Organic and Inorganic Chemistry

The book consists of two parts

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Metabolism

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Content

Metabolism

The biochemical reactions that happen inside the body.

Metabolism divided into to process

1- Catabolim
2- Anabolism

Catabolism

The biochemical processes of metabolism by which large molecules are breakdown to small molecules or oxidizing to producing energy.

Anabolism

The biochemical processes of metabolism by which molecules are synthesized or built up.

Note

Catabolism and anabolism are separated process, catabolism process occur to produce energy, but anabolism need energy.

INTRODUCTION

The carbohydrates are source of energy for animal nutrition. The

monosaccharides and oligosaccharides are efficiently metabolized by simple stomach animals. On the other hand, ruminants contain microbes, which secrete enzymes capable of degrading cellulose. Glycogen is a polysaccharide found in animal and fungal cells. Glycogen is a storage form of carbohydrate and is readily utilized when there is deficiency of energy.

Digestion

The dietary carbohydrates that are most important nutritionally are polysaccharides and disaccharides, since free monosaccharides are not commonly present in the diet in significant quantities. There is, however, some free glucose and fructose in honey, in certain fruits, and in the carbohydrates that are added to processed foods. The cellular use of carbohydrates depends on their absorption from the Gastrointestinal (GI) tract into the blood stream, a process normally restricted to monosaccharides. Therefore, poly saccharides and disaccharides must be hydrolyzed to their constituent monosaccharide units. The hydrolytic enzymes involved are collectively called glycosidases, or, alternatively, carbohydrases.

1 Disaccharides

Virtually no digestion of disaccharides or small oligo saccharides occurs in the mouth or stomach. In the human it takes place entirely in the upper small intestine. Unlike amylase, disaccharidase activity is associated with the mucosal cells of the microvilli or brush border rather than with the intestinal lumen. Among the types of enzyme activities located in the mucosal cells are lactase, invertase (sucrase), and isomaltase. The latter is not a disaccharidase but instead hydrolyses branched dextrins, as mentioned in an earlier section. Lactase catalyses the cleavage of lactose to equimolar amounts of galactose and glucose, and sucrase hydrolyses sucrose to yield glucose and one fructose residue; sucrase also hydrolyses maltose and maltotriose to free glucose.

2 Polysaccharides

The glycosidase, a-amylase, assumes a particularly important role in polysaccharide digestion because of its specific hydrolytic action on the α-1,4 bonds of the starches. Resistant to the action of this enzyme, therefore, are the β-1,4 bonds of cellulose and the α -1,6 linkages that form branch points in the starch amylopectin. The a-amylase hydrolyses the unbranched amylose rapidly into units of the disaccharide maltose and into the trisaccharide malltotriose, the latter subsequently undergoing slower hydrolysis to maltose and glucose. The enzyme's hydrolytic action on amylopectin produces, in addition to glucose, maltose, and maltotriose, a mixture of branched oligo saccharides, or dextrins, the smallest of which are tetrasaccharides and pentasaccharides. Together with the complementary activity of another glycosidase, α-dextrinase, which hydrolyses the α-1, 6 bonds at the branches, the dextrins are consequently hydrolysed to free glucose.

Metabolism of carbohydrates

- تحليل الجلوكوز	Glycolysis
- دورة كربس	Krebs Cycle
- بناء الجلايكوجين	Glycogenesis
- إستحداث الجلايكوجين	Gluconeogenesis
- تحليل الجلايكوجين	Glycogenolysis

Glycolysis

Glycolysis is, by definition, the pathway by which glucose is converted into two units of lactic acid, a triose. The pathway can function anaerobically, and in situations in which oxygen debt is in effect, as in times of strenuous exercise, lactate accumulates in the muscle cells, causing the aches and pains associated with overexertion. The importance of glycolysis in energy metabolism is that it provides the initial sequence of reactions necessary for glucose to be oxidized completely to CO_2 and H_2O via the citric acid cycle. In cells that lack mitochondria, such as the erythrocyte, the pathway of glycolysis is the sole provider of ATP by substrate level phosphorylation of ADP. The glycolytic enzymes function within the cytoplasmic matrix of the cell, while the enzymes catalyzing the citric acid (Krebs) cycle reactions are located within the mitochondrion (pp. 8, 9). Further metabolism of the products of glycolysis in the Krebs cycle allows complete oxidation of glucose to CO_2 and H_2O, with maximal energy production. Some of the energy liberated is salvaged as ATP, while the remainder maintains body temperature. Many cell types are involved in glycolysis, but most of the energy derived from carbohydrates originates in liver, muscle, and adipose tissue. The pathway of glycolysis, showing the entry of dietary fructose and galactose, the following are comments on selected reactions:

1 .The hexokinase/glucokinase reaction consumes 1mol ATP/mol

glucose. Hexokinase (not glucokinase) is negatively regulated by

the product of the reaction, glucose 6-phosphate.

2 .Glucose phosphate isomerase catalyses this inter-conversion of

isomers.

3 .The phosphofructokinase reaction, an important regulatory site, is modulated negatively by ATP and citrate and positively by AMP.

Another ATP is consumed in the reaction.

3 .The aldolase reaction results in the splitting of a hexose bisphosphate into two triose phosphates.

4 .The isomers glyceraldehyde 3-phosphate and dihydroxyacetone phosphate (DHAP) are interconverted by the enzyme triosephosphate isomerase. In an isolated system the equilibrium favors DHAP formation. However, in the cellular environment it is shifted completely toward the production of glyceraldehyde 3- phosphate, since this metabolite is being continuously removed from the equilibrium by the subsequent reaction catalysed by glyceraldehyde 3-phosphate dehydrogenase.

5 .In this reaction, glyceraldehyde 3-phosphate is oxidised to a carboxylic acid, while inorganic phossphate is incorporated as a high-energy anhydride bond. The enzyme is glyceraldehyde 3-phosphate dehydrogenase, which uses NAD as its hydrogen accepting substrate. Under aerobic conditions, the NADH formed is deoxidized to NAD by O_2 via the electron transport chain in the mitochondria. The reason the O_2 is not necessary to sustain this reaction under anaerobic conditions is that the NAD consumed is restored by a subsequent reaction

6 .This reaction, catalyzed by phosphoglycerate kinase, exemplifies a substrate level phosphorylation of ADP. Do a little extensive reading, for a more detailed review of this mechanism by which ATP can be formed from ADP by the transfer of a phosphate from a high-energy donor molecule.

7 .Phosphoglyceromutase catalysis the transfer of the phosphate group from the carbon-3 to carbon-2 of the glyceric acid.

8 .Dehydration of 2-phosphoglycerate by the enzyme enolase introduces a double bond that imparts high energy to the phosphate bond.

9 .The product of reaction (9), phosphoenolpyruvate (PEP), donates its phosphate group to ADP in a reaction catalysed by pyruvate kinase. This is the second site of substrate level phosphorylation of ADP in the glycolytic pathway.

10 .The lactate dehydrogenase reaction transfers two hydrogen from NADH and H+ to pyruvate, reducing it to lactate. NAD is formed in the reaction and can replace the NAD consumed in reaction (6) under anaerobic conditions. It must be emphasized that this reaction is most active in situations of oxygen debt, as in prolonged muscular activity. Under normal, aerobic conditions, pyruvate enters the mitochondrion for complete oxidation. A third important option available to pyruvate is its conversion to the amino acid alanine through trans-amination with the amino group donor glutamate. This, together with the fact that pyruvate is also the product of the catabolism of various amino acids, makes it an important link between protein and carbohydrate metabolism.

11 .These two reactions provide the means by which dietary fructose enters the glycolytic pathway. Fructose is an important factor in the average American diet, since nearly half of the carbohydrate consumed is sucrose, and high fructose corn sugar is becoming more popular as a food sweetener. Reaction 12 functions in extrahepatic tissues and involves the direct phosphorylation by hexokinase to form fructose 6-phosphate. This is a relatively unimportant reaction. It is slow and occurs only in the presence of high levels of the ketose. Reaction 13 is the major means by which fructose is converted to glycolysis metabolites.

The phosphorylation occurs at carbon-l and is catalysed by fructokinase, an enzyme found only in hepatocytes. The fructose Iphosphate is subsequently split by aldolase, designated aldolase B to distinguish it from the enzyme acting on fructose 1,6-bisphosphate, forming DHAP and glyceraldehyde. The latter can then be phosphorylated by glyceraldehyde kinase (or triokinase) at the expense of a second ATP to produce glyceraldehyde 3-phosphate. Fructose is therefore converted to glycolytic intermediates and as such can follow the pathway to pyruvate formation and Krebs cycle oxidation. Alternatively, they can be used in the liver to produce free glucose by a reversal of the first part of the pathway through the action of gluconeogenic enzymes.

Glucose formation from fructose would be particularly important

if fructose provides the major source of carbohydrate in the diet.

Since the phosphorylation of fructose is essentially the responsibility of the liver, the ingestion of large amounts of the ketose can cause a depletion of hepaatocyte ATP, leading to reduction in the rate of various biosynthetic processes such as protein synthesis.

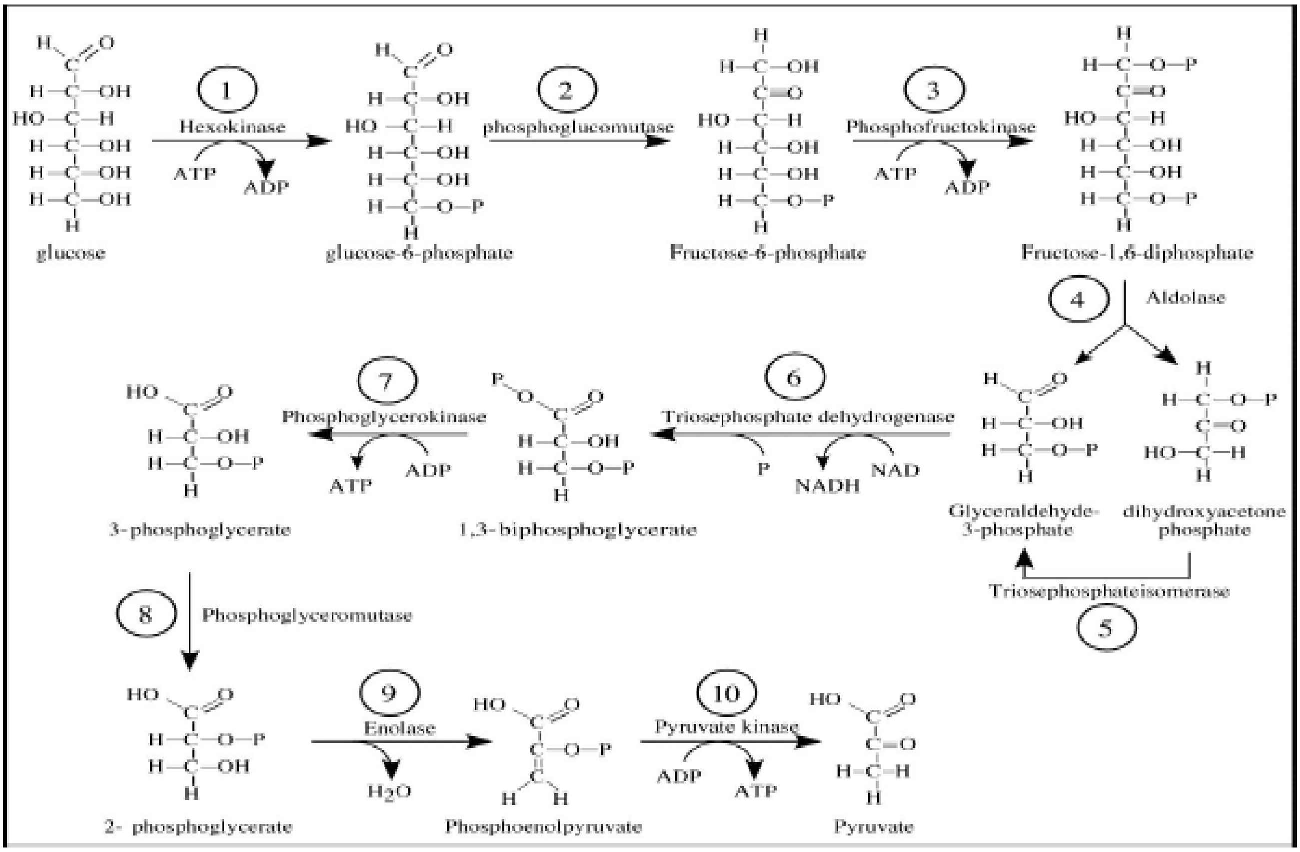
12 Like glucose and fructose, galactose is first phosphorylated. The transfer of the phosphate from ATP is catalysed by galactokinase and the resulting phosphate ester is at carbon-I of the sugar. The major dietary source of galactose is lactose, from which the monosaccharide is hydrolytically released by lactase.

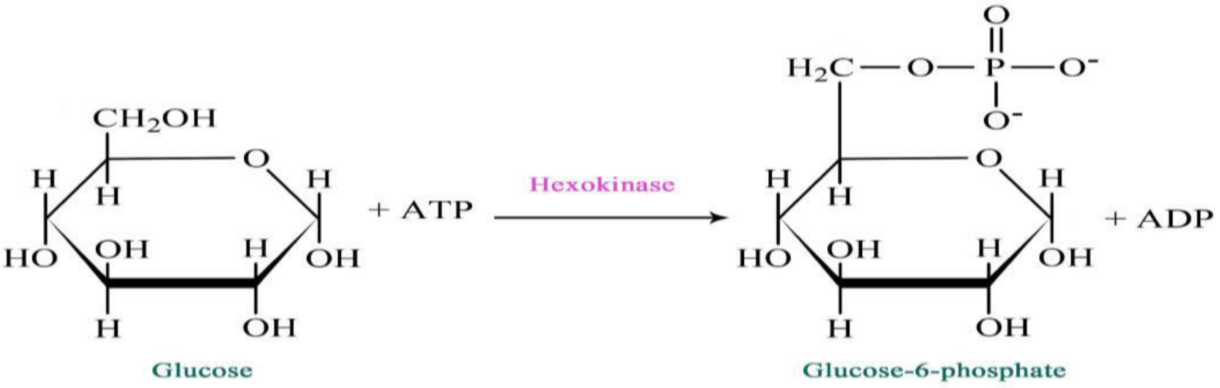
13 .Galactose 1-phosphate can be converted to glucose I phosphate by the enzyme galactose 1-phosphate uridyl transferase. The reaction involves the transfer of a uridyl phosphate residue from UDP glucose to the galactose I-phosphate, yielding glucose 1-phosphate and UDP galactose. As glucose 1-phosphate, galactose can be incorporated into glyycogen through reactions discussed previously. It can enter the

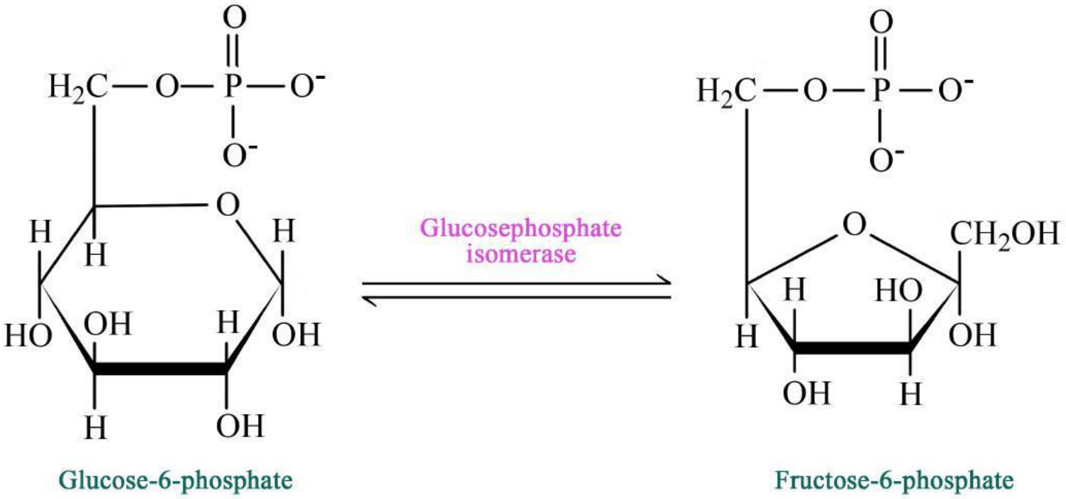
glycolytic pathway following isomerisation to glucose 6-phosphate and be hydrolysed to free glucose in liver cells.

