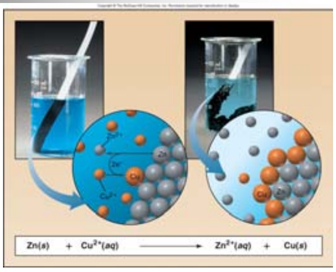
Electrochemistry & Redox

An oxidation-reduction (redox) reaction involves the transfer of electrons from the *reducing agent* to the *oxidising agent.*



OXIDATION - is the LOSS of electrons $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}(aq)$

REDUCTION - is the GAIN of electrons $Cu^{2+}(aq) + 2e^{-}(aq) \rightarrow Cu(s)$

These represents the redox HALF-EQUATIONS

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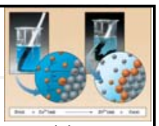
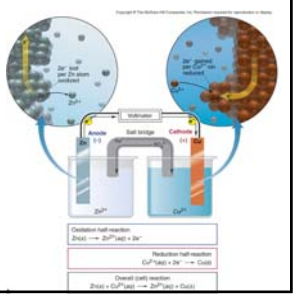
Voltaic Cells



- A voltaic electrochemical cell involves two half cells one containing an oxidising agent and the other a reducing agent.

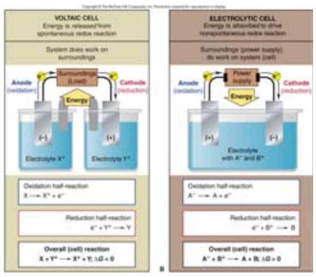


- These cells are connected with a wire, to allow electron flow and a salt bridge to complete the circuit and maintain electrical neutrality.
- The PULL or DRIVING FORCE on the electrons is the cell potential (E_{cell}) or the electromotive force (emf) of the cell, measured in volts.

Electrochemical Cells

An ox, red cat
Anode: oxidation
Reduction: cathode

- Voltaic (Galvanic) cells are those in which spontaneous chemical reactions produce electricity and supply it to other circuits.
  $\Delta G < 0$
- Electrolytic cells are those in which electrical energy causes non-spontaneous chemical reactions to occur.
  $\Delta G > 0$



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Balancing Redox Equations

- The concept of Oxidation Number is artificial. In simple ions it is equivalent to the charge on the ion.
  - Oxidation involves an increase in oxidation number
  - Reduction involves a decrease in oxidation number
- As half cells, determine oxidation numbers and balance electrons.
- Combine half cells balancing gain/loss of electrons.
- Balance with H_2O and H^+ or H_2O and OH^-.
- Check charges balance.

$0 \rightarrow +II$	$Zn(s)$	$\rightarrow Zn^{2+}(aq) + 2e^-(aq)$
$+II \rightarrow 0$	$Cu^{2+}(aq) + 2e^-(aq)$	$\rightarrow Cu(s)$
	$Zn(s) + Cu^{2+}(aq)$	$\rightarrow Zn^{2+}(aq) + Cu(s)$

Standard Reduction Potentials

- In data tables half cells are written as reductions.
- Standard hydrogen electrode defined as $E^\circ = 0$ V (1 atm H_2, $[H^+] = 1$ M, at all temperatures).
- The more negative E, the greater the tendency to release electrons (act as a reducing agent).

$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$E^\circ = 0.77$ V
$Cu^{2+} + 2e^- \rightarrow Cu$	$E^\circ = 0.34$ V
$2H^+ + 2e^- \rightarrow H_2\,(g)$	$E^\circ = 0.00$ V
$Zn^{2+} + 2e^- \rightarrow Zn$	$E^\circ = -0.76$ V

Calculating Cell Potential

- When combining two half-reactions:
  - One half-cell reaction is reversed (thus the sign of the reduction potential is reversed).
  - Number of electrons lost must equal the number gained.
  - Note cell potential is an INTENSIVE PROPERTY i.e. when a half-reaction is multiplied by and integer E° stays the SAME.

