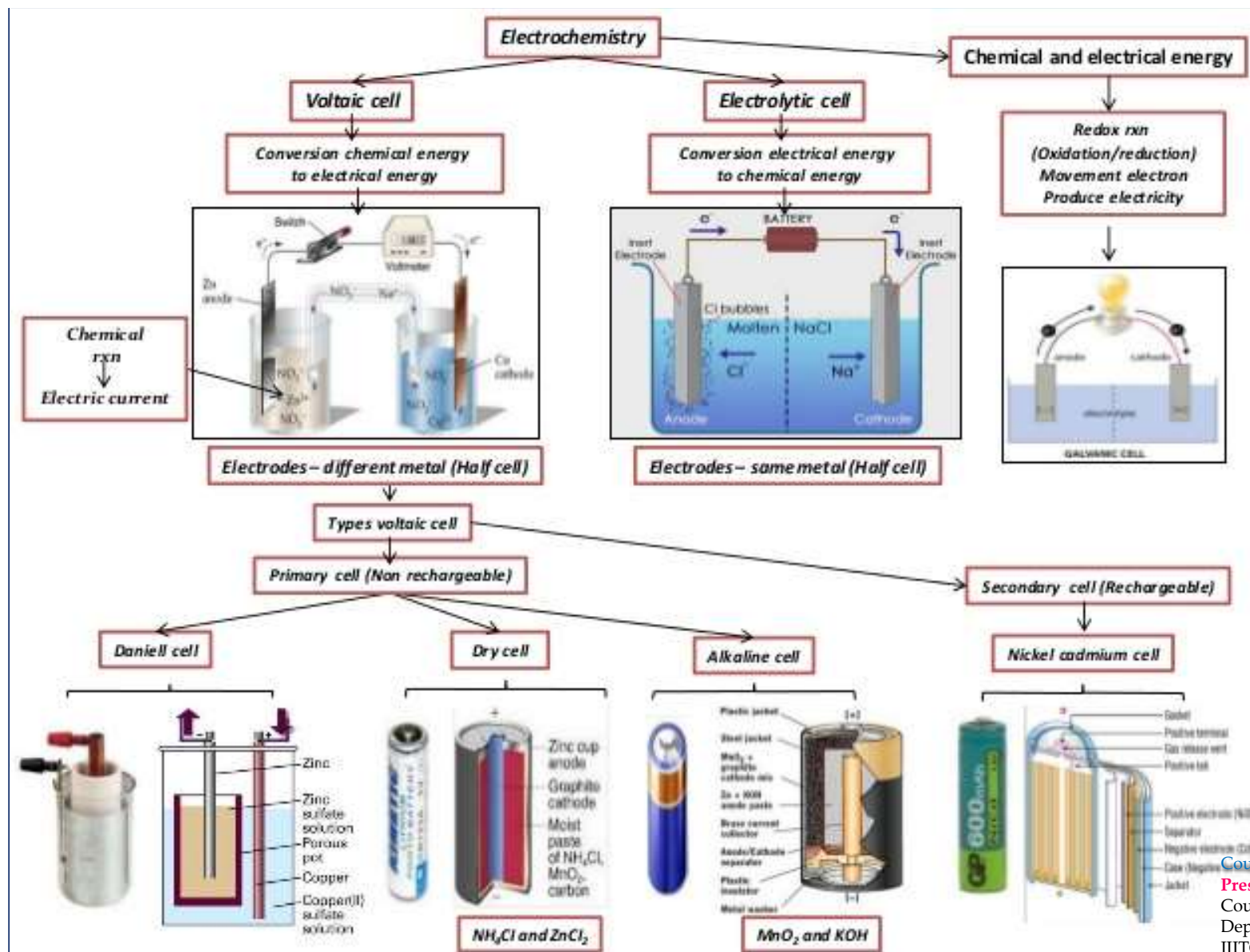
In an **electrolyte concentration cell**, the electrode compartments are identical except for the concentrations of the electrolytes.

In an **electrode concentration cell** the electrodes themselves have different concentrations.

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Electrochemistry

Voltaic cell — Electrolytic cell — Chemical and electrical energy

Conversion chemical energy to electrical energy

Conversion electrical energy to chemical energy

Redox rxn (Oxidation/reduction) Movement electron Produce electricity

Chemical rxn → Electric current

Electrodes – different metal (Half cell)

Electrodes – same metal (Half cell)

Types voltaic cell

Primary cell (Non rechargeable)

Secondary cell (Rechargeable)

Daniell cell

Dry cell

Alkaline cell

Nickel cadmium cell

NH₄Cl and ZnCl₂

MnO₂ and KOH

| Electrochemical cell (Galvanic Cell) | Electrolytic cell |
|---|---|
| A Galvanic cell converts chemical energy into electrical energy. | An electrolytic cell converts electrical energy into chemical energy. |
| Here, the redox reaction is spontaneous and is responsible for the production of electrical energy. | The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction. |
| The two half-cells are set up in different containers, being connected through the salt bridge or porous partition. | Both the electrodes are placed in a same container in the solution of molten electrolyte. |
| Here the anode is negative and cathode is the positive electrode. The reaction at the anode is oxidation and that at the cathode is reduction. | Here, the anode is positive and cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction. |
| The electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit. | The external battery supplies the electrons. They enter through the cathode and come out through the anode. |

*Liquid junction potential:* In a cell with 2 different electrolyte solutions in contact, (Daniell cell), an additional source of potential difference across the interface of two electrolytes exists, called liquid junction potential, $E_{lj}$.