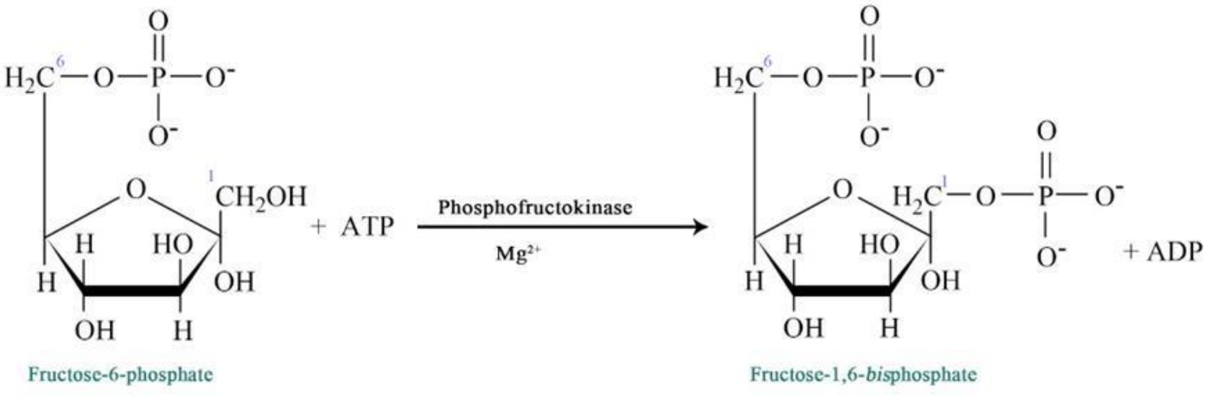
14 .This indicates the entry of glucose 6-phosphate into another pathway called the hexose monophosphate shunt (pentose phosphate pathway), which will be considered next.

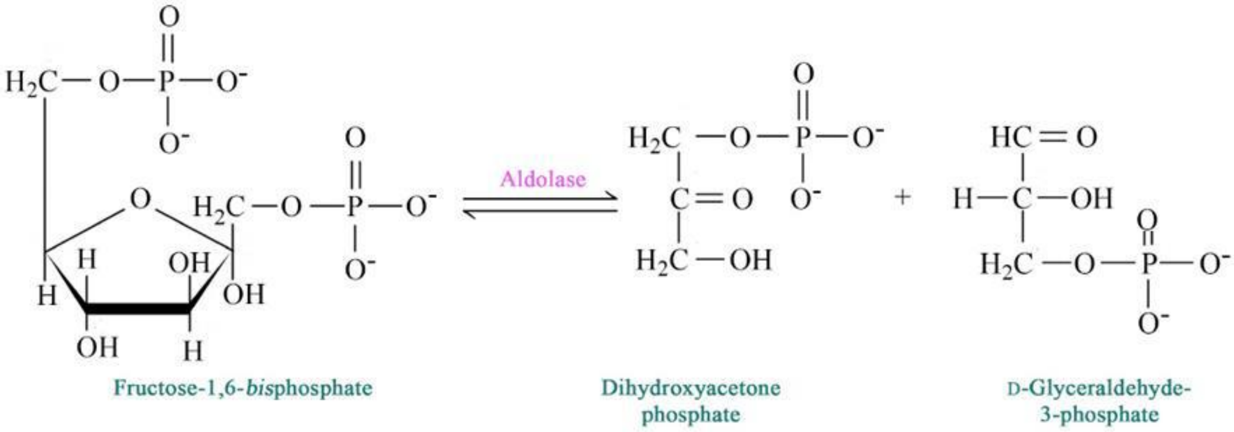
Glucose + 2 Pi + 2 ADP ⟶ 2 Pyruvate + 2 ATP

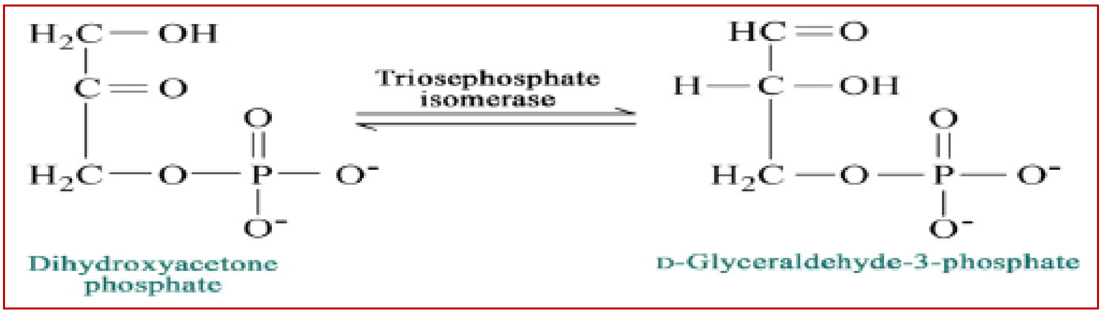


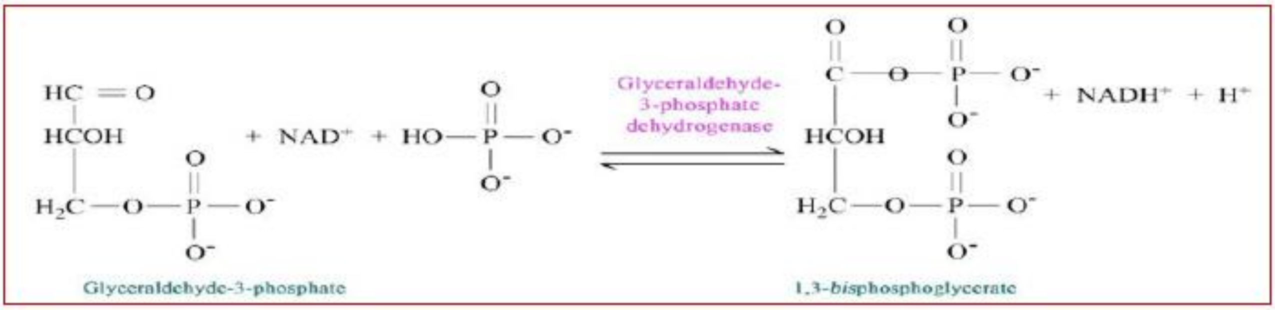

Glucose
+ ATP
Hexokinase
+ ADP
Glucose-6-phosphate

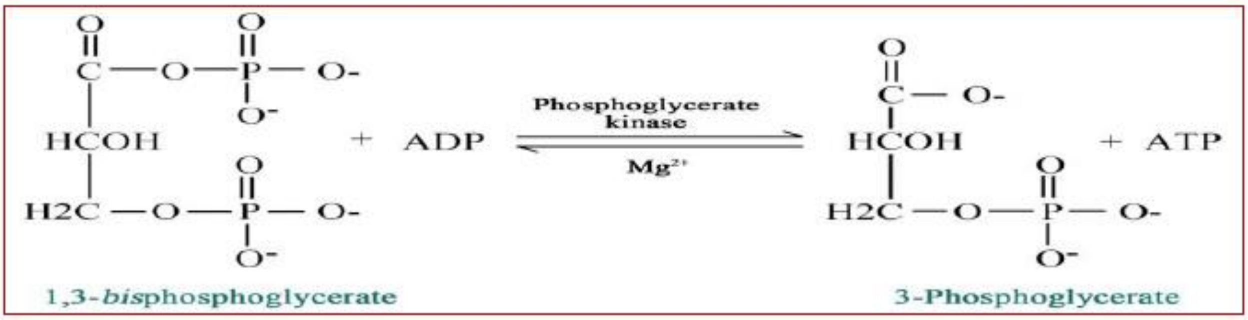

Glucosephosphate isomerase
Glucose-6-phosphate
Fructose-6-phosphate

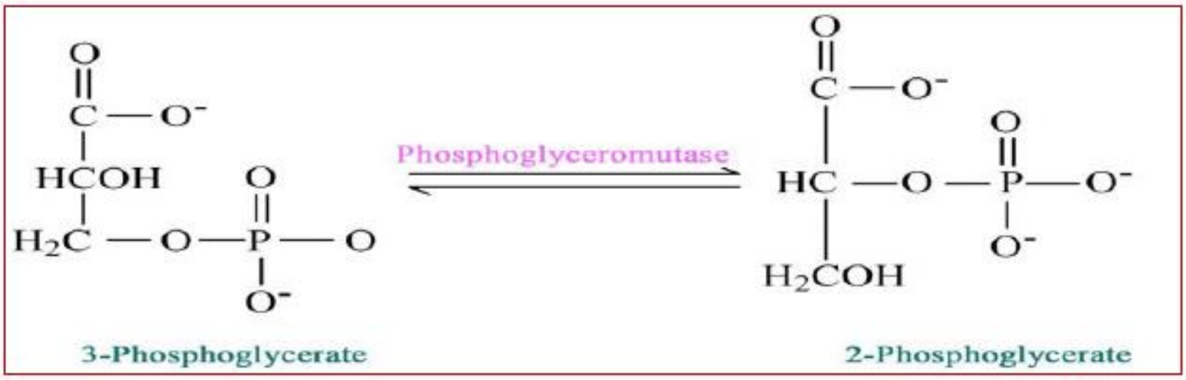

+ ATP
Phosphofructokinase
Mg2+
+ ADP
Fructose-6-phosphate
Fructose-1,6-bisphosphate

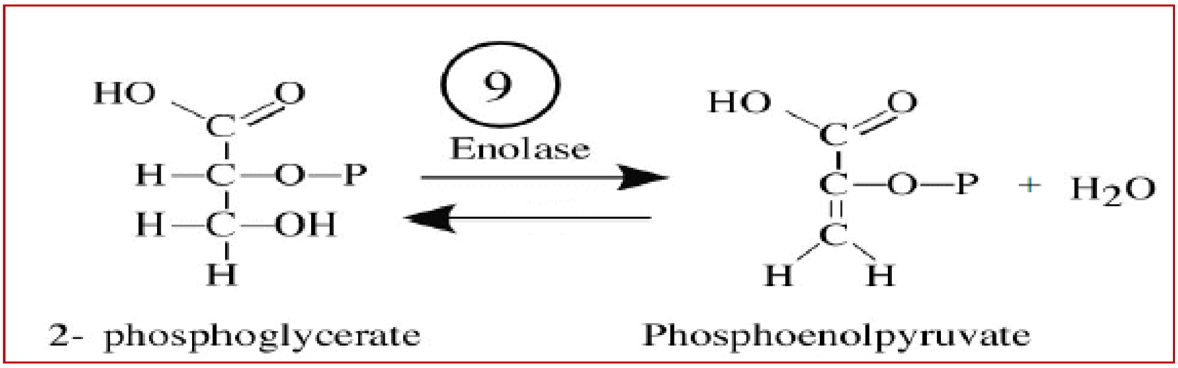

Aldolase
Fructose-1,6-bisphosphate
Dihydroxyacetone phosphate
D-Glyceraldehyde-3-phosphate

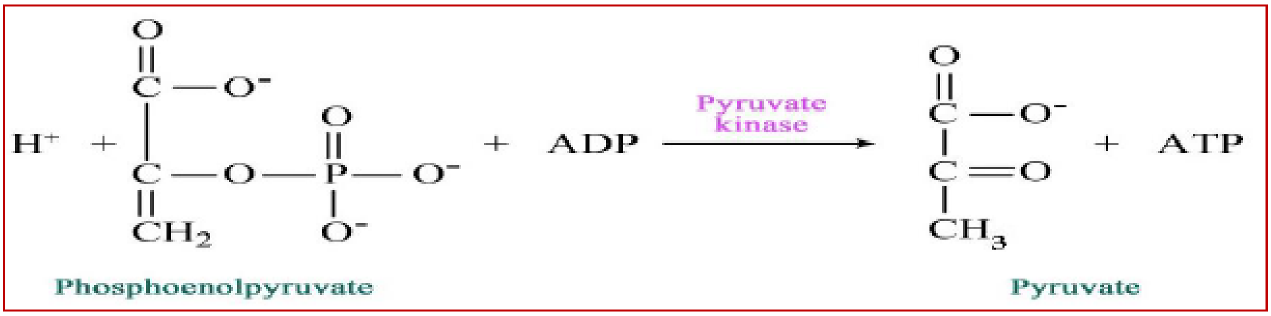

Triosephosphate isomerase
Dihydroxyacetone phosphate
D-Glyceraldehyde-3-phosphate


+ NAD+ + HO—P—O-
Glyceraldehyde-3-phosphate dehydrogenase
+ NADH+ + H+
Glyceraldehyde-3-phosphate
1,3-bisphosphoglycerate


+ ADP
Phosphoglycerate kinase
Mg2+
+ ATP
1,3-bisphosphoglycerate
3-Phosphoglycerate



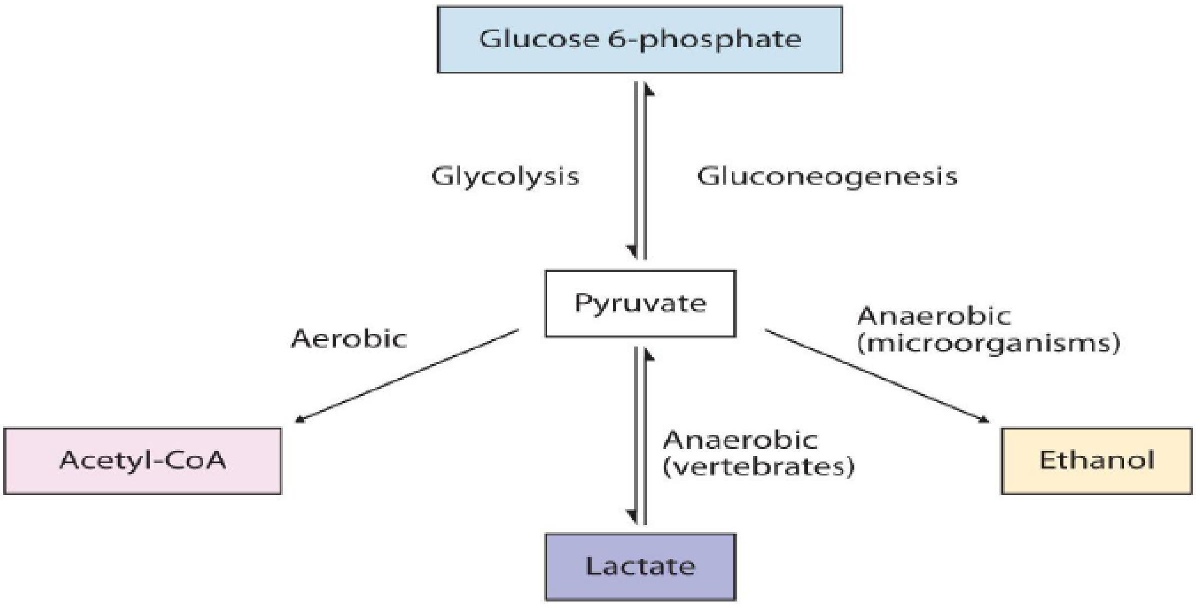


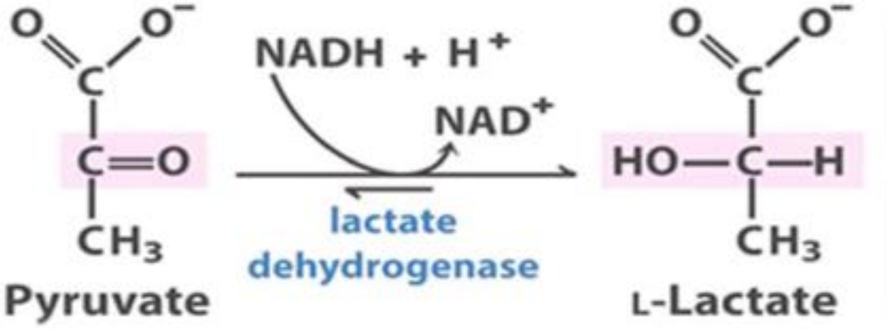


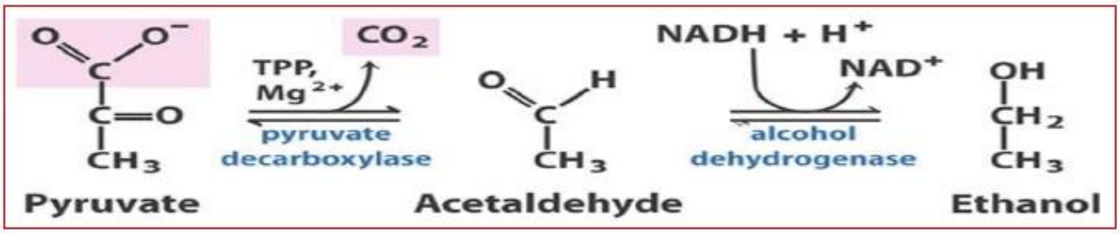
محصلة الطاقة الناتجة من تحلل جزيء من الجلوكوز إلي جزيئين من البيروفيت