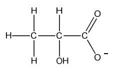
E.g.	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$E^\circ = 0.77$ V ...1
	$Cu^{2+} + 2e^- \rightarrow Cu$	$E^\circ = 0.34$ V ...2
reverse ...2	$Cu \rightarrow Cu^{2+} + 2e^-$	$E^\circ = -0.34$ V
double ...1	$2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$	$E^\circ = 0.77$ V
add equations	$2Fe^{3+} + Cu \rightarrow 2Fe^{2+} + Cu^{2+}$	$E^\circ_{cell} = 0.77+(-0.34) = 0.43$ V

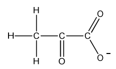
Question

Write a balanced equation for the oxidation of lactate to pyruvate and calculate the cell potential.

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E^\circ = 0.82$ V

pyruvate $+ 2H^+ + 2e^- \rightarrow$ lactate $E^\circ = -0.19$ V





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$\Delta G^\circ = -nFE^\circ_{max}$

Example: Calculate ΔG° for a cell reaction:

$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$

Is this a spontaneous reaction?

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^\circ = 0.34$ V

$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $E^\circ = -0.44$ V

$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$

$E^\circ_{cell} = 0.34 + (+0.44) = 0.78$ V

$\Delta G^\circ = -2 \times 96485 \times 0.78$ ($F = 96485$ C mol^{-1})

$= -1.5 \times 10^5$ J

This process is spontaneous as indicated by the negative sign of ΔG° and the positive sign for E°_{cell}.

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Glucose metabolism

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ $\Delta G^\circ = -2875$ kJ mol^{-1}

- If all this energy was released at once it would totally swamp the cell.
- Instead energy in food used to create an electrochemical potential which is used to create the high energy molecule ATP.
- The energy can be released in small steps rather than all at once.

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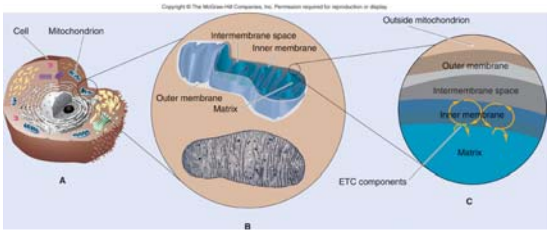
Metabolism and energy storage



- Redox reactions involved form part of the electron-transport chain (ETC).
- The ETC lies on the inner membrane of mitochondria.
- The ETC involves a series of large molecules, mostly proteins, that use Fe^{2+}/Fe^{3+} to pass electrons down the chain.

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Electron transport chain ETC

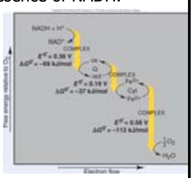
- The reaction that ultimately powers ETC is $H_2 + ½O_2 \rightarrow H_2O$

but do not have $H_2(g)$ but rather $2H^+ + 2e^-$ in the presence of NADH.

$2H^+ + 2e^- + ½O_2 \rightarrow H_2O$

$NADH + H^+ \rightarrow NAD^+ + 2H^+ + 2e^-$

$NADH(aq) + H^+(aq) + ½O_2(aq) \rightarrow NAD^+(aq) + H_2O(l)$



$E°'_{overall} = 1.13$ V and $\Delta G° = -218$ kJ mol^{-1}.

At each of the points shown there is enough free energy released to drive

$ADP^{3-} + HPO_4^{2-} + H^+ \rightarrow ATP^{4-} + H_2O$ $\quad \Delta G°' = 30.5$ kJ mol^{-1}

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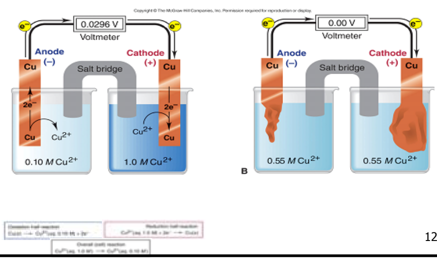
Concentration Cells

Imagine a cell: $Cu(s)|Cu^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$

Low $[Cu^{2+}]$ — High $[Cu^{2+}]$

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ — $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$



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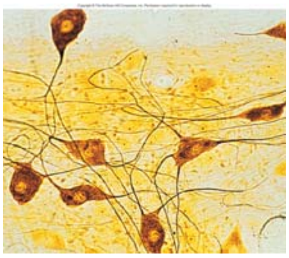
Concentration Cells

- Nerve cells operate as concentration cells.
- Inside cell $[Na^+]$ low, $[K^+]$ high; outside cell $[Na^+]$ high, $[K^+]$ low.
- Outer cell membrane is positive. One third of our ATP is used to maintain this difference.
- On nerve stimulation, Na^+ enters cell, inner membrane becomes more positive, then K^+ ions leave cell to re-establish positive potential on outside.
- These changes occur on a millisecond timescale.
- Large changes in charge in one region of the membrane stimulate the neighbouring region and the impulse moves down the length of the cell.