An **ion-selective electrode** is an electrode that generates a potential in response to the presence of a solution of specific ions. E.g. **glass electrode.**

The **cell reaction** is the reaction in the cell written on the assumption that the right-hand electrode is the cathode, and hence that the spontaneous reaction is one in which reduction is taking place in the right-hand compartment. If the left-hand electrode is the cathode, then the reverse of the cell reaction is spontaneous.

In the cell $Zn(s) \,|\, ZnSO_4(aq) \,||\, CuSO_4(aq) \,|\, Cu(s)$, the two electrodes and their reduction half-reactions are

Right-hand electrode: $Cu^{2+}(aq) + 2\ e{-}{\longrightarrow}Cu(s)$

Left-hand electrode: $Zn^{2+}(aq) + 2\ e{-}{\longrightarrow}Zn(s)$

Hence, the overall cell reaction is the difference:
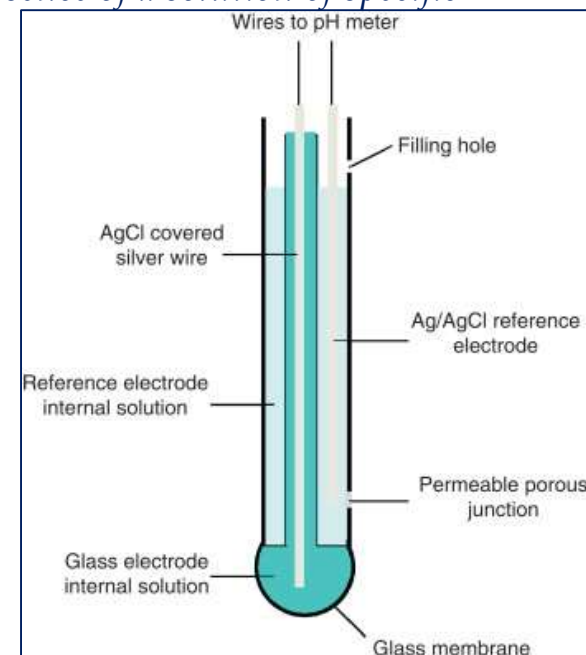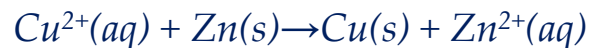
$Cu^{2+}(aq) + Zn(s){\longrightarrow}Cu(s) + Zn^{2+}(aq)$

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*Cell potential*: *A cell in which the overall cell reaction has not reached chemical equilibrium can do electrical work which depends on the potential difference between the two electrodes. This potential difference is called the* **cell potential** *and is measured in volts, V (1 V = 1 J C $^{-1}$ s).*

*When the cell potential is large, a given transfer of electrons between the two electrodes can do a large amount of electrical work.*

*When the cell potential is small, the same number of electrons can do only a small amount of work.*

*A cell in which the overall reaction is at equilibrium can do no work, and then the cell potential is zero.The cell potential when balanced by an exactly opposing source of potential so that the cell reaction occurs reversibly, the composition is constant, and no current flows: in effect, the cell reaction is poised for change, but not actually changing. In such a case, the resulting potential difference is called the* **electromotive force** *(emf), E, of the cell.*

$$-\nu FE = \Delta_r G$$

*Where F is Faraday's constant, and $\nu$ is the stoichiometric coefficient of the electrons in the half-reactions.*

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*Change in Gibb's energy G when the extent of cell reaction increases by an infinitesimal amount $d\xi$ (at constant temperature and pressure) is $dG = \Delta_r G d\xi$* ----------- eqn. (1)

*The maximum non-expansion electrical work that the reaction can do therefore is $dw_e = \Delta_r G d\xi$------- eqn. (2)*

*This work is infinitesimal, and the composition of the system is virtually constant when it occurs.*

*When the reaction advances by $d\xi$, then $vd\xi$ electrons must travel from the anode to the cathode, $v$ is the stoichiometric coefficient of the electrons in the half-reactions. The total charge transfer between the electrodes when this change occurs is $-veN_A d\xi$ (because $vd\xi$ is the amount of electrons and the charge per mole of electrons is $-eN_A$, e: charge of $e^-$ : $1.602 \times 10^{-19}$ C, $N_A$: Avogadro's constant: $6.022 \times 10^{23}$ mol$^{-1}$). Hence, the total charge transported is $-vFd\xi$ because $eN_A = F$. The work done when an infinitesimal charge $-vFd\xi$ travels from the anode to the cathode is equal to the product of the charge and the potential diff. E. $dw_e = -vFEd\xi$*

*From eqns. (3) & (4),*

**$dG = \Delta_r G d\xi = dw_e = -vFEd\xi$**

**$\Delta_r G = -vFE$**      *Since $\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q$,*

$$E = -\frac{\Delta_r G^{\ominus}}{vF} - \frac{RT}{vF} \ln Q$$

**$E^{\ominus} = -\Delta_r G^{\ominus}/vF$**, *standard emf of the cell. The standard emf is the standard reaction Gibbs energy expressed as a potential (in volts) . Therefore,*

$$E = E^{\ominus} - \frac{RT}{vF} \ln Q$$ ---------- **Nerst eqn.**

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Since $RT/F = 25.7$ mV at 25°C, the Nernst equation becomes $E = E^{\ominus} - (25.7\ mV/v)\ ln\ Q$

Therefore, for a reaction in which $v = 1$, if $Q$ is increased by a factor of 10, then the emf *decreases by 59.2 mV.*