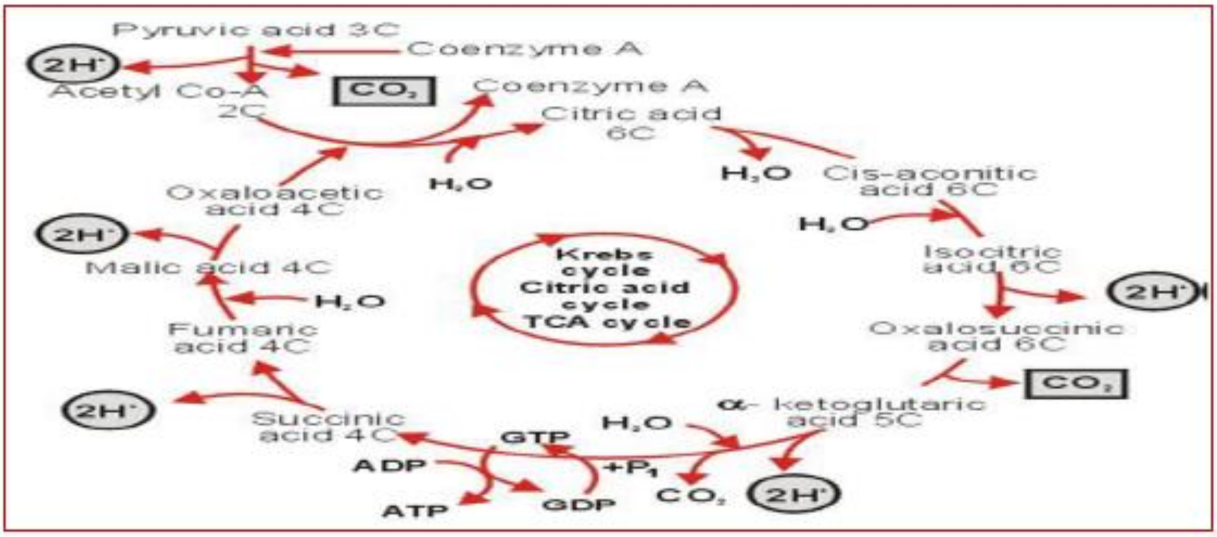
- إستهلاك 1 ATP في الخطوة رقم 1 .
- إستهلاك 1 ATP في الخطوة رقم 3 .
- إنتاج جزيئين من ال (NADH) باعتبار أن الجلوكوز إنشطر إلى جزئيين في الخطوة رقم 6 . كل جزيء من ال NADH عند أكسدته يعطي 3 ATP .
- إنتاج 2 ATP في الخطوة رقم 7 باعتبار أن الجلوكوز إنشطر إلى جزئيين من الجليسر ألدهيد 3 -فوسفات وكل جزء يعطي 1 ATP .
- إنتاج 2 ATP في الخطوة رقم 10 باعتبار وجود جزئيين من 3 -فوسفو إنول بيروفيت ليعطي كلا منهما 1 ATP .

وبالتالي يكون الناتج: 6+2+2+1-1 = 8 ATP









Krebs Cycle

Alternatively designated the tricarboxylic acid cycle or the citric acid cycle, this sequence of reactions represents the forefront of energy metabolism in the body. It can be thought of as the common and final catabolic pathway because products of carbohydrate, fat, and amino acids feed into the cycle where they can be totally oxidised to CO_2 and H_2O, with the accompanying generation of large amounts of ATP. Not all entrant substances are totally oxidised. Some Krebs cycle intermediates are used to form glucose by the process of gluconeogenesis, which will be discussed in the next section, and some can be converted to certain amino acids by transamination. However, the importance of the cycle as the nucleus of energy production is evidenced by the estimation that over 90 per cent of energy released from food occurs here.

The high energy output of the Krebs cycle is attributed to mitochondrial electron transport, with oxidative phosphorylation providing the means for ATP formation. The oxidation reactions occurring in the cycle are actually dehydrogenations in which an enzyme catalyses the removal of two hydrogens to an acceptor co-substrate such as NAD or FAD. Since the enzymes of the cycle and the enzymes and electron carriers of electron transport are both compartmentalised within the mitochondria,

the reduced cosubstrates, NADH and FADH2 are readily reoxidised by O_2 via the electron transport chain. In addition to its production of the reduced co-substrates NADH and FADH2, which furnish the energy through their oxidation via electron transport, the Krebs cycle produces most of the carbon dioxide through decarboxylation reactions. Viewing this in its proper perspective with regard to glucose metabolism, it must be recalled that two pyruvates are produced from one glucose during cytoplasmic glycolysis. These pyruvates are in turn transferred into the mitochondria, where decarboxylation leads to the formation of two acetyl CoA units and two molecules of CO_2. The two carbons represented by the acetyl CoA are additionally lost as CO_2 through Krebs cycle decarboxylations. Most of the CO_2 produced is exhaled through the lungs, although some is used in certain synthetic reactions called carboxylation. The Krebs cycle is shown in figure below. It is usually visualized as beginning with the condensation of acetyl CoA with oxaloacetate to form citrate. The acetyl CoA is formed from numerous sources, including the breakdown of fatty acids, glucose (through pyruvate), and certain amino acids. Its formation from pyruvate will be considered now, since this compound links cytoplasmic glycolysis to the mitochondrial Krebs cycle activity. The reaction shown below is generally referred to as the pyruvate dehydrogenase reaction. However, the reaction is a complex one requiring a multienzyme system and various cofactors. The enzymes

and cofactors are contained within an isolable unit called the pyruvate dehydrogenase complex. The cofactors include coenzyme A (CoA)thiamine diphosphate (TDP), Mg+2, NAD, FAD, and lipoic acid. Four vitamins are therefore necessary for the activity of the complex pantothenic acid (a component of CoA), thiamine, niacin, and riboflavin.

The role of these vitamins and others as precursors of coenzymes will be discussed in another unit. The enzymes include pyruvate decarboxylase, dihydroolipoyl dehydrogenase, and dihydrolipoyl transacetylase. The net effect of the complex results in decarboxylation and dehydrogenation of pyruvate with NAD serving as the terminal hydrogen acceptor. This reaction therefore yields energy, since the reoxidation by electron transport of the NADH produces three mol of ATP by oxidative phosphorylation. The reaction is regulated negatively by ATP and by NADH. The condensation of acetyl CoA with oxaloacetate initiates the Krebs cycle reactions. The following are comments on reactions:

1 .The formation of citrate from oxaloacetate and acetyl CoA is catalysed by citrate synthetase. The reaction is regulated negatively by ATP. The isomerisation of citrate to isocitrate involves cis aconitate as an intermediate. The isomerisation, catalysed by aconitase, involves dehydration followed by sterically reversed hydration, resulting in the repositioning of the-OH group onto an adjacent carbon. The first of four

dehydrogenation reactions within the cycle, the isocitratede hydrogenase reaction supplies energy through the respiratory chain reoxidation of the NADH. Note that the first loss of CO_2 in the cycle occurs at this site. It arises from the spontaneous decarboxylation of an intermediate compound, oxalosuccinate. The reaction is positively modulated by ADP and negatively modulated by ATP and NADH.

2 .The decarboxylation/dehydrogenation of aglutarate is mechanistically identical to the pyruvate dehydrogenase complex reaction in its multi-enzyme/cofactor requirement. In the reaction, referred to as the α

ketoglutarate dehydrogenase reaction, NAD serves as hydrogen acceptor, and a second carbon is lost as CO_2 The pyruvate dehydrogenase, isocitrate dehydrogenase, and aglutarate dehydrogenase reactions account for the loss of the three-carbon equivalent of pyruvate as CO_2.

3 .Energy is conserved in the thioester bond of succcinyl CoA. The hydrolysis of that bond by succinyl thiokinase releases enough energy to drive the phosphorylation of guanosine diphosphate (GDP) by inorganic phosphate. The resulting GTP is a high energy phosphate anhydride compound like ATP; as such, GTP can serve as phosphate donor in certain phosphorylation reactions. One such reaction occurs in the gluconeogenesis pathway.

4 .The succinate dehydrogenase reaction uses FAD instead of NAD as hydrogen acceptor. The FADH2 is reoxidised by electron transport to O_2, but only two ATPs are formed by oxidative phosphorylation instead of three.

5 .Fumarase incorporates the elements of H_2O across the double bond of fumarate to form malate.

6 .The conversion of malate to oxaloacetate completes the cycle. NAD acts as a hydrogen acceptor in this dehydrogenation reaction catalysed by malate dehydrogenase. It is the fourth site of reduced co substrate formation and therefore of energy release in the cycle.

In summary the complete oxidation of glucose to CO_2 and H_2O can be shown by the equation:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6\ CO_2 + 6\ H_2O + \text{energy}.$$

This is achieved by the combined reaction sequences of the glycolytic and Krebs cycle pathways. The amount of released energy conserved as ATP under aerobic conditions is as follows:

The glycolytic sequence, glucose →2 pyruvates, produces two ATPs by substrate level phosphoryllation and either four or six by oxidative phosphoorylation, depending on the shuttle system for NADH-reducing equivalents. Generally, six will be formed due to the overall greater activity of the malate shuttle system. The intra mitochondrial pyruvate dehydrogenase reaction yields two mol of NADH, one for each pyruvate oxidised and therefore six additional ATPs by oxidative phosphorylation.

The oxidation of 1 mol of acetyl CoA in the Krebs cycle yields a total of

12 ATPs. The sites of formation, indicated by reaction number, follow.

3 - 3 .ATP

4 -3 .ATP

5 -1 .ATP (as GTP)

6 -2 .ATP

8-3 .ATP

Total 12 ATP

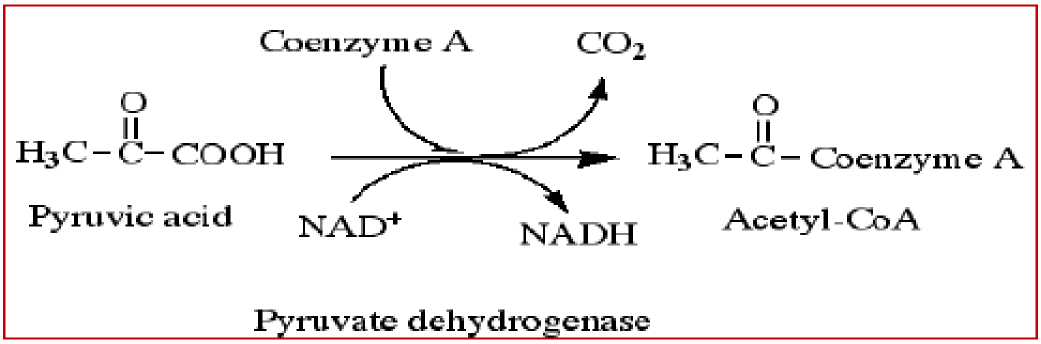
Since 2 mol acetyl CoA derived from one glucose, however, the actual

total is 24 ATPs. The total number of ATPs realized for the complete

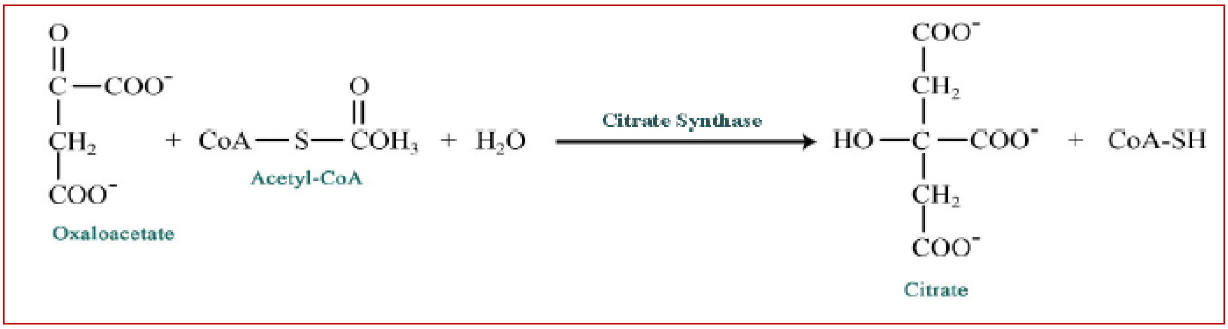
oxidation of 1 mol of glucose is therefore 38, equivalent to 262.8 kcal. It will be recalled that this figure represents only about 40% of the total energy released by mitochondrial electron transport. The remaining 60 per cent, or approximately 394 kcal, is released as heat to maintain body temperature has already been mentioned that acetyl CoA is produced by fatty acid oxidation and amino acid catabolism as well as from the glycolytically

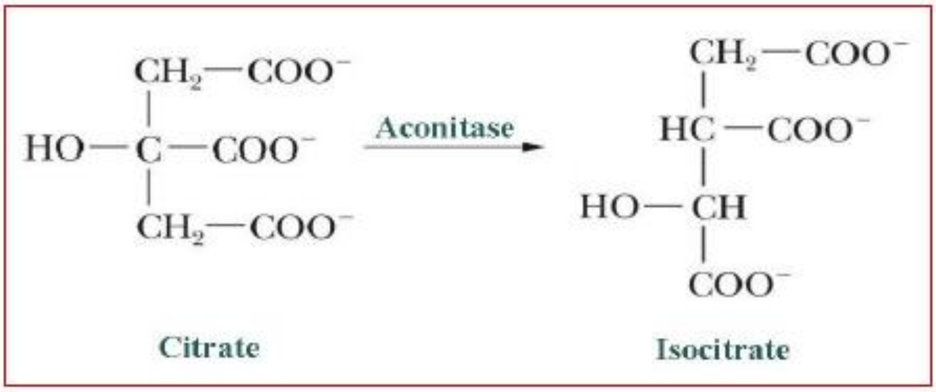
derived pyruvate. This clearly leads to an imbalance between the amount of acetyl CoA and oxaloacetate, which condense one to one stoichiometrically in the citrate synthetase reaction. It is therefore important that oxaloacetate and/or Krebs cycle intermediates, which can form oxaloacetate, be replenished in the cycle. Such a mechanism does indeed exist. Oxaloacetate, fumarate, succinyl CoA, and a rate can all be formed from certain amino acids, but the single most important mechanism for ensuring an ample supply of oxaloacetate is the reaction

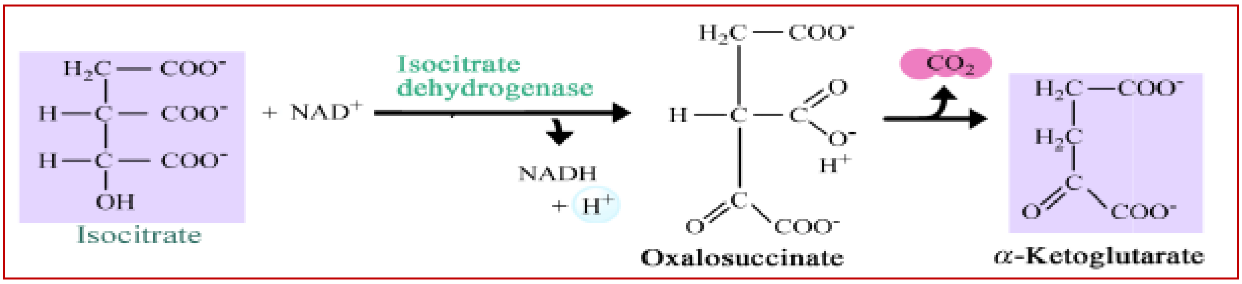
by which it is formed directly from pyruvate. This reaction, shown below, is catalysed by pyruvate carboxxylase. The "uphill" incorporation of CO_2 is accomplished at the expense of ATP, and the reaction requires the participation of biotin. The diversion of pyruvate into oxaloacetate is called an anaplerotic (filling up) process because of its role in restoring oxaloacetate to the cycle. It is of interest that pyruvate carboxylase is regulated positively by acetyl CoA, thereby accelerating oxaloacetate formation in answer to increasing levels of acetyl CoA.