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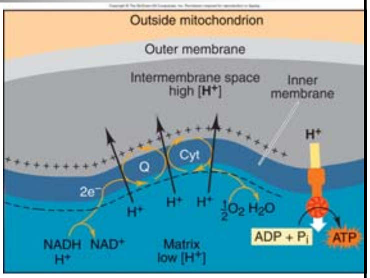
ATP Synthesis

- So far looked at electrons, but what about the protons?

$NADH + H^+ \rightarrow NAD^+ + 2H^+ + 2e^-$

- As redox processes occur, free energy used to force protons into the intermembrane space.
- This creates a concentration cell across the membrane.



- When $[H^+]_{intermembrane}/[H^+]_{matrix} \sim 2.5$ a trigger allows protons to flow back across membrane and this spontaneous process drives the non-spontaneous formation of ATP.

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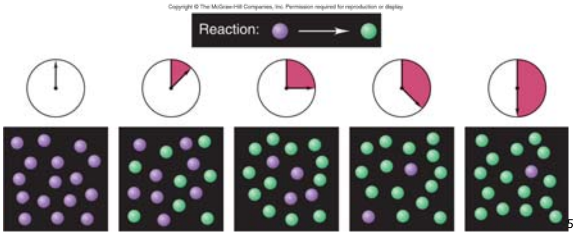
Chemical Kinetics

- The rate of a reaction is the speed with which the concentrations of the molecules present change. The rate is given by the gradient of a concentration vs time graph.



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Decomposition of H_2O_2

$2H_2O_2\ (aq) \rightarrow 2H_2O + O_2\ (g)$

- Start 1.000 M H_2O_2 — After 10 s $[H_2O_2]$ = 0.983 M
- $\Delta[H_2O_2]$ = - 0.017 M — Time interval Δt = 10.0 s

Rate of reaction = Rate of change of $[H_2O_2]$
= $\Delta[H_2O_2] / \Delta t$
= - 0.017/10.0 = -1.7×10^{-3} M s^{-1}

To avoid negative rates….
Rate is defined as $-\Delta$[reactant]/Δt

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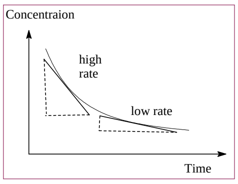
Decomposition of H_2O_2

- The rate of removal of H_2O_2 is not constant.
- The lower the concentration of H_2O_2 the slower the rate.
- The rate is dependent on concentration.



$2H_2O_2\ (aq) \rightarrow 2H_2O\ (l) + O_2\ (g)$

Time s	Δt s	$[H_2O_2]$ M	$\Delta[H_2O_2]$ M	Reaction rate x 10^{-4} M s^{-1}
0		2.32		
	400		-0.60	15.0
400		1.72		
	400		-0.42	10.5
800		1.30		
	400		-0.32	8.0
1200		0.98		
	400		-0.25	6.3
1600		0.73		
	400		-0.19	4.8
2000		0.54		
	400		-0.15	3.8
2400		0.39		
	400		-0.11	2.8
2800		0.28		
	400			

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The rate of reaction

The rate of reaction depends on (among other factors) ...

- Concentration of some or all of the molecules present
- Temperature
- The presence of a catalyst
- The 'rate equation' can only be determined by experiment, not from the stoichiometric equation

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The Rate Equation

This relates the rate of reaction to the concentration terms which affect it.

For the general reaction: A + B $\rightarrow$ M + N

$$-d[A]/dt = k\,[A]^x\,[B]^y$$

- Rate constant, *k*, is a characteristic of the reaction and depends on temperature.
- 'Order' of the reaction is given by x + y.
- x is the order with respect to A, y is the order with respect to B etc.