For cells at equilibrium, $E = 0$ and $Q = K$, equilibrium constant of the cell reaction, therefore

$$ln\ K = \frac{vFE^{\ominus}}{RT}$$

**Standard potentials:** *It is not possible to measure the contribution of a single electrode, we can define the potential of one of the electrodes as zero and then assign values to others on that basis.*

*The selected reference electrode is the* **standard hydrogen electrode** *(SHE): Pt(s) $|H_2(g)|H^+(aq)$ $E^{\ominus} = 0$*



Temperature 298 K

Hydrogen 1 bar

Platinum wire

Platinum foil

Dilute $H_2SO_4$

*This holds for all temperatures. For standard conditions, the activity of the hydrogen ions must be 1 (that is, pH = 0) and the hydrogen gas must be at 1 bar pressure. The* **standard potential**, *$E^{\ominus}$, of another electrode couple is designated by constructing a cell where it is the right-hand electrode and the standard hydrogen electrode is the left-hand electrode.*

*E.g.  Harned cell: Pt(s) $|H_2(g)|$ HCl(aq) $|$ AgCl(s) $|$ Ag(s)*

*Cell reaction: $1/2\ H_2(g) + AgCl(s) \rightarrow HCl(aq) + Ag(s)$*

*It is pertinent to note that standard emf of cells and standard potentials of electrodes is that they are unchanged if the chemical equation for the cell reaction or a half-reaction is multiplied by a numerical factor.*
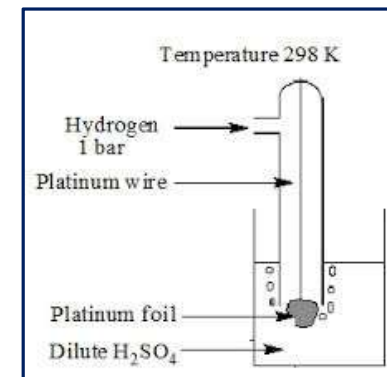
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# Chemical Kinetics

*The branch of kinetics that studies the rates and mechanisms of chemical reactions is **chemical kinetics** or*

***reaction kinetics.*** *A reacting system is not in equilibrium, so reaction kinetics is not part of thermodynamics.*

Stoichiometry tells us what and how many reactants/products there are
Thermodynamics tells us if the reaction is energetically favorable ($-\Delta H$)
Kinetics describes how fast or slow a reaction occurs

*There are two types of reactions:*

**Homogeneous reaction:** *is a reaction that occurs entirely in one phase**. Homogeneous reactions are divided into gas-phase reactions and reactions in liquid solutions.*

**Heterogeneous reaction:** *involves species present in two or more phases.*

***Rate of a reaction:*** *The rate of a chemical reaction depends on variables such as pressure, temperature, presence of a catalyst, and it is possible to optimize the rate by appropriate choice of conditions. It is measured by using techniques that monitor the concentration of species present in the reaction mixture. e.g. real-time and quenching procedures, flow techniques, flash photolysis.*

*Methods of determining composition include spectrophotometry, emission spectroscopy, mass spectrometry, gas chromatography, nuclear magnetic resonance, and electron paramagnetic resonance.*

**Reaction Rates** = Change in concentration (conc) of a reactant or product per unit time.

$$\text{Rate} = \frac{\Delta[A]}{\Delta t} = \frac{[A]_2 - [A]_1}{t_2 - t_1}$$

# Main Factors which influence reaction rate:

- **Concentrations of Reactants** - Rates usually increase as reactant concentrations increase.

- **Reaction Temperature** - An increase in temperature increases the rate of a reaction.

- **Presence of a Catalyst** (not all rxns have catalysts)
  - A catalyst is a substance which increases the rate of a reaction without being consumed in the overall reaction.
  - The concentration of the catalyst or its surface area (if insoluble) are variables which influence the rate.
  - Some catalysts are incredibly complex - like enzymes; and others are quite simple: $H^+ + H_2O + CH_2 = CH_2$ ------) $CH_3\text{-}CH_2\text{-}OH + H^+$

Various Rates can be determined: **1)** instantaneous rate at a given time; **2)** average rate over a long period of time; or **3)** the initial rate – rate at the beginning of the rxn; ie rate at t=0.0 (this is used the most).

## Examples of what one might follow to obtain rates:
- a change in **pressure**      (if gas produced or consumed in the rxn)
- a change in **pH**      (if acidity changes in the rxn)
- a change in **absorbance** of electromagnetic radiation (EMR)

$A = Ebc$ at given $\lambda$ (wavelength) **This is Beer's Law**

A = absorbance; use spectrophotometer to measure; has no units.
E = molar absorptivity = a constant @ given $\lambda$; has units of $M^{-1}cm^{-1}$
b = pathlength of EMR through sample; usually 1.00 cm cuvette used.
c = concentration in $M$

For the balanced homogeneous reaction $A + 2B \rightarrow 3C + D$, the instantaneous **rate of consumption** of reactant A at a given time is $-d[A]/dt$, and **rate of formation** of product C is $d[C]/dt$. Following stoichiometry of the reaction
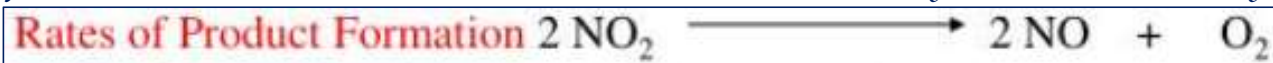
$$\frac{d[D]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}.$$