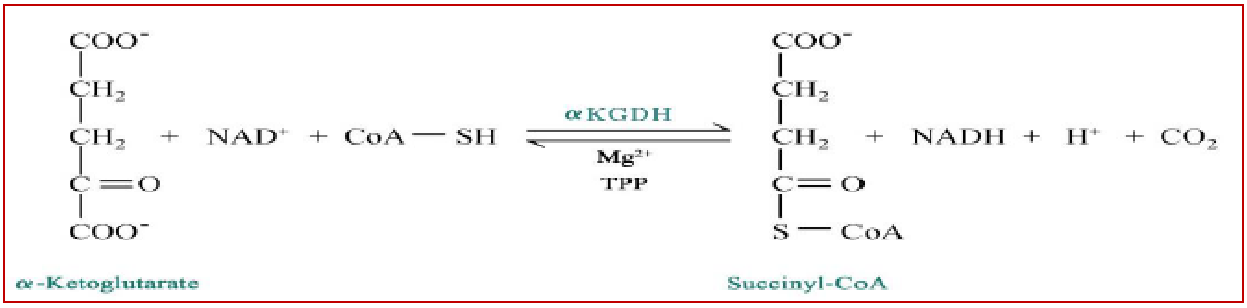


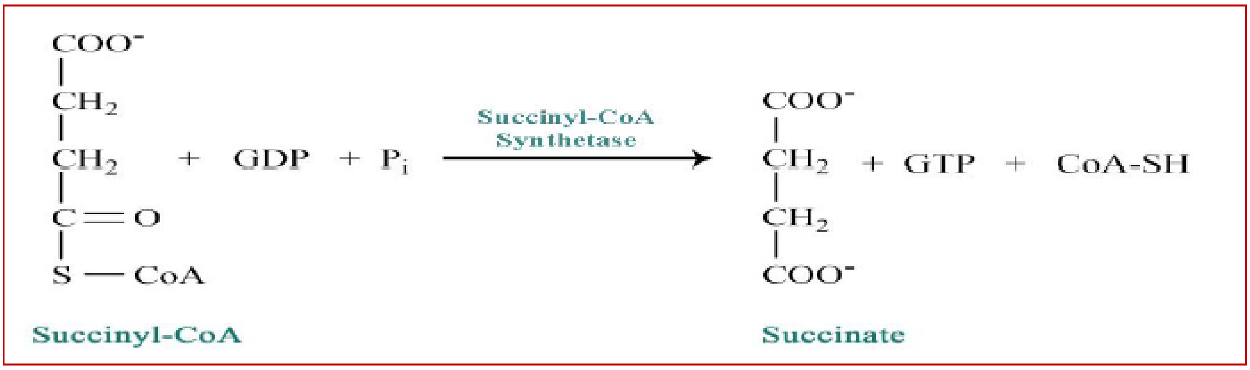
خطوات دورة كربس

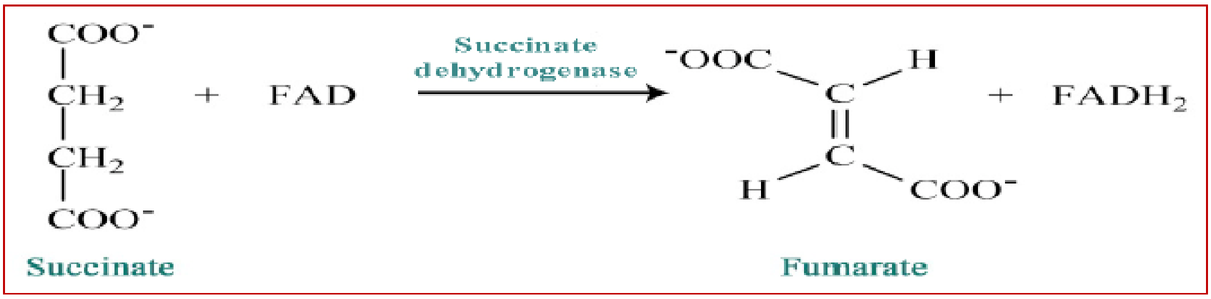

Oxaloacetate
Acetyl-CoA
Citrate Synthase
Citrate
CoA-SH
H2O

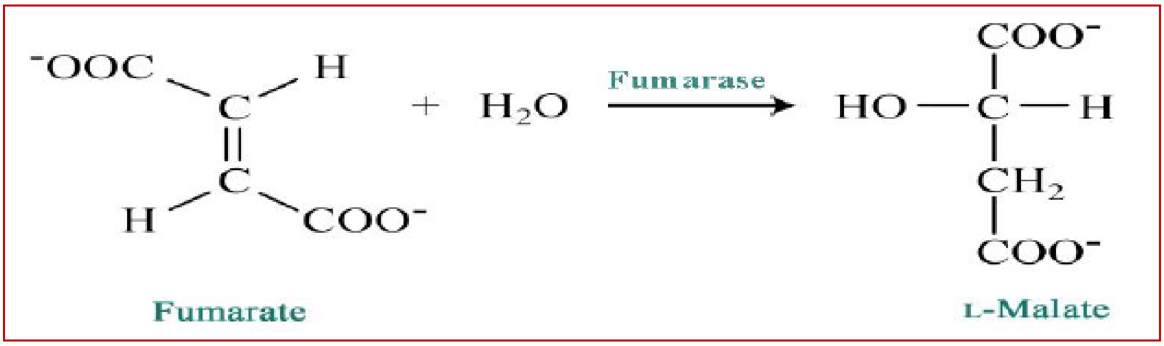

Aconitase
Citrate
Isocitrate

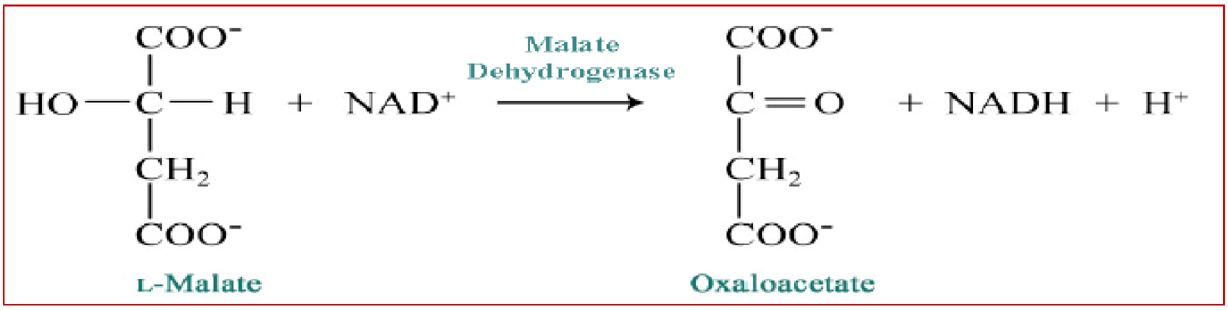

Isocitrate
NAD+
Isocitrate dehydrogenase
NADH
+ H+
Oxalosuccinate
CO2
α-Ketoglutarate


α-Ketoglutarate
NAD+
CoA — SH
αKGDH
Mg2+
TPP
NADH
H+
CO2
Succinyl-CoA

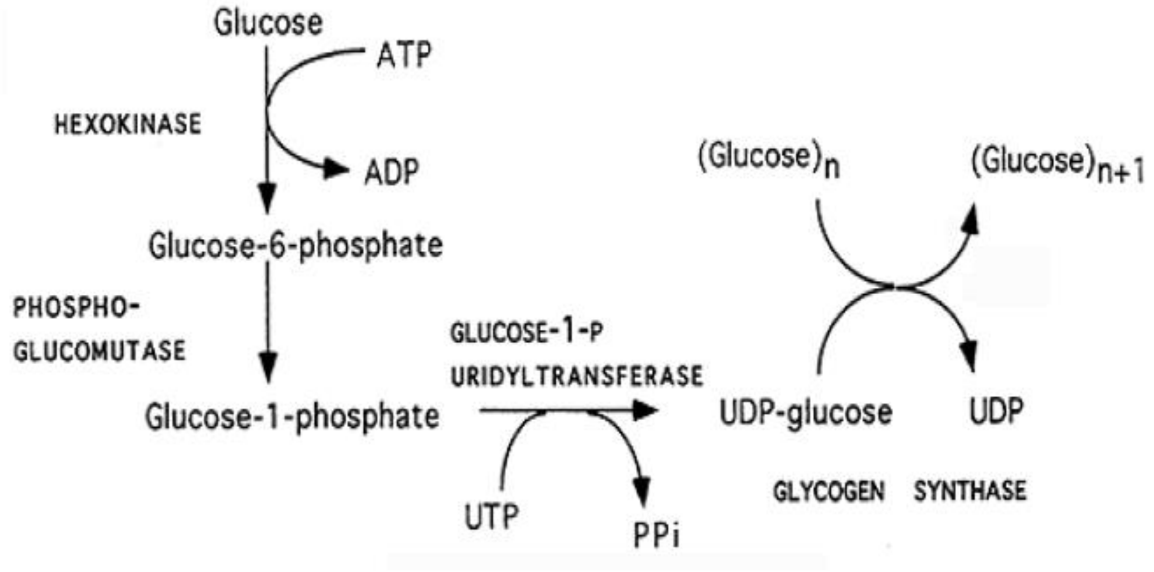

COO⁻
CH2
CH2
C=O
S — CoA
+ GDP + Pi
Succinyl-CoA Synthetase
COO⁻
CH2
CH2
COO⁻
+ GTP + CoA-SH
Succinyl-CoA
Succinate


COO⁻
CH2
CH2
COO⁻
+ FAD
Succinate dehydrogenase
⁻OOC
H
C
C
H
COO⁻
+ FADH2
Succinate
Fumarate

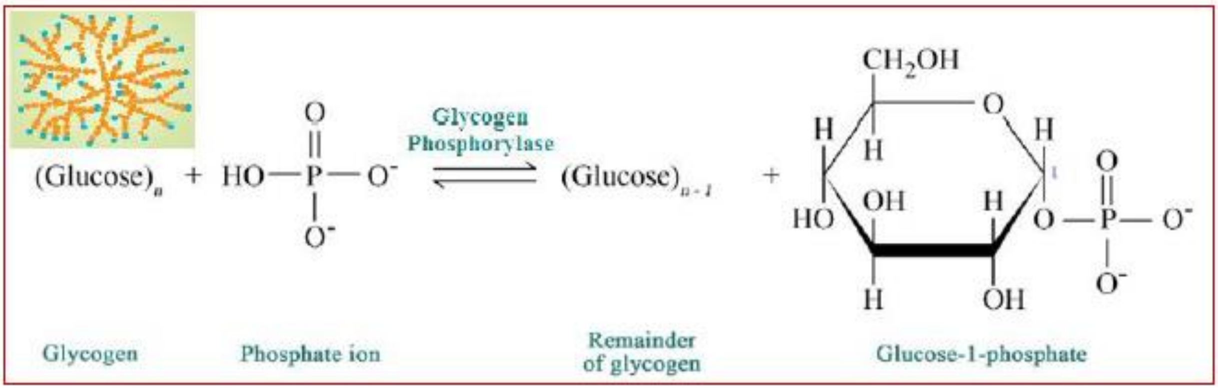

⁻OOC
H
C
C
H
COO⁻
+ H2O
Fumarase
COO⁻
HO — C — H
CH2
COO⁻
Fumarate
L-Malate

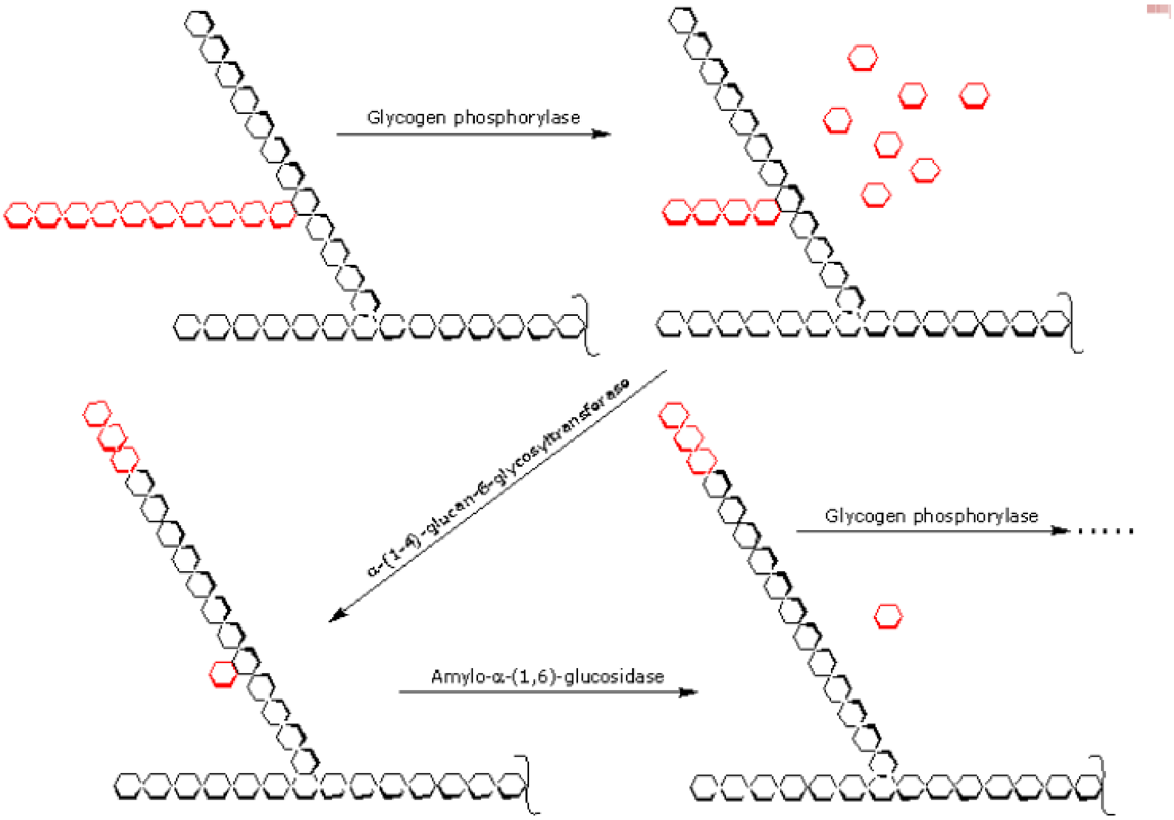

COO⁻
HO — C — H
CH2
COO⁻
+ NAD⁺
Malate Dehydrogenase
COO⁻
C=O
CH2
COO⁻
+ NADH + H⁺
L-Malate
Oxaloacetate

بناء الجلايكوجين (Glycogenesis)



إستحداث الجلايكوجين (Gluconeogenesis)



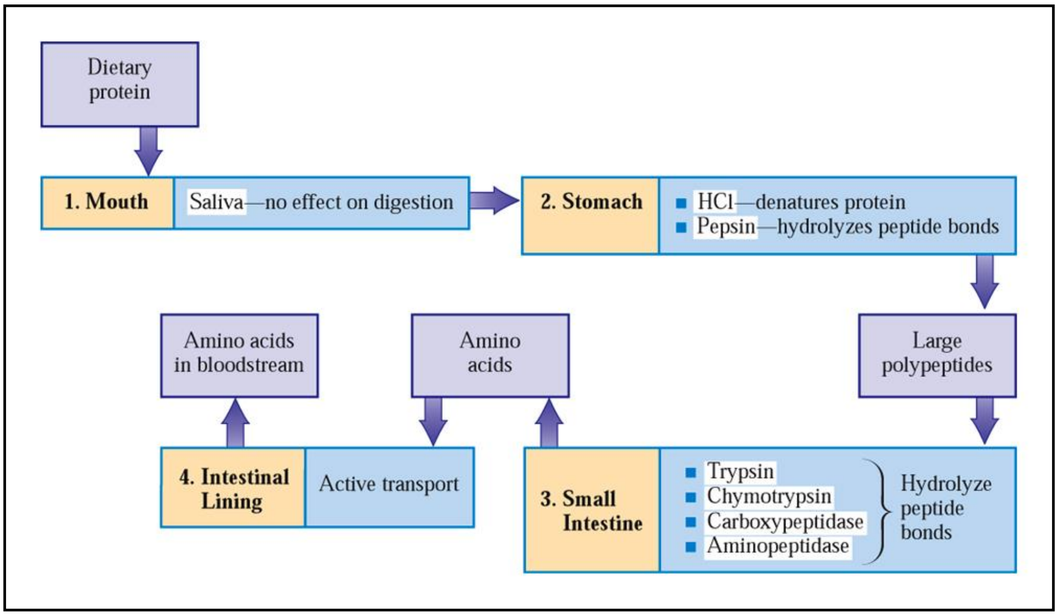

Glycogen phosphorylase
α-(1-4)-glucan-6-glycosyltransferase
Glycogen phosphorylase
Amylo-α-(1,6)-glucosidase