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Example

$H_2\,(g) + 2\,ICl\,(g) \rightarrow 2\,HCl\,(g) + I_2\,(s)$

Rate $= -d[H_2] / dt = k[H_2][ICl]$ (by experiment)

- This reaction is *first order* with respect to H_2, *first order* with respect to ICl and *second order overall.*

Question:

For the reaction: $2NO_2\,(g) + F_2\,(g) \rightarrow 2NO_2F\,(g)$ Rate = $k[NO_2][F_2]$

What is the order of reaction with respect to NO_2, F_2 and the overall order of reaction?

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Determine the Rate Equation

$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$

	$[O_2]$ / M	[NO] / M	Initial Rate / M s^{-1}
1	1.10×10^{-2}	1.30×10^{-2}	3.21×10^{-3}
2	2.20×10^{-2}	1.30×10^{-2}	6.40×10^{-3}
3	1.10×10^{-2}	2.60×10^{-2}	12.8×10^{-3}
4	3.30×10^{-2}	1.30×10^{-2}	9.60×10^{-3}

Rate $= k\,[O_2]^x\,[NO]^y$

keep one conc constant, alter other conc and see what happens to rate.

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Determine the Rate Equation

$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$

	$[O_2]$ / M	[NO] / M	Initial Rate / M s^{-1}
1	1.10×10^{-2}	1.30×10^{-2}	3.21×10^{-3}
2	2.20×10^{-2}	1.30×10^{-2}	6.40×10^{-3}
3	1.10×10^{-2}	2.60×10^{-2}	12.8×10^{-3}
4	3.30×10^{-2}	1.30×10^{-2}	9.60×10^{-3}

Rate = $k [O_2]^x [NO]^y$

↑ double ↑ double therefore x = 1 $(2 = (2)^1)$

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Determine the Rate Equation

$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$

	$[O_2]$ / M	[NO] / M	Initial Rate / M s^{-1}
1	1.10×10^{-2}	1.30×10^{-2}	3.21×10^{-3}
2	2.20×10^{-2}	1.30×10^{-2}	6.40×10^{-3}
3	1.10×10^{-2}	2.60×10^{-2}	12.8×10^{-3}
4	3.30×10^{-2}	1.30×10^{-2}	9.60×10^{-3}

Rate = $k [O_2]^1 [NO]^y$

↑ four times ↑ double therefore y = 2 $(4 = (2)^2)$

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Determine the Rate Equation

$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$

	$[O_2]$ / M	[NO] / M	Initial Rate / M s^{-1}
1	1.10×10^{-2}	1.30×10^{-2}	3.21×10^{-3}
2	2.20×10^{-2}	1.30×10^{-2}	6.40×10^{-3}
3	1.10×10^{-2}	2.60×10^{-2}	12.8×10^{-3}
4	3.30×10^{-2}	1.30×10^{-2}	9.60×10^{-3}

Rate = $k [O_2]^1 [NO]^2$ substitute values to get k

$3.21 \times 10^{-3} = k (1.10 \times 10^{-2})(1.30 \times 10^{-2})^2$

Rate constant, $k = 1.73 \times 10^3$ $s^{-1}M^{-2}$

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Question:

Determine the rate equation and value of the rate constant for the reaction:

NO_2 (g) + CO (g) → NO (g) + CO_2 (g)

	$[NO_2]$ / M	[CO] / M	Initial Rate / M s^{-1}
1	0.10	0.10	0.0050
2	0.40	0.10	0.080
3	0.10	0.20	0.0050

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Half Life, $t_{1/2}$

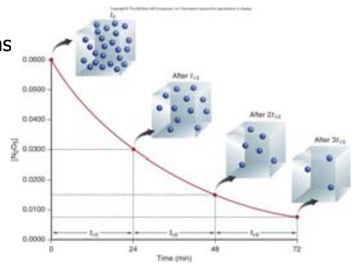
The half life of a reaction is the time required for the concentration to fall to half its initial value. For first order reactions this is a constant.

First Order Reactions

$t_{1/2}$ = Ln 2 / k

and

$Ln[A]=Ln[A]_o-k\,t$



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Example

An antibiotic breaks down in the body with a first order rate constant of k = 1.9 x 10^{-2} min^{-1}. How long does it take for the concentration to drop to 10% of the initial value?

rearrange $Ln[A]=Ln[A]_o-kt$ to give $Ln([A]/[A]_o)= -k\,t$

We do not know the actual concentrations but can use the ratio of concentrations:

$$Ln (10/100) = -(1.9 \times 10^{-2})\ t$$

$$\therefore \quad Ln\ 0.1 = -2.303 = -(1.9 \times 10^{-2})\ t$$

and $t = 2.303 / 1.9 \times 10^{-2} = 120$ min

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Question

The radioactive isotope ^{15}O is used in medical imaging and has a half life of 122.2 seconds. What percentage is left up after 10 minutes?