The **rate of conversion** J for the homogeneous reaction is defined as $J \equiv -\frac{1}{a}\frac{dn_A}{dt} = -\frac{1}{b}\frac{dn_B}{dt} = \cdots$

The conversion rate J is an extensive quantity and depends on the system's size. The conversion rate per unit volume, J/V, is called the **rate of reaction** r: $r \equiv \frac{J}{V} = \frac{1}{V}\left(-\frac{1}{a}\frac{dn_A}{dt}\right)$

r is an intensive quantity and depends on T, P, and the concentrations in the homogeneous system. When V is essentially constant, we have $(1/V)(dn_A/dt) = d(n_A/V)/dt = dc_A/dt = d[A]/dt$, where $c_A = [A]$ is the **molar concentration.** Thus $r = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \cdots = \frac{1}{e}\frac{d[E]}{dt} = \frac{1}{f}\frac{d[F]}{dt} = \cdots$ const. V

Common units for r are mol dm$^{-3}$ s$^{-1}$ (1 dm$^3$= 1 L) and mol cm$^{-3}$ s$^{-1}$. (The symbol v is commonly used instead of r.)

Rates of Product Formation $2\,NO_2 \longrightarrow 2\,NO + O_2$

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO]}{\Delta t} = \frac{1}{1}\frac{\Delta[O_2]}{\Delta t}$$

<u>_Rate law_</u> _is an equation that expresses the rate of reaction as a function of the concentrations of all the species present in the overall chemical equation for the reaction at time t, at a fixed temperature._

$r$ _(or v) = f ([A],[B], . . . )_

_For homogeneous gas-phase reactions, rate law is expressed in terms of partial pressures, $p_J = RT$ [J], J: no. of components. Thus r (or v) = f ($p_A$, $p_B$,...)_

| Overall Rxn Order, x | Units for k |
|---|---|
| zero | $Ms^{-1}$ |
| first | $s^{-1}$ |
| second | $M^{-1}s^{-1}$ |
| third | $M^{-2}s^{-1}$ |

_For most reactions, the rate r at time t is experimentally found to be related to the concentrations of all components present at that time t by as_ $r = k[A]^{\alpha}[B]^{\beta} \cdots [L]^{\lambda}$

_The power to which the concentration of a species (a product or a reactant) is raised in a rate law of this kind is the **order** of the reaction with respect to that species. An order may be an integer or half-integer. Thus for a reaction with two reactants A and B, v = k[A][B], coefficient k is called the **rate constant** or **rate coefficient,** and is a function of temperature and pressure. The reaction having rate law first-order in A and first-order in B. The exponents $\alpha$, $\beta$ , . . . are also called **partial orders**. The sum $\alpha + \beta +....+ \lambda = n$ is the **overall order** of the reaction. Few reactions follow **zero-order rate law**, i.e. they have a rate that is independent of the_ ⟶ $Rate = -k[A]^0$
$Rate = -k$
_concentration of the reactant. E.g. the catalytic decomposition of phosphine ($PH_3$) on hot tungsten at high pressures has the rate law v = k. A rate law is a guide to the mechanism of the reaction and can predict the composition of the reaction mixture at any given stage of the reaction._

## Determination of Order by varying $\underline{M}$

$$2N_2O_5 \text{ ---) } 4NO_2 + 1O_2 \qquad rate = k\,[N_2O_5]^m$$

**Exp #1:** Rate $= 4.8 \times 10^{-6}$ $\underline{M}s^{-1}$ at $1.0 \times 10^{-2}$ $\underline{M}$ $N_2O_5$

**Exp #2:** Rate $= 9.6 \times 10^{-6}$ $\underline{M}s^{-1}$ at $2.0 \times 10^{-2}$ $\underline{M}$ $N_2O_5$

**Order:** Note that when $[N_2O_5]$ doubles, the rate doubles. Since rate $\alpha\,[N_2O_5]^m$ & rate doubles when $[N_2O_5]$ doubles, the value of must be 1; the order is 1.

- rate $\alpha\,[N_2O_5]^m$ & rate doubles when $[N_2O_5]$ doubles, then:
  go from $[1]^m = 1$ to $[2]^m = 2$     m has to be 1

**Rate law:**     rate $= k \times [N_2O_5]^1$

---

**EFFECTS** of doubling reagent $\underline{M}$ while keeping others constant:

| | |
|---|---|
| Rate remains the same | 0th order: $[\underline{M}]^0$ |
| Rate doubles | 1st order: $[\underline{M}]^1$ |
| Rate quadruples | 2nd order: $[\underline{M}]^2$ |
| Rate increases eightfold | 3rd order: $[\underline{M}]^3$ |

# Determination of Order by varying $M$

**2 NO + $Cl_2$ -----) 2 NOCl - Calculate order of Rxn**

| Exp | Initial [NO] | Initial [$Cl_2$] | Initial Rate, $Ms^{-1}$ |
|-----|--------------|------------------|-------------------------|
| 1   | 0.0125       | 0.0255           | $2.27 \times 10^{-5}$   |
| 2   | 0.0125       | 0.0510           | $4.57 \times 10^{-5}$   |
| 3   | 0.0250       | 0.0255           | $9.08 \times 10^{-5}$   |

Rate = $k[NO]^m[Cl_2]^n$

a) calculate n:   From 1 & 2 - double [$Cl_2$] & keep [NO] constant
   & rate increases by factor of 2.01;  n = 1

b) calculate m:   From 1 & 3 - double [NO] & keep [$Cl_2$] constant
   & rate increases by factor of 4.00;  m = 2