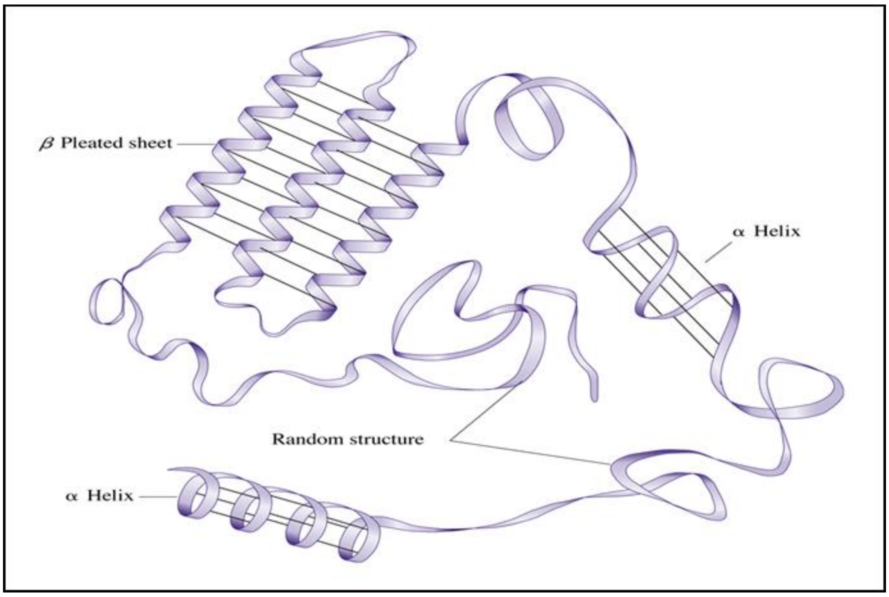
Proteins Metabolism

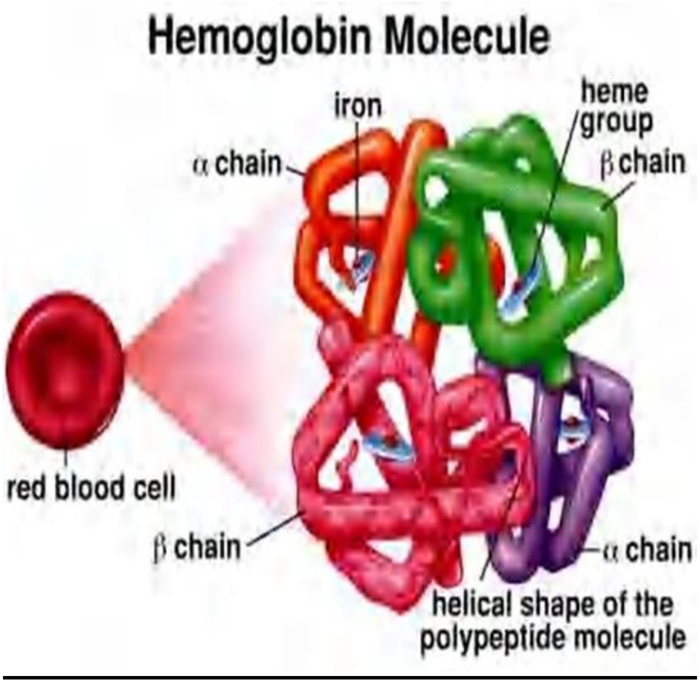
Protein Digestion

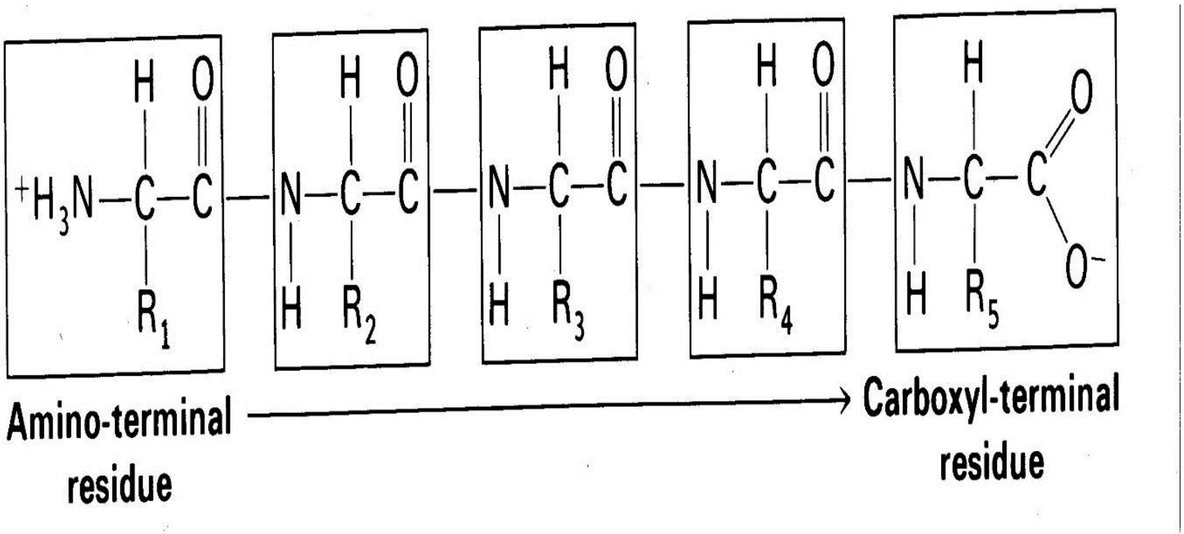
Protein breakdown begins in the **stomach**.

No protein hydrolyzing enzymes are found in saliva.






Hemoglobin Molecule
iron
heme group
α chain
β chain
red blood cell
β chain
α chain
helical shape of the polypeptide molecule


Amino-terminal residue
Carboxyl-terminal residue
R1
R2
R3
R4
R5

Hydrolysis (10% of peptide bonds) & **denaturization** by pepsin enzyme & HCl acid produce **short chain polypeptides** in the stomach.

Trypsin, chymotrypsin, & carboxypeptidase from Pancreatic juices, and **Aminopeptidase** from cells in the small intestine Brush Zone create “free” **amino acids**.

Free amino acids are absorbed thru intestinal wall via active transport.

Enter bloodstream and are brought to cells.

The total supply of free amino acids available is called: the **Amino Acid Pool**.

3 sources of “free” amino acids:

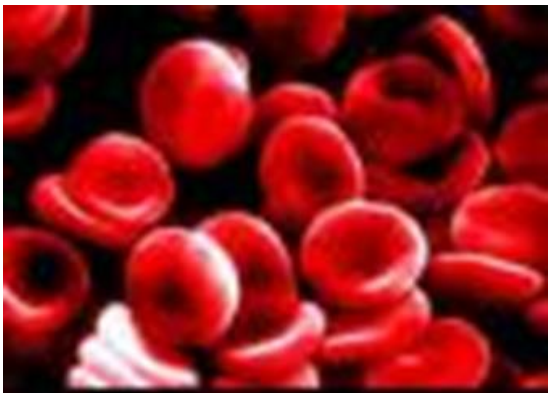
1. Dietary protein breakdown
2. Biosynthesis of amino acids in the Liver
3. Protein turnover (I prefer apple turnovers)

Protein turnover is the breakdown & re-synthesis of body protein:

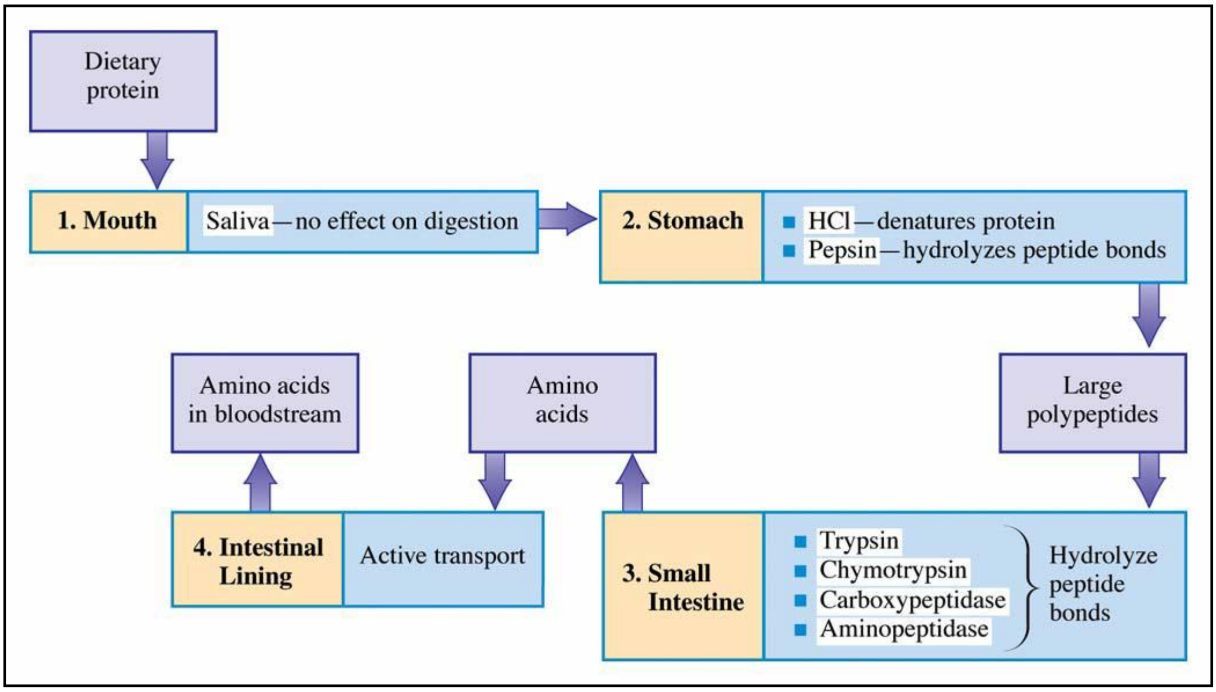
Old tissues

Damage

Recycling enzymes & hormones



Summary of protein digestion in the human body. Possible fates for amino acid degradation products.



Transamination and Oxidative Deamination:

Two steps in degrading amino acids

1) remove a-amino group

2) breakdown & process carbon skeleton

Release of an **amino group** is also two steps:

1) **Transamination**

2) **Oxidative deamination**

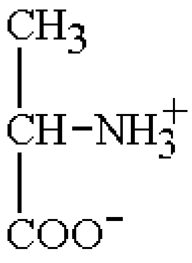
Central role of glutamate:

Amino acids:

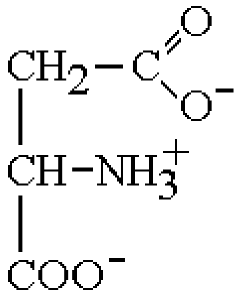
Glutamate, **aspartate**, **alanine** & **glutamine**

present in higher concentrations in mammalian cells. Have metabolic functions as well as roles in proteins.

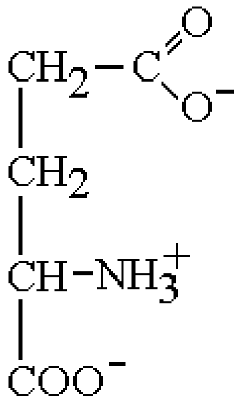
Glutamate is the most important, metabolically



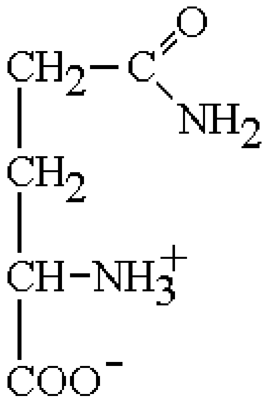
Alanine



Aspartate



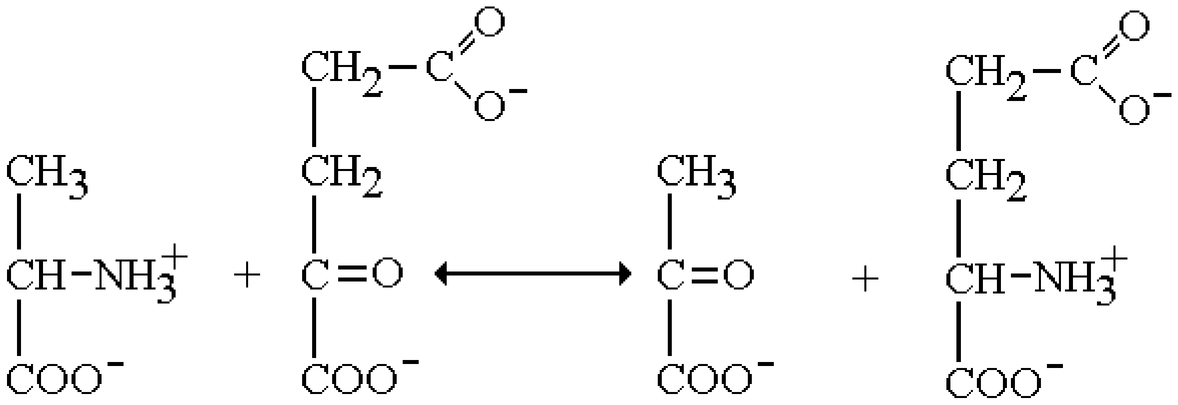
Glutamate



Glutamine

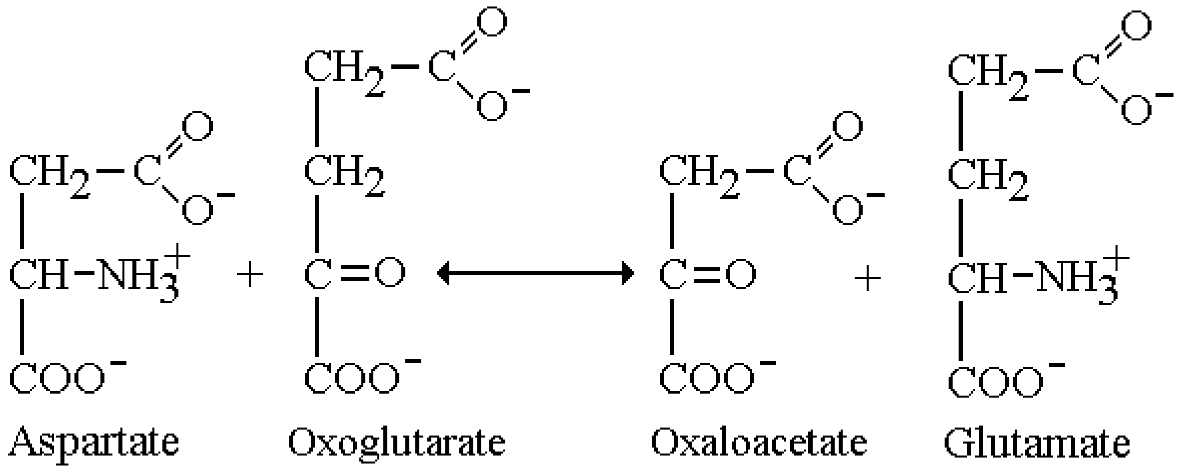
Some **transaminases** are used for diagnosing disorders:

enzyme **alanine aminotransferase**. Escapes in large amounts from dead or dying liver tissue. Measured in blood samples for diagnostic purposes.



Alanine Oxoglutarate Pyruvate Glutamate

Transaminase enzyme **aspartate aminotransferase** very active enzyme inside heart cells. Also escapes in large amounts from dead or dying heart tissues & enters bloodstream. Measured in blood for diagnosing myocardial infarction.

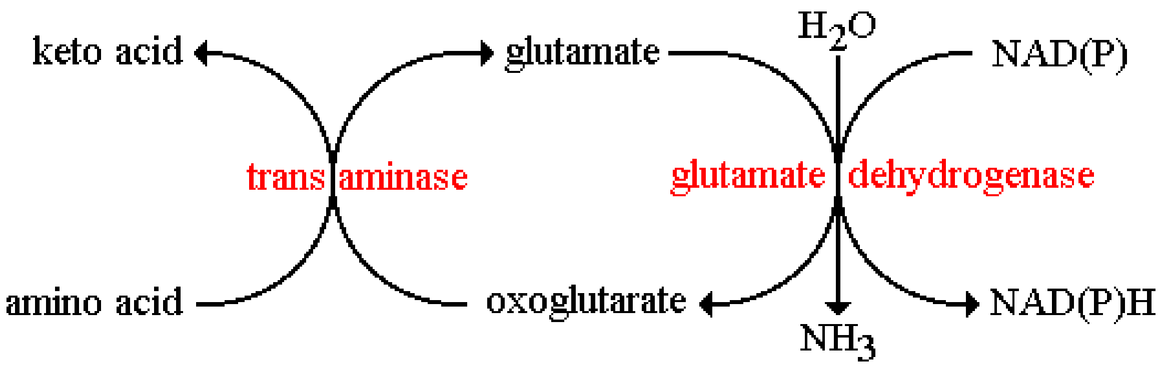


Trans-deamination (sum it up)

Most **transaminases** share a common substrate and product (oxoglutarate and glutamate) with the enzyme **glutamate dehydrogenase**.

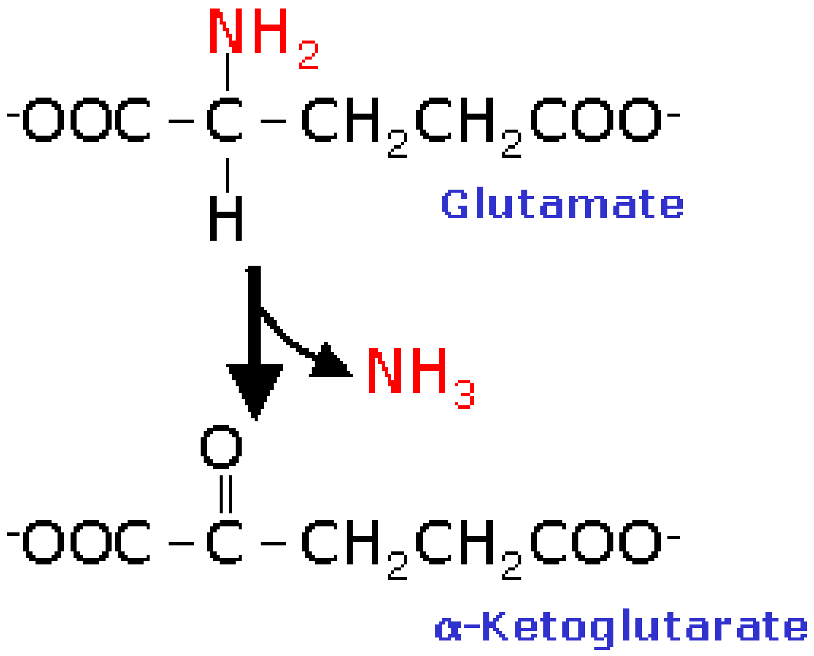
This permits a ***combined*** N excretion pathway for individual amino acids: "trans-deamination."