Use $k = \text{Ln}2/t_{½}$ and $\text{Ln}[A]=\text{Ln}[A]_o - kt$

Note: $\text{Ln}\{ [A]/[A]_o \} = -kt$ and $[A]/[A]_o$ is amount left.

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Reaction Mechanisms

A balanced chemical equation describes the overall chemical reaction

e.g. $2\ NO_2\ (g) + F_2\ (g) \rightarrow 2\ NO_2F\ (g)$

A reaction mechanism is a series of 'elementary' reaction steps that add up to give a detailed description of a chemical reaction.

e.g.					
NO_2 +	F_2	$\rightarrow$	NO_2F +	F	Step 1
NO_2 +	F	$\rightarrow$	NO_2F		Step 2
$2\ NO_2$ +	F_2	$\rightarrow$	$2\ NO_2F$		Overall

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Reaction Mechanisms

A rate determining step in a reaction mechanism is an elementary process that is the slowest step in the mechanism

e.g. Step 1 $NO_2 + F_2 \rightarrow NO_2F + F$ (slow)

- In simple reactions, the exponents in the rate equation are the same as the coefficients of the molecules of the rate determining elementary process. So in this case,

$$\text{Rate} = k[NO_2][F_2]$$

- Note the overall reaction is: $2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$

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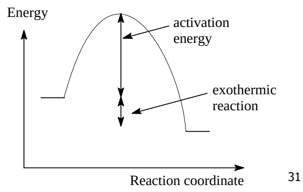
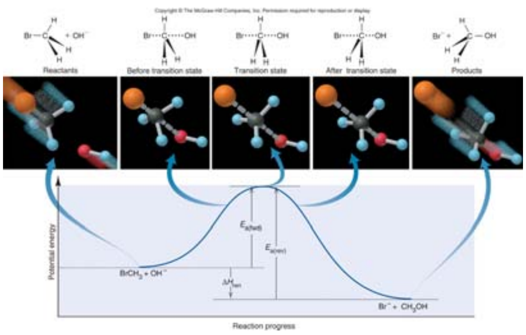
Arrhenius Equation $k = Ae^{-E_a/RT}$

- The activation energy, E_a, of a reaction is the minimum amount of energy that the reacting molecules must possess if the reaction is to be successful.
- The Arrhenius equation describes the temperature dependence of the rate constant that is exponentially related to the activation energy (A is the pre-exponential factor, or the "A factor").

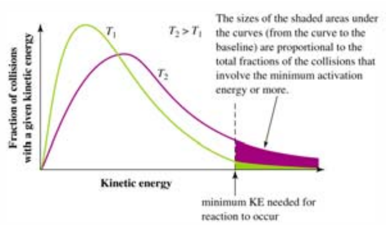


Reaction Profile



Arrhenius Equation $k = Ae^{-E_a/RT}$

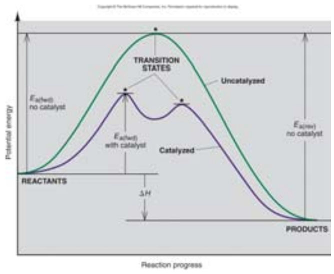
At higher temperatures, more molecules have the minimum required energy (E_a) and hence the faster the reaction.



Catalysis

A catalyst provides an alternative reaction pathway of lower activation energy.

In this case more molecules have the minimum energy required for successful reaction and the reaction proceeds at a faster rate.



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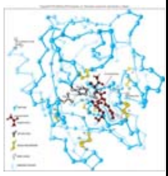
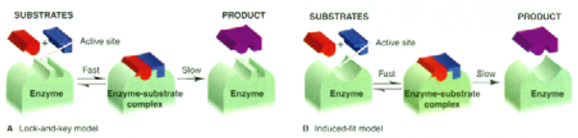
Enzyme Catalysis

- Efficient: rate enhancements of 10^8 to 10^{20} possible.
- Specific.
- But low tolerance to temperature and pH changes.





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