Rate = $k[NO]^2[Cl_2]^1$

2nd order wrt [NO];   1st order wrt [$Cl_2$];   3rd order overall

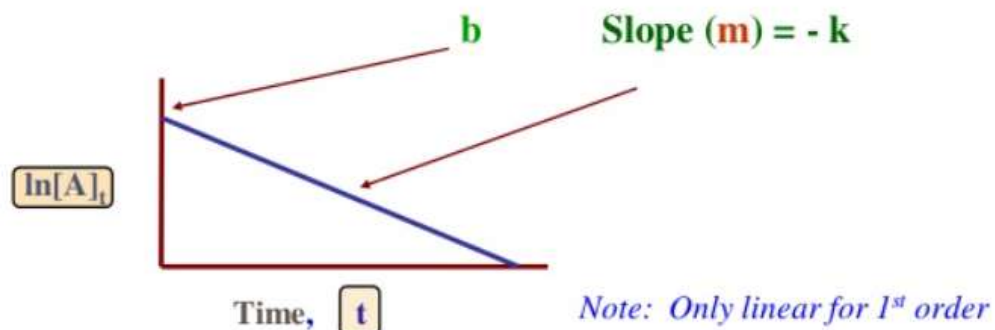## Determination of Order by Integrated Rate Expression

$$Y = mX + b$$

$$\ln[A]_t = -kt + \ln[A]_o \qquad \text{or} \qquad \ln\{[A]_t/[A]_o\} = -kt$$

where $[A]_t = \underline{M}$ of A at time $= t$ & $[A]_o = \underline{M}$ of A at $t = 0$

- **A plot of $\ln[A]_t$ versus $t$ gives a straight line** $(Y = mX + b)$:

b          Slope $(m) = -k$

$\boxed{\ln[A]_t}$

Time, $\boxed{t}$          *Note: Only linear for 1st order*

---

■ **Half-Life $(t_{1/2})$ of 1st Order Reaction:**

$t_{1/2} =$ time it takes for $[A]_o$ to decrease to 1/2 initial $\underline{M} = \frac{1}{2}[A]_o$

$\ln [A]_t/[A]_o = -kt$          $\ln \frac{1}{2}[A]_o /[A]_o = -kt_{1/2}$

$\ln 1/2 = -kt_{1/2}$     $-0.693 = -kt_{1/2}$     $\boxed{t_{1/2} = 0.693 / k}$

_Determination of the rate law_:

_Four methods for the experimental determination of the rate law are_

1. _**Half-life method**: The **half-life** $t_{1/2}$ of a reaction is the time it takes for the concentration of a species to be reduced to half its_

   _initial value._

   > **Example:** If $t_{1/2} = 189$ sec for $1^{st}$ order decomposition of 1.0 mole of $H_2O_2$, then how much $H_2O_2$ will be left after 378 sec?
   >
   > **Note:** $378/189 = 2$     **Goes through two half lives**
   >
   > 1.0 mol ---) 0.50 mol ---) 0.25 mol

2. _**Powell-plot method**: is applied when the rate law has the form $r = k[A]^n$._

3. _**Initial-rate method**: The initial rate $r_0$ is measured for several runs, varying the initial concentration of one reactant at a_

   _time. The initial rate $r_0$ is found by plotting $[A]$ versus t, drawing the tangent line at $t = 0$._

4. _**Isolation method**: The determination of a rate law is simplified by the **isolation method** where the concentrations of all the_

   _reactants except one are in large excess. If B is in large excess, when the rate of a reaction is proportional to the molar_

   _concentrations of two reactants A and B, the true rate law might be $v = k[A][B]$, which becomes $v = k'[A]$, $k' = k[B]_0$ as $[B] \approx$_

   _$[B]_0$. Thus the reaction is said to have a **pseudofirst-order rate law**._

> **Example 1 for a multistep reaction:** $1\ CH_2Br_2 + 2\ KI$ ---) $1\ CH_2I_2 + 2\ KBr$
>
> If experimentation found that m & n were both first order; then:
>
> $$rate = k\ [CH_2Br_2]^1\ [KI]^1$$
>
> **Example 2 for an elementary reaction:**   $2\ O_3$ ---) $3\ O_2$   (told it is elementary)
>
> No need for experimentation; order comes from balancing coefficients:
>
> $$rate = k[O_3]^2$$

*It is possible to predict the rate law from the overall chemical equation only in case of an elementary reaction. There are two forms of a rate law for chemical kinetics: the **differential rate law** and the **integrated rate law**.*

**Differential Rate Law** tells us how rate changes with concentration
a)   This is what we will call the rate law

b)   $\text{rate} = k[A]^n = -\dfrac{\Delta[A]}{\Delta t}$

**Integrated Rate Law** tells us how concentrations depend on time
a)   This can be derived from the differential rate law (and vice versa)
b)   We will look at integrated rate laws later

*An **differential rate law** is an expression for the rate of reaction w.r.t. the concentrations of the various species in the system.*

$$r = k[A]^\alpha[B]^\beta \cdots [L]^\lambda$$

*An **integrated rate law** is an expression for the concentration of a reactant or product as a function of time:*

### *First-order reactions*

*The integrated form of the first-order rate law* $r = -\dfrac{d[A]}{dt} = k[A]$ *is* $\ln\left(\dfrac{[A]}{[A]_0}\right) = -kt$ *or* $\boxed{[A] = [A]_0\, e^{-kt}}$