Glutamate has a central role in the overall control of nitrogen metabolism.



Oxidative Deamination

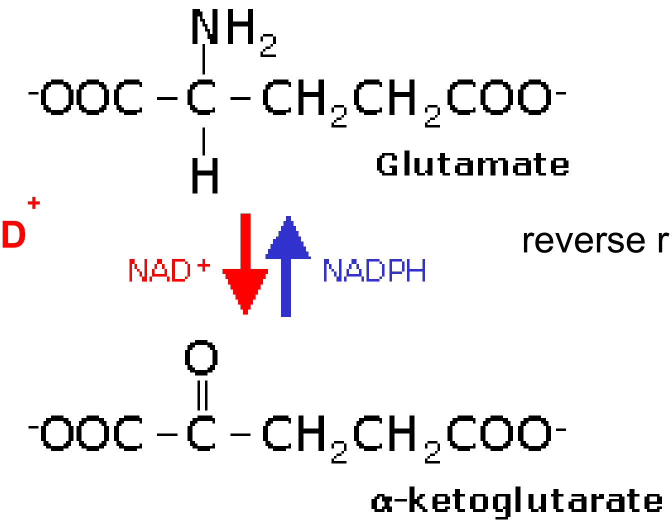
The **glutamate** produced from the transamination step is then deaminated by **oxidative deamination** using the enzyme **glutamate dehydrogenase**



Recycles back to a ketodiacid & releases ammonia

Glutamate dehydrogenase **[GluDH]** will reversibly convert

glutamate to **a-ketoglutarate** and **a-ketoglutarate** to **glutamate**.



Deamination reaction uses **NAD$^+$**

reverse reaction uses **NADPH**

Uses ***both*** **NAD$^+$** and **NADPH** – how to regulate it?

Urea cycle:

Ammonium salts (**NH_4^+**) are toxic compounds.

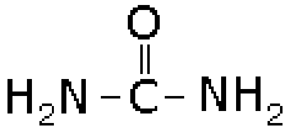
Oxidative deamination converting glutamate to a-ketoglutarate is an easily shifted equilibrium reaction.

Ammonium ions building up favors the synthesis of excessive amounts of glutamate, decreasing the Krebs cycle intermediate

a-ketoglutarate.

This in turn decreases **ATP production**, and that affects the nervous system.

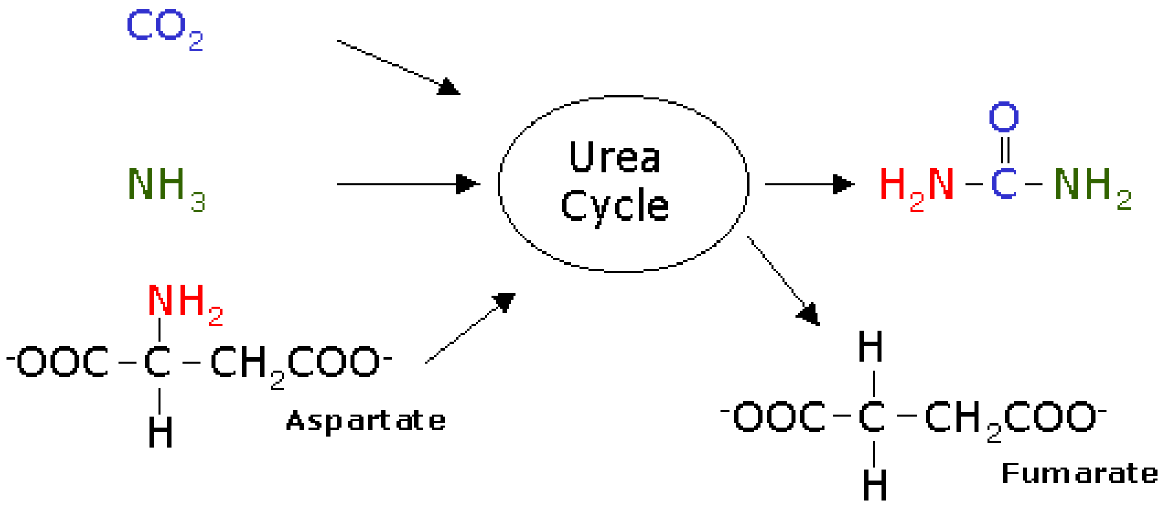
The answer is Urea:



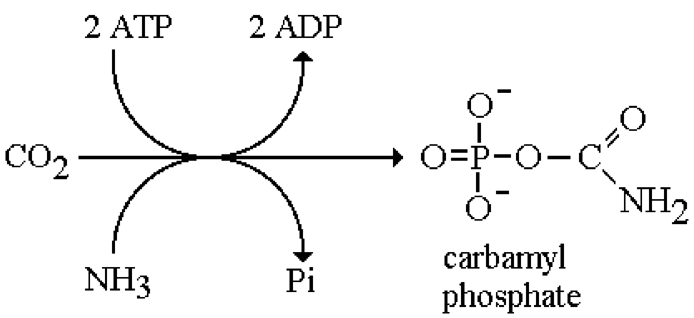
$$H_2N-\overset{\overset{O}{\|}}{C}-NH_2$$

The **inputs** to the urea cycle are NH_3, CO_2 and aspartic acid and ATP.

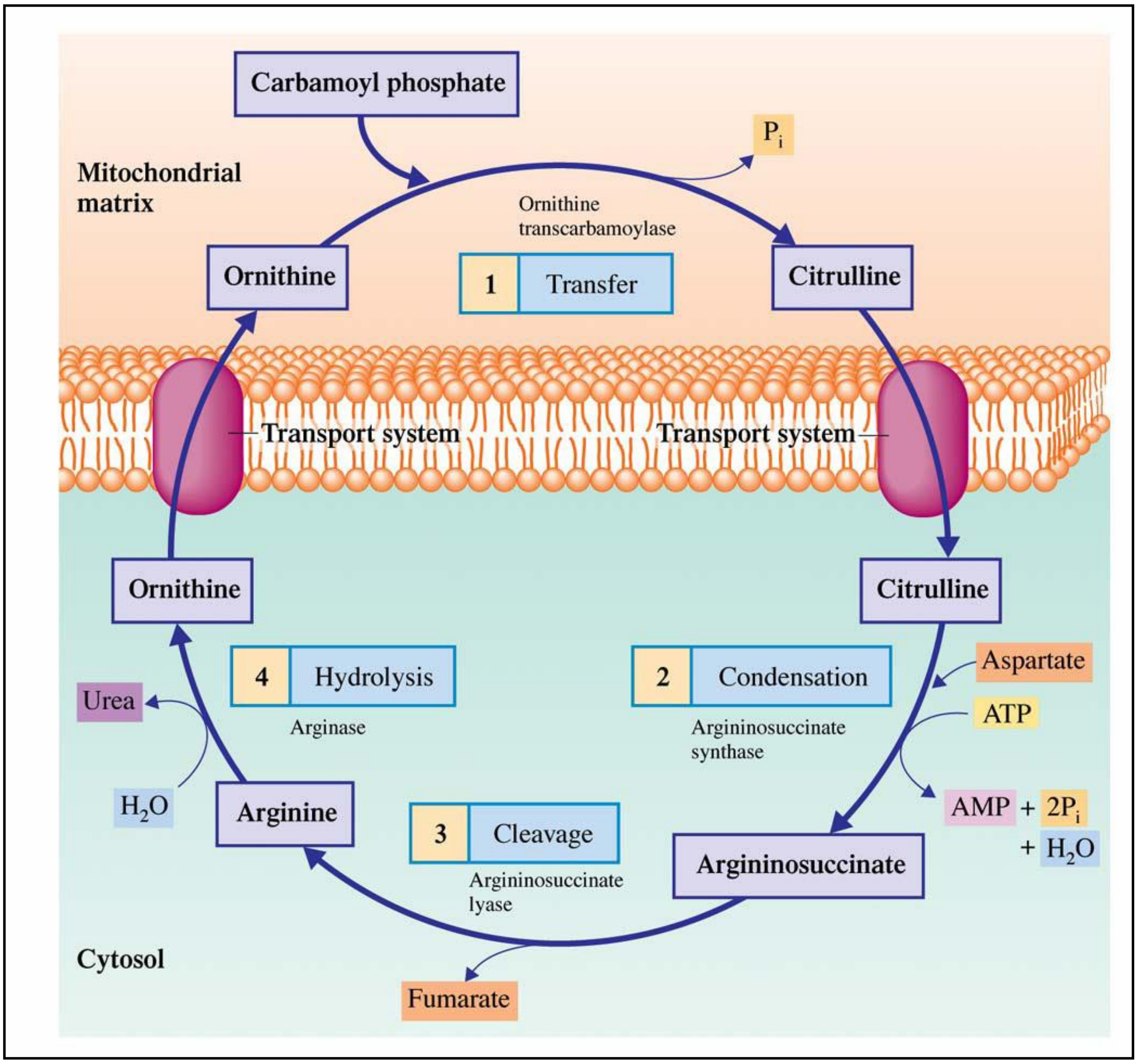
The **outputs** are urea, ADP and fumaric acid.



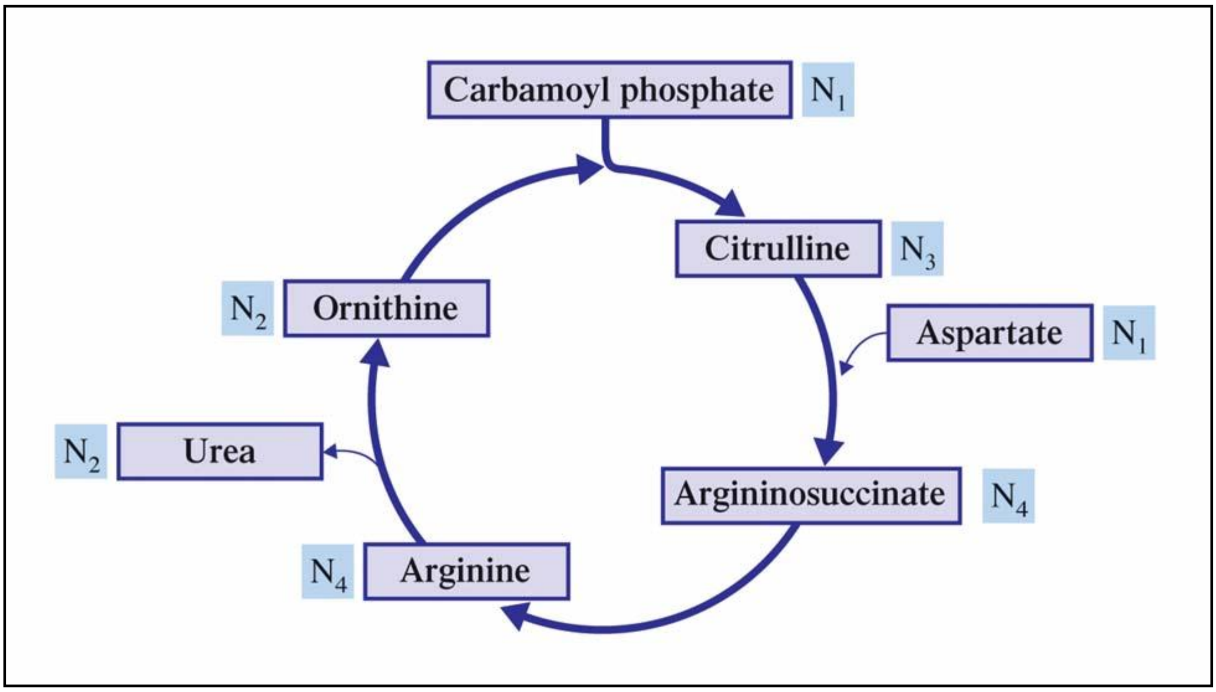
The carbonyl group of urea is derived from **CO_2** , **Ammonia** contributes one of the amine groups on urea



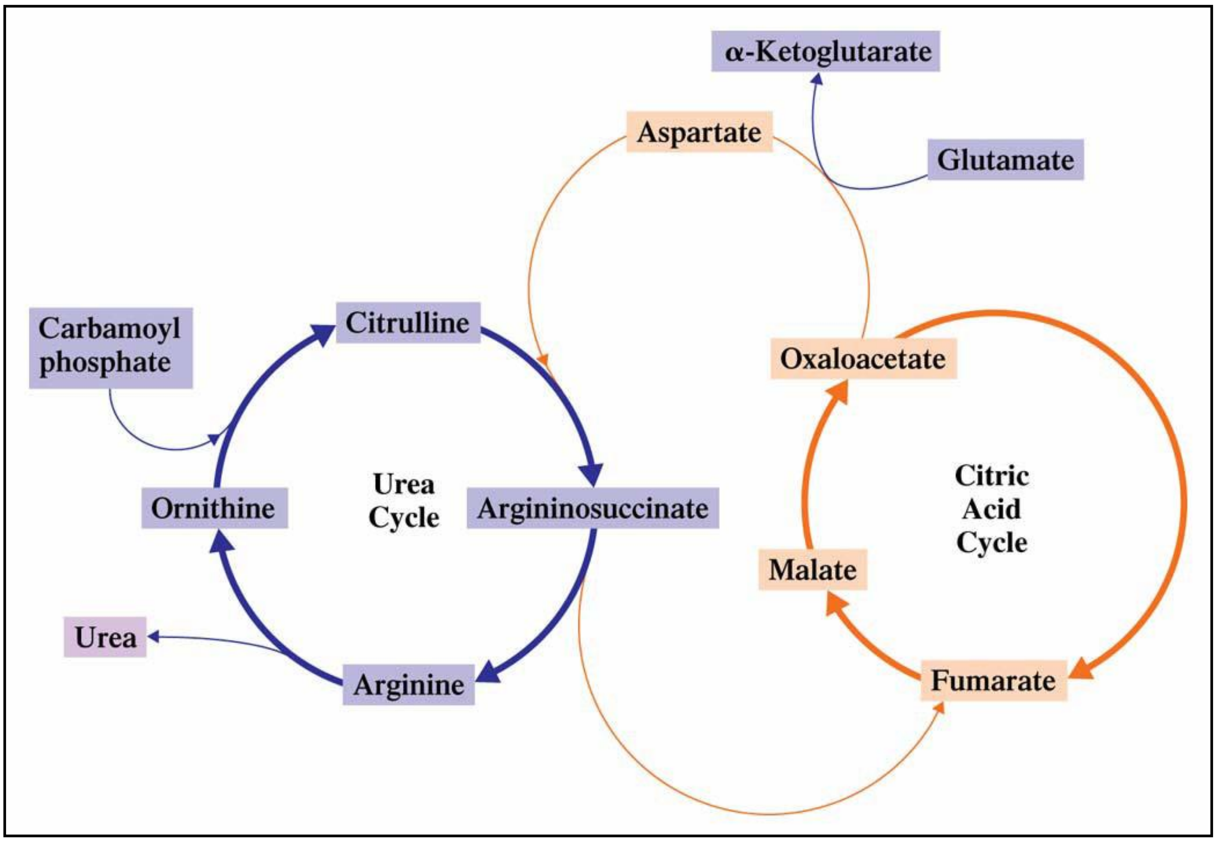
The **four-step** urea cycle in which **carbamoyl phosphate** is converted to **urea**.



The nitrogen content of the various compounds that participate in the urea cycle



Fumarate from the urea cycle enters the Krebs cycle. **Aspartate** produced from **oxaloacetate** of the Krebs cycle enters the urea cycle.