*at t = 0, the initial concentration of A is $[A]_0$.*

### *Second-order reactions*

Th $\dfrac{d[A]}{[A]^2} = -k dt$ *rate law* $r = -\dfrac{d[A]}{dt} = k[A]^2$ *(or r = k[A][B], where A and B are two different reactants)*

Integrating from A to $A_0$ $\quad \dfrac{1}{[A]} - \dfrac{1}{[A]_0} = kt$

*The integrated form of the second-order rate law r is* $\quad [A] = \dfrac{[A]_0}{1 + kt\,[A]_0}$

# Reactant Concentration versus Time
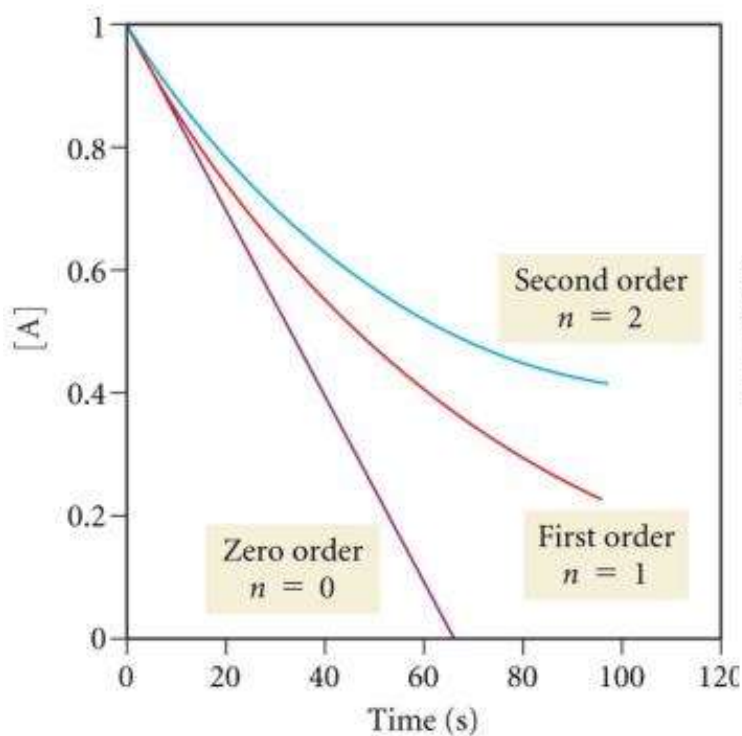


# Rate versus Reactant Concentration
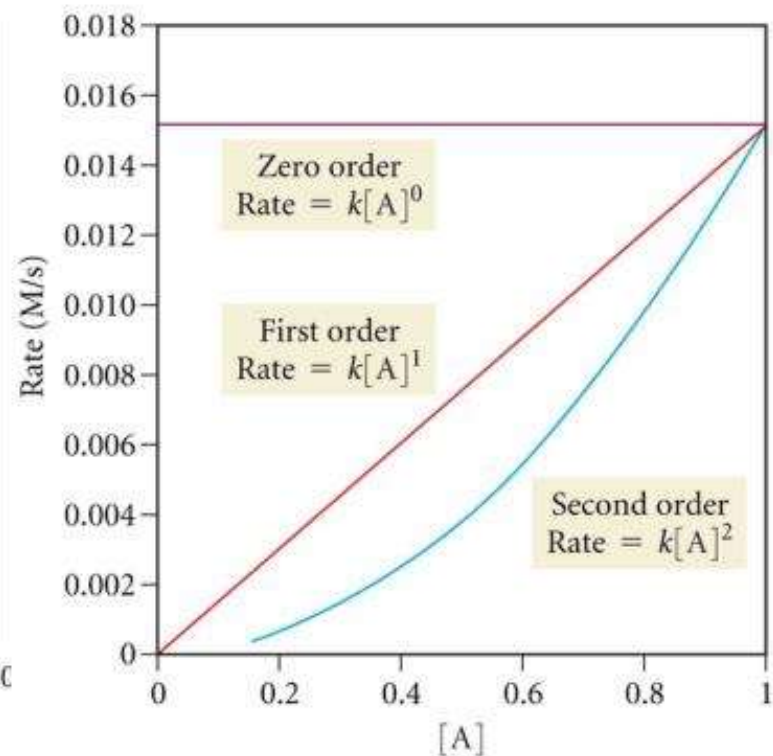


Left graph axes: [A] (vertical), Time (s) (horizontal). Curves labeled: Zero order $n = 0$, First order $n = 1$, Second order $n = 2$.

Right graph axes: Rate (M/s) (vertical), [A] (horizontal). Curves labeled: Zero order Rate $= k[A]^0$, First order Rate $= k[A]^1$, Second order Rate $= k[A]^2$.

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## Half-lives and time constants

The **half-life $t_{1/2}$** of a reaction is the time it takes for the concentration of a species to be reduced to half its initial value. In a first-order reaction, time taken for [A] to decrease from $[A]_0$ to 1/2 $[A]_0$ in a **1st**-order reaction is

$$kt_{1/2} = -\ln\left(\frac{\frac{1}{2}[A]_0}{[A]_0}\right) = -\ln\frac{1}{2} = \ln 2$$

Thus, $t_{1/2} = \dfrac{\ln 2}{k}$ or $\boxed{t_{1/2} = 0.693 / k}$

The **time constant $\tau$** is the time required for the concentration of a reaction to fall to **1/e** of its initial value.

Thus, $k\tau = -\ln\left(\dfrac{[A]_0/e}{[A]_0}\right) = -\ln\dfrac{1}{e} = 1$

In a **second**-order reaction, substituting $t = t_{1/2}$ and $[A] = 1/2\,[A]_0$ in the half-life of a species A that is consumed in a second-order reaction is

$$[A] = \frac{[A]_0}{1 + kt\,[A]_0}$$

$$t_{1/2} = \frac{1}{k[A]_0} \qquad \boxed{\tau = \frac{1}{k}}$$

Rate $= -\Delta[A] / \Delta t = k\,[A]^2$

Integrate rate expression from time t to 0 & get following:

$\boxed{1/[A]_t = k\,t + 1/[A]_0}$ So, a plot of $1/[A]_t$ vs t should give a straight line with slope $= k$ and y intercept $= 1/[A]_0$

$t_{1/2} = \dfrac{1}{k \times [A]_0}$ Note: Now $t_{1/2}$ depends on initial M

For a **zero**-order reaction, $\boxed{[A]_t = -k \times t + [A]_0}$

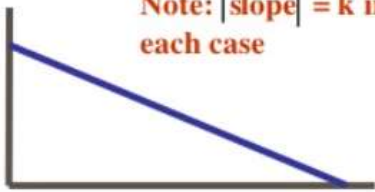Again, if you let $[A]_t = 1/2\,[A]_0$ then $t = t_{1/2}$

$t_{1/2} = [A]_0 / 2k$
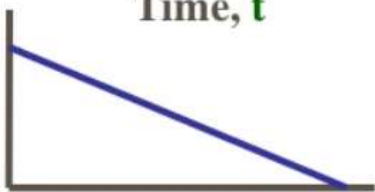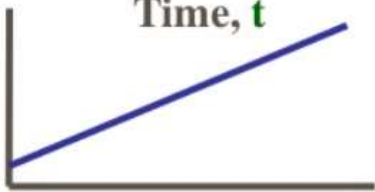
| Reaction Order | Integrated Rate Law | Characteristic Kinetic Plot | Slope of Kinetic Plot | Units of Rate Constant |
|---|---|---|---|---|
| Zero | $[E]_t = -kt + [E]_0$ | $[E]$ vs $t$ | $-kt$ | $mol\ L^{-1}\ s^{-1}$ |
| First | $\ln[A]_t = -kt + \ln[A]_0$ | $\ln[A]$ vs $t$ | $-k$ | $s^{-1}$ |
| Second | $\dfrac{1}{[C]_t} = kt + \dfrac{1}{[C]_0}$ | $1/[C]$ vs $t$ | $k$ | $L\ mol^{-1}\ s^{-1}$ |

**Order**

**Integrated Rate Law - Summary**

$A \rightarrow B \quad \Delta[A]/\Delta t = k[A]^n$

Note: $|slope| = k$ in each case

$0^{th}$ Order $n=0$
$[A]_t = -kt + [A]_0$

$[A]_t$

Time, t

$1^{st}$ Order $n=1$
$\ln[A]_t = -kt + \ln[A]_0$

$\ln[A]_t$

Time, t

$2^{th}$ Order $n=2$
$1/[A]_t = kt + 1/[A]_0$

$1/[A]_t$

Time, t

*Each step in the sequence of steps/ mechanism of a reaction is called an **elementary reaction.** A **simple reaction** consists of a single elementary step.* $H_2 + Cl_2 \longrightarrow 2HCl$

*The molecularity of an elementary reaction is the no. of molecules reacting together. e.g. isomerization of cyclopropane to propene is an **elementary unimolecular reaction** having first-order kinetics. Etherification of alcohols, dimerization of alkenes and dienes are **elementary bimolecular reactions** having second-order kinetics.*

*A **complex** (or **composite**) **reaction** consists of two or more elementary steps. Most chemical reactions are composite.*

*A **chain reaction** contains a series of steps in which a reactive intermediate is consumed, reactants are converted to products, and the intermediate is regenerated. Regeneration of the intermediate allows this cycle to be repeated over and over again. Thus a small amount of intermediate produces a large amount of product. Most combustions, explosions, and addition polymerizations are chain reactions and usually involve free radicals as intermediates. It comprises of **initiation step, propagation step and termination step.** [Refer Macromolecules]*

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*Consecutive elementary reactions: are those which proceed thro.' the formation of an intermediate.*

$A \xrightarrow{k_a} I \xrightarrow{k_b} P$   *e.g. radioactive decay of uranium* $^{239}U$       $^{239}U \xrightarrow{23.5 \text{ min}} {}^{239}Np \xrightarrow{2.35 \text{ day}} {}^{239}Pu$

*A reaction scheme involving many steps has to integrate the rate laws numerically and make an approximation. This* **steady-state approximation,** *also called the* **quasi-steady state approximation,** *QSSA,  (different from a true steady state) assumes that, after an initial* **induction period**, *an interval during which the concentrations of intermediates I, rise from zero, the rates of change of concentrations of all reaction intermediates are negligibly small throughout the major part of the reaction.*  $\dfrac{d[I]}{dt} \approx 0$

*Applying the approximation to the consecutive first-order mechanism, we set d[I]/dt = 0, to the net rate of formation of I is therefore*  $k_a[A] - k_b[I] \approx 0$  *{intermediate I is formed from A (at a rate $k_a[A]$) but decays to P (at a rate $k_b[I]$)}. Thus*  $[I] \approx (k_a/k_b)[A]$  *Assumption made is $k_a/k_b$ << 1 (although [A] does depend on the time, the dependence of [I] on the time is negligible). Thus the eqn. becomes*   $\dfrac{d[P]}{dt} = k_b[I] \approx k_a[A]$

$$[P] = k_a[A]_0 \int_0^t e^{-k_a t} dt = (1 - e^{-k_a t})[A]_0$$

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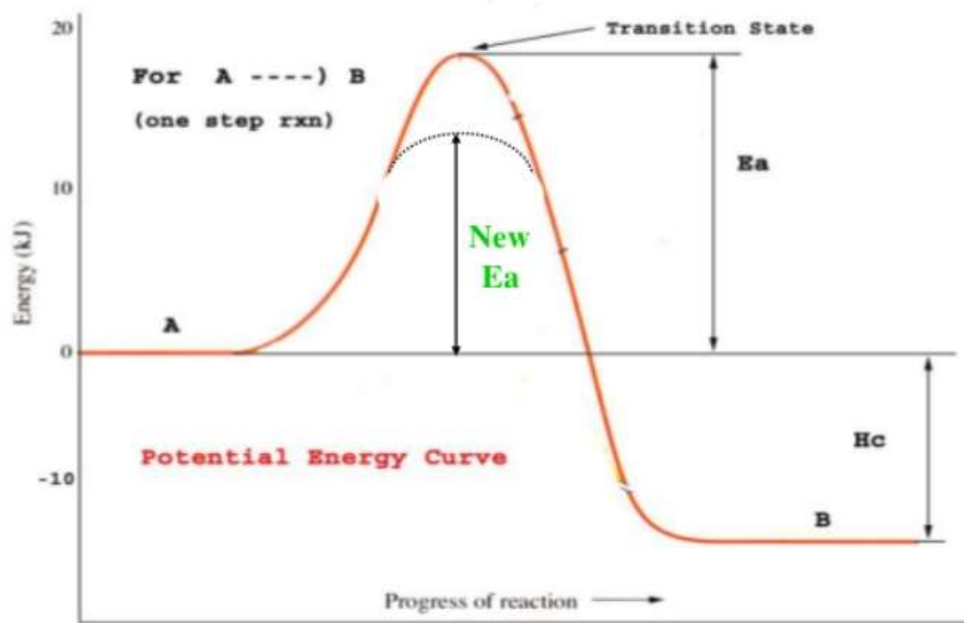Dept. of Science & Mathematics
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## Rate Determining Step:

*In case of consecutive elementary reactions (which proceed thro.' the formation of an intermediate), the rate determining step is the slowest step within a reaction mechanism that controls the overall rate of the reaction.*

Catalyst = A chemical which speeds up a reaction without being consumed in the reaction.
- They operate by lowering the Ea for the rate determining step.

A catalyst speeds up the rxn by lowering the Ea – provides a different mechanism with a lower Ea



For   A ----) B
(one step rxn)

Transition State

Ea

New Ea

A

Potential Energy Curve

Hc

B

Progress of reaction

Energy (kJ)

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- A collision needs to occur before a reaction can take place, & the rate constant (& rate) of the reaction depends upon the:

1) collision frequency      (temperature)
2) number of collisions having enough energy for rxn      (Ea)
3) orientation of particles upon collision

- Ea = energy of activation = minimum energy of collision in order for the reaction to take place.

- Ea & ΔH can be represented by **Potential Energy Diagram**; can draw for one step or for several steps in a mechanism.

**Catalyst = A chemical which speeds up a reaction without being consumed in the reaction.**

- They operate by lowering the Ea for the rate determining step.

## Temperature & Reaction Rate      Arrhenius Equation

- Arrhenius Equation relates: rate constant (**k**), temperature (**T**), energy of activation (**Ea in J/mole**), & orientation factor.

$$k = A\, e^{-Ea/RT}$$      R = gas constant;  use R = 8.31 J/(Kmole)

Take ln of both sides:  $\ln k = -(Ea/R)\, 1/T + \ln A$

$$Y = mX + b$$

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**Arrhenius equation**

$$k = Ae^{\frac{-E_a}{RT}}$$

$k$ is the rate constant                     $T$ is the temperature in K

$E_a$ is the activation energy          $R$ is the ideal-gas constant (8.314 J/Kmol)

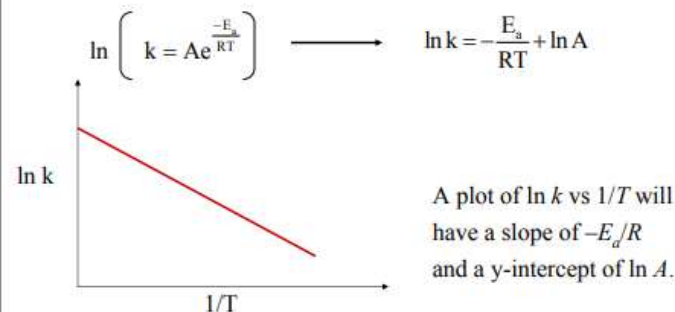$A$ is known the *frequency or pre–exponential factor*

In addition to carrying the units of the rate constant, "**A**" relates to the frequency of collisions and the orientation of a favorable collision probability

Both $A$ and $E_a$ are *specific to a given reaction.*

---

**Determining the Activation Energy**

$E_a$ may be determined experimentally.
First take natural log of both sides of the Arrhenius equation:

$$\ln\left(k = Ae^{\frac{-E_a}{RT}}\right) \longrightarrow \ln k = -\frac{E_a}{RT} + \ln A$$

A plot of ln $k$ vs $1/T$ will have a slope of $-E_a/R$ and a y-intercept of ln $A$.