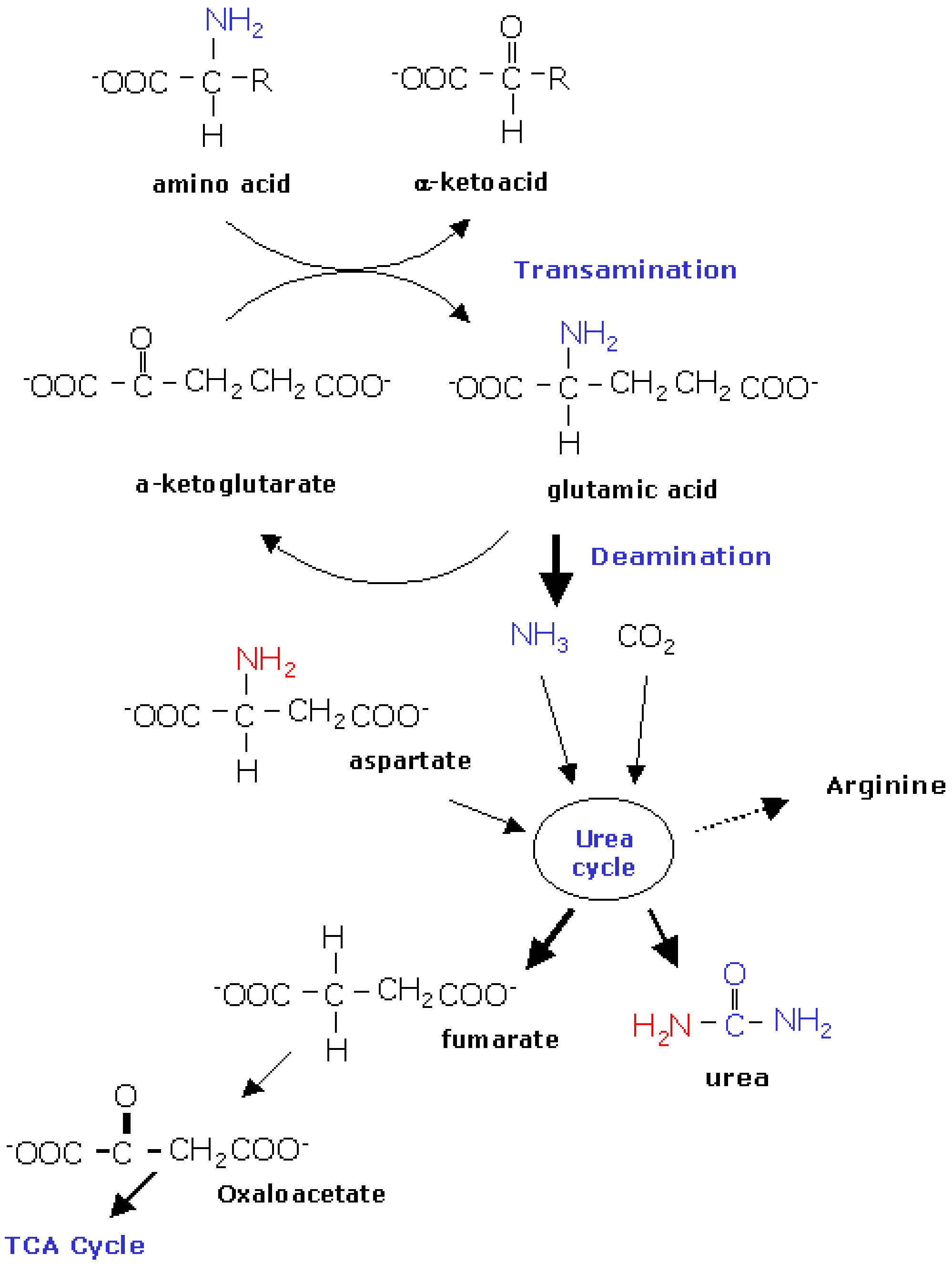
Oxaloacetate has 4 potential fates: transamination; conversion to glucose; formation of citrate; conversion to pyruvate

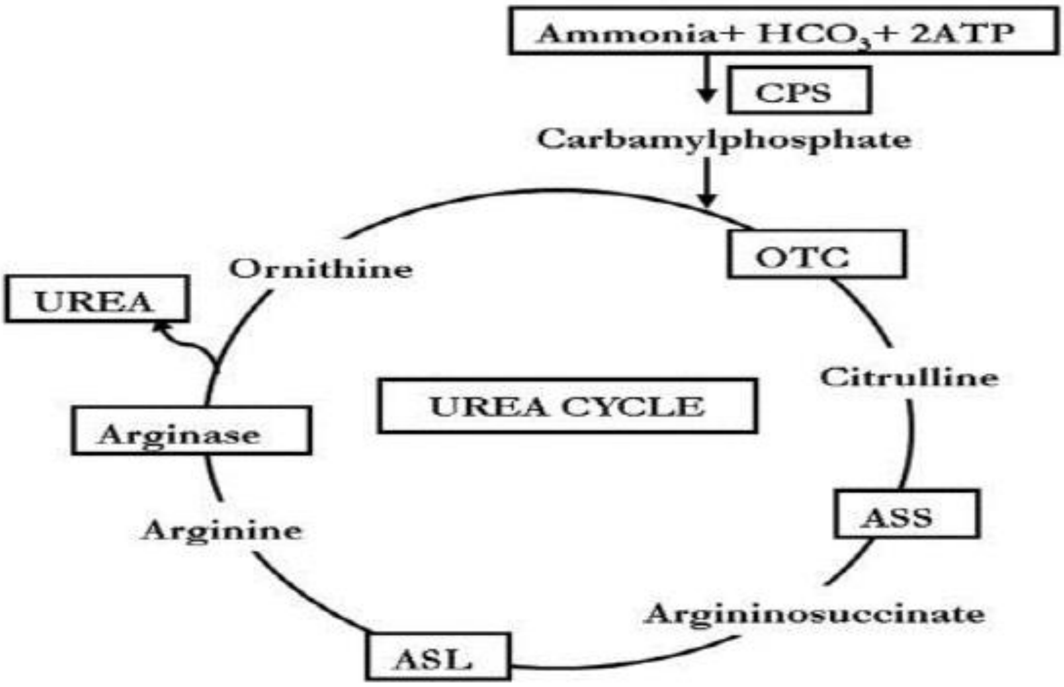
Summary:

Transamination takes off amine groups from amino acids and forms **glutamate**
(ionized glutamic acid)

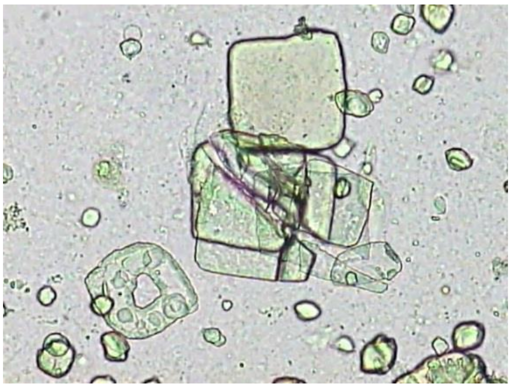
Amine groups form **ammonia** when removed in **deamination**
This combines with **CO_2** & **Aspartate**.

Forms **urea**, **Arginine**,
& **Fumarate**

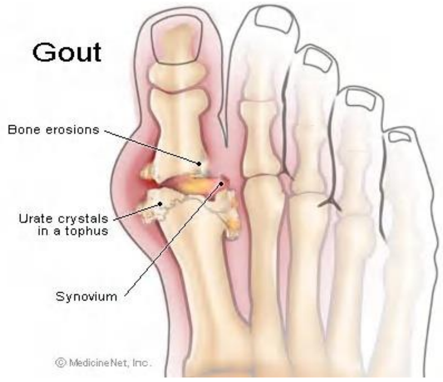




Reptiles & birds excrete **uric acid** – very ***insoluble*** purine compound – forms supersaturated solutions. Concentrated urine, supersaturated with uric acid, goes from cloaca into hindgut – uric acid crystalizes & water is reabsorbed.



In humans uric acid deposits crystals & causes gout



Processing Amino Acid Carbon Skeletons

Transamination or Oxidative deamination both produce a-keto acids

Degradation of these carbon skeletons may take several different pathways:

Amino acid C skeletons that degrade to form a Krebs cycle intermediate can then be used to make glucose via **gluconeogenesis**.

These are called **Glucogenic Amino Acids**.

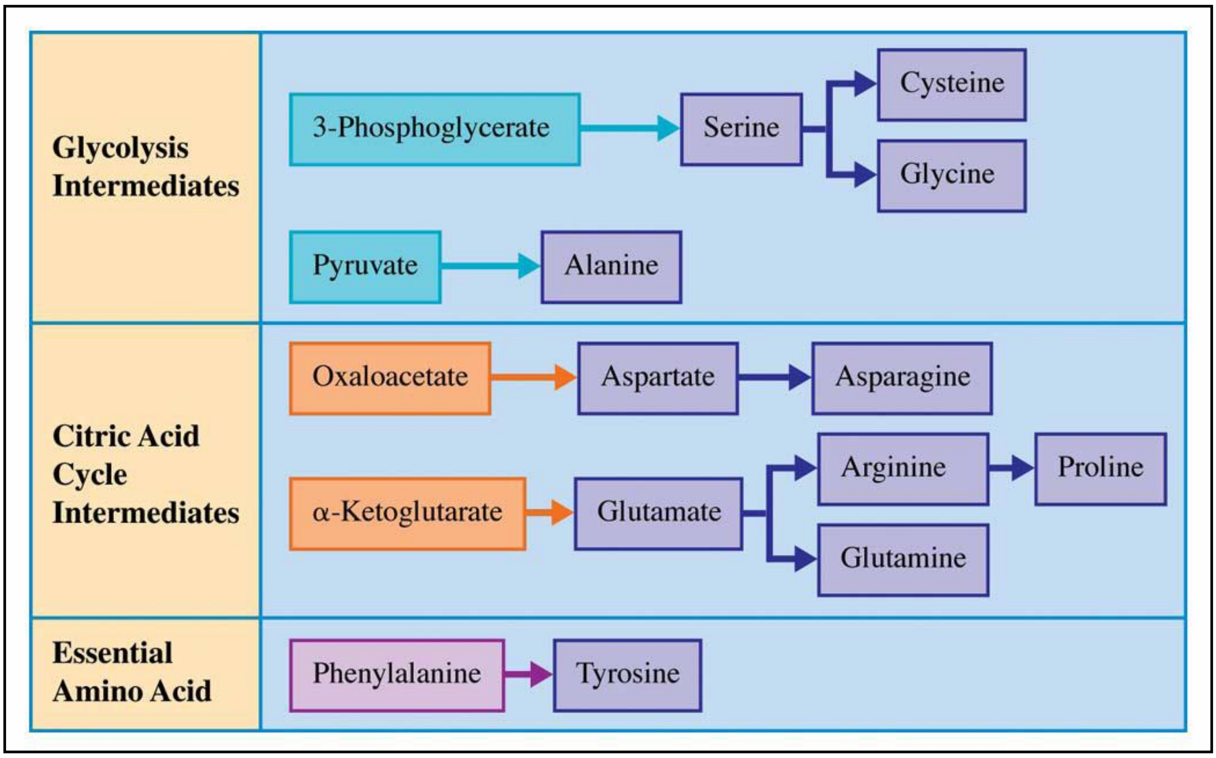
Amino acid C skeletons that degrade to form **acetyl CoA** or **Acetoacetyl CoA** can form fatty acids or ketone bodies.

These are called **Ketogenic Amino Acids**.

Amino Acid Biosynthesis

Essential amino acids can be made by plants & bacteria in 7 to 10 steps. We obtain these amino acids by eating plants.11 Non-essential amino acids synthesized in 1 to 3 steps. Use glycolysis intermediates: **3-phosphoglycerate** & pyruvate Krebs cycle intermediates: **Oxaloacetate** & **a-ketoglutarate**.

Starting materials for biosynthesis of 11 **nonessential** amino acids: 1 step, 2 steps, or 3 steps



Alanine, aspartate, & glutamate use transamination

Phenylketonuria (PKU):

Defective phenylalanine hydroxylase – **phenylalanine** accumulates in body. Phenylalanine is transaminated to **phenylpyruvate**.

Accumulation of phenylpyruvate leads to severe mental retardation in infants. Persons suffering from phenylketonuria should not consume foods containing high levels of phenylalanine, such as aspartame.

Hemoglobin catabolism

Red blood cells contain oxygen carrying pigments of a conjugated protein: Protein part is ***Globin*** Non-protein prosthetic group is ***Heme***. **Heme** contains four pyrrole (**tetrapyrrole**) groups held together by an **iron** atom. Old red blood cells degraded in the spleen. Globin is hydrolyzed into amino acids. Iron atom stored in a protein (***ferritin***) **Tetrapyrrole** degraded to **bile pigments**.

Review: can you…

- Describe the steps in Protein digestion & absorption
- Explain how Amino Acids are utilized in the body
- Explain **Transamination** and **Oxidative De-amination**
- Describe **The Urea Cycle** – purpose and steps
- Describe how a.a. Carbon Skeletons are processed
- Define and explain Amino Acid Biosynthesis.
- Describe the chemical composition of urine.

Lipid Metabolism

Fatty acids (F.A.s) are taken up by cells.

They may serve as:

- precursors in synthesis of other compounds
- fuels for energy production
- substrates for ketone body synthesis.

Ketone bodies may be exported to other tissues: used for **energy production**. Some cells **synthesize fatty acids** for storage or export.

Energy

Fats are an important source of calories. Typically 30-40% of calories in American diet are from **fat**. Fat is the major form of **energy storage**.

Typical body fuel *reserves* are:

fat:	**100,000 kcal.**
protein:	**25,000 kcal**.
carbohydrate:	**650 kcal.**

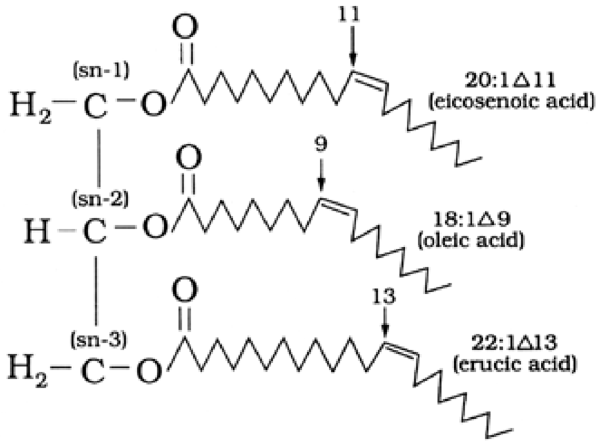
Provides 60% of energy needs for body at restTAG reserves would enable someone to survive starvation for ~30 days.

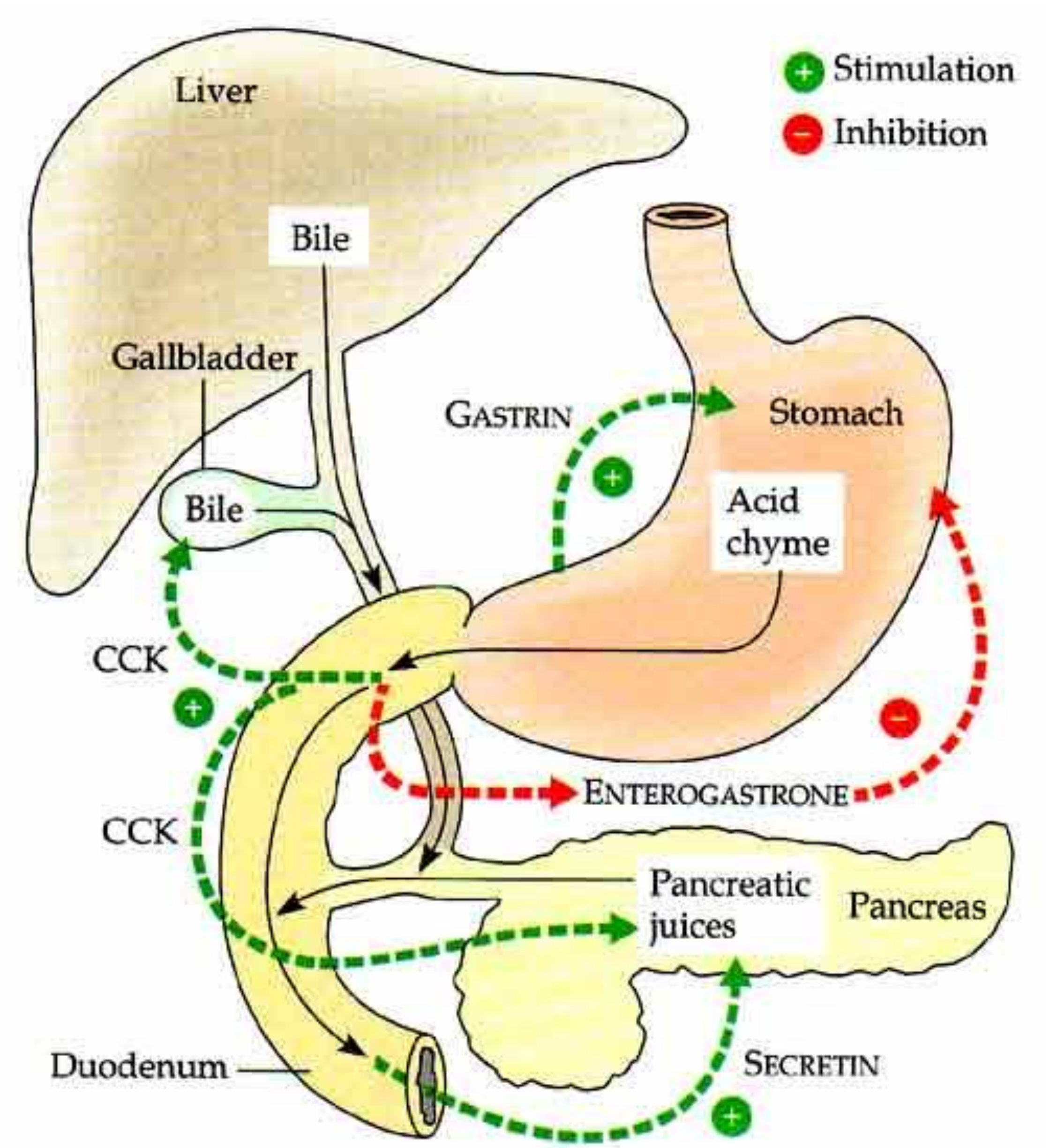
Digestion and Absorption of Lipids

- 98% of ingested lipids are triacylglycerols (TAGs)
- Digestion in the Mouth: enzymes are **aqueous**-little effect on lipids
- Digestion in the Stomach:causes a large ***physical*** change- Churned into droplets:

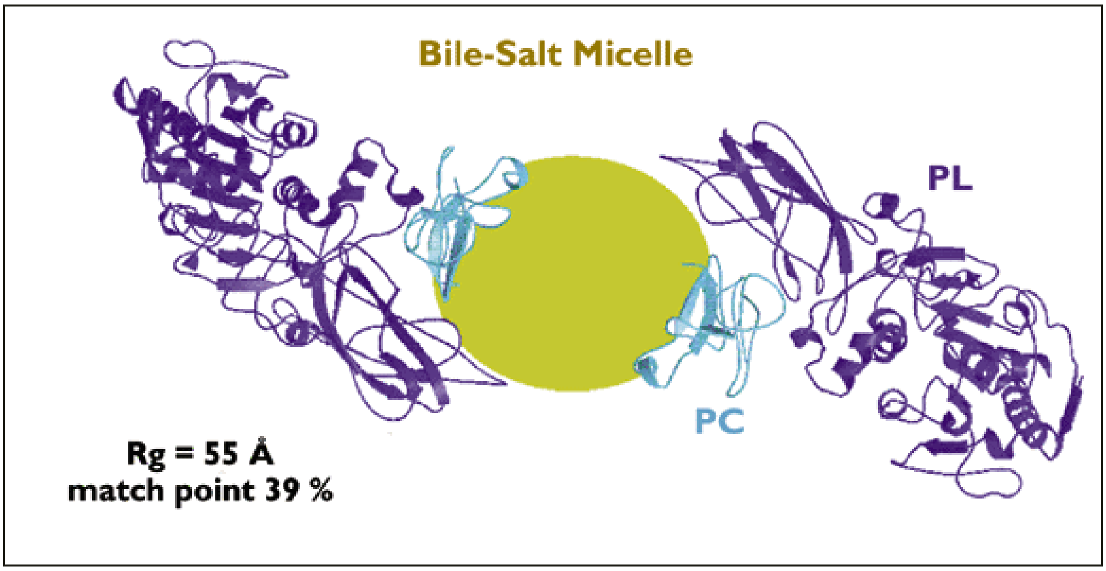
  “Chyme”

TRIACYLGLYCEROL



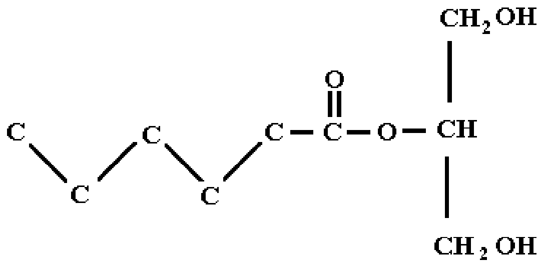


Gastric Lipase: Begins actual lipid digestion.~10% of TAGs are hydrolyzed in the **stomach**.Chyme stimulates **cholecystokinin** (CCK) to release **bile** from gallbladder.Bile is an emulsifier

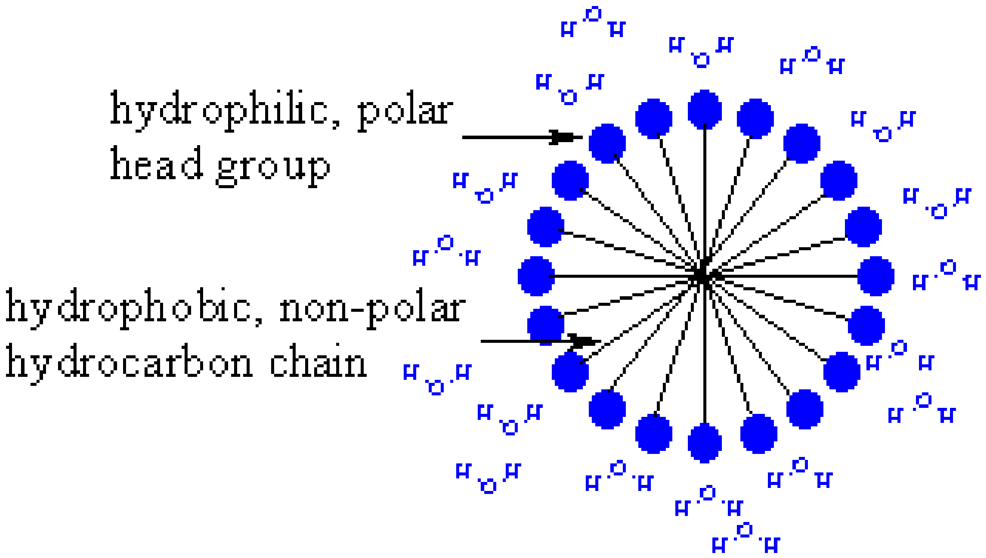


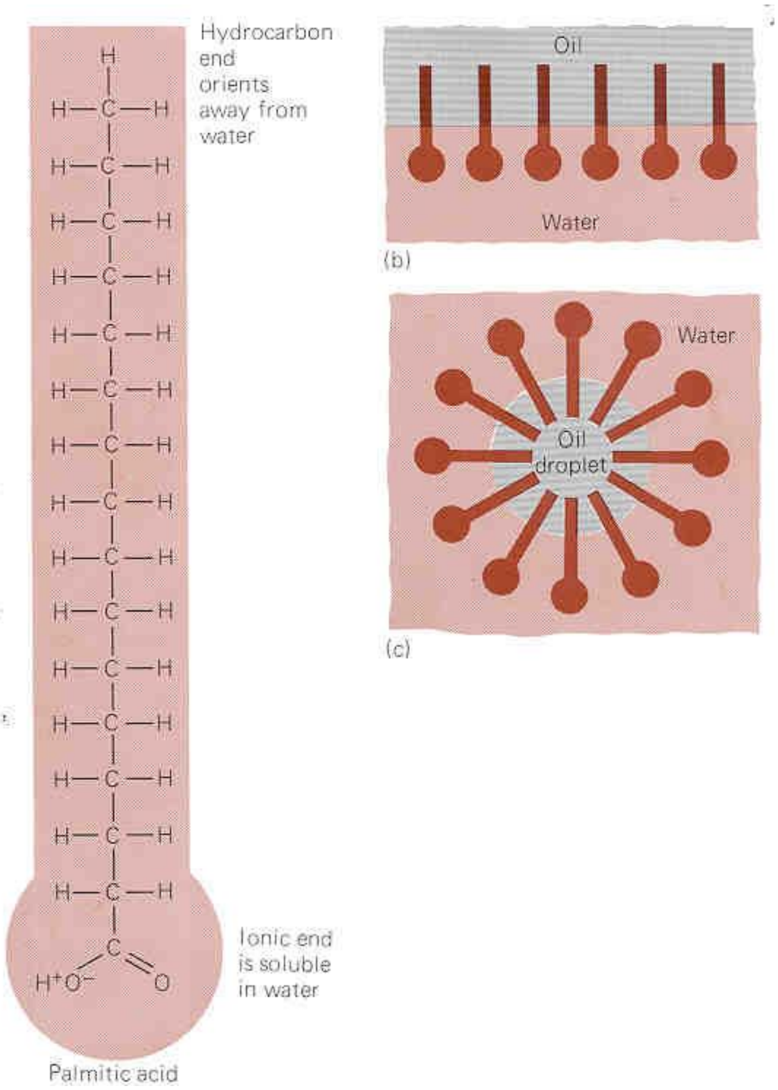
Pancreatic lipase (PL) hydrolyzes insoluble triglyceride by binding to the **bile-salt micelles**TAGs are ***partially*** hydrolyzed: 2 of the 3 F.A.s have ester linkages hydrolyzed and are released.

Monoacylglycerol remains = glycerol and 1 fatty acid



Oil droplets will form spherical **micelle** shapes.Bile salts aid this process clumping fatty acids and monacylglycerols.

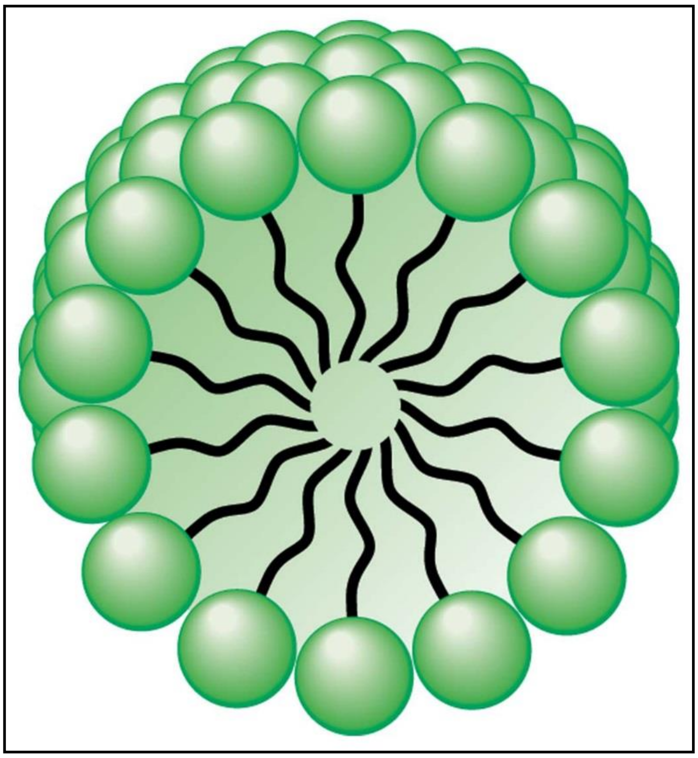

hydrophilic, polar head group
hydrophobic, non-polar hydrocarbon chain
H O H


Hydrocarbon end orients away from water
H
H—C—H
H⁺O⁻
C
O
Ionic end is soluble in water
Palmitic acid
Oil
Water
(b)
Water
Oil droplet
(c)

Fatty acid micelle: **hydrophobic** fatty acids & monoacylglycerols are in the interior. Bile salts on exterior.

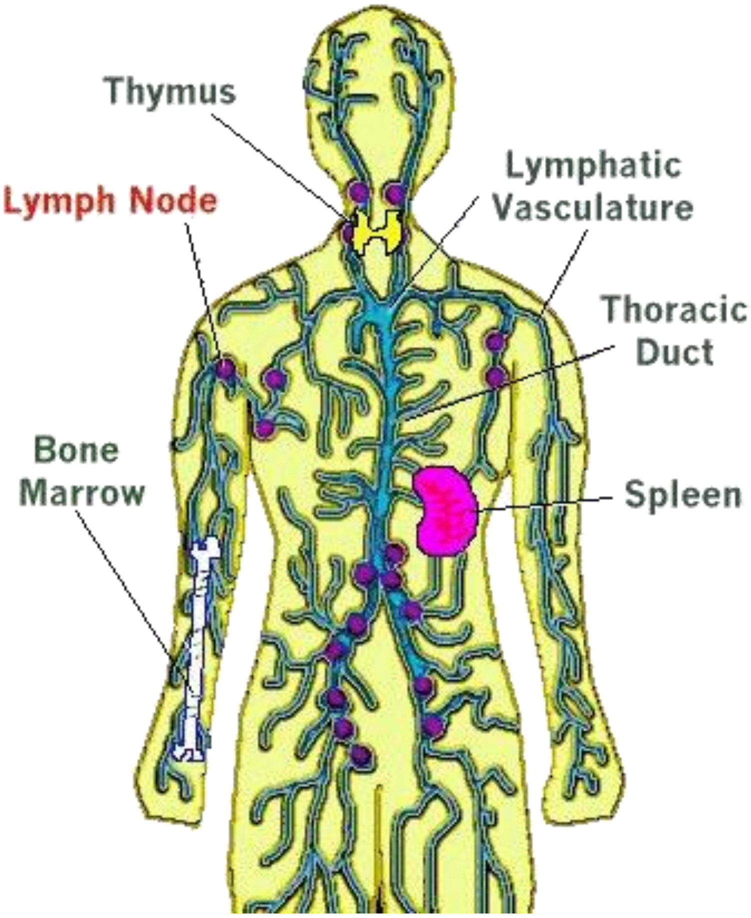
Micelles are small enough to penetrate membrane of intestinal cells. Free fatty acids & monoacylglycerols are reformed into

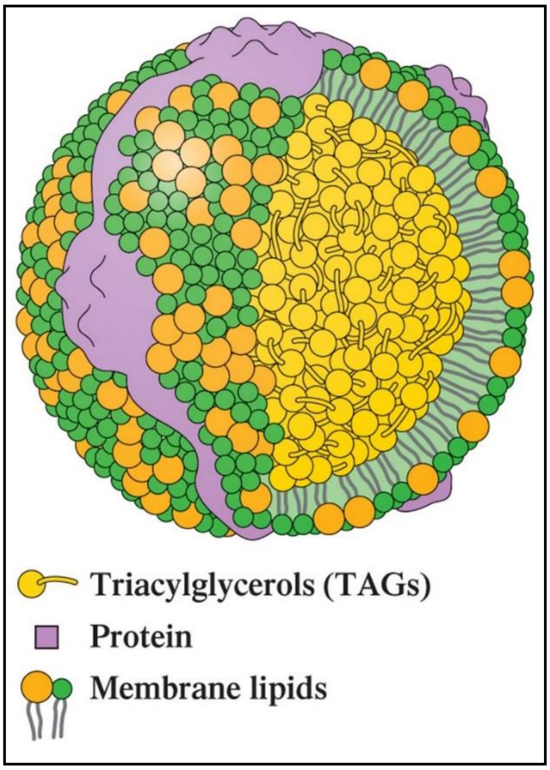
triacylglycerols.



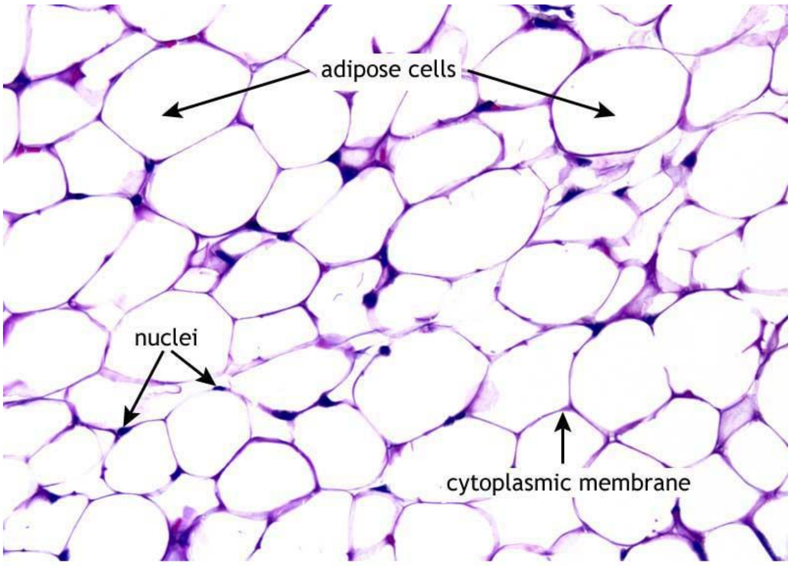
TAGs are combined with membrane & water soluble proteins to form a **chylomicron**, a lipoprotein.

Chylomicrons carry TAGs from intestinal cells into bloodstream via the **lymph system**.


Thymus
Lymph Node
Lymphatic Vasculature
Thoracic Duct
Bone Marrow
Spleen


Triacylglycerols (TAGs)
Protein
Membrane lipids

Triacylglycerols reach bloodstream & are hydrolyzed down to **glycerol** and **fatty acids**.These are absorbed by cells and processed further for energy by forming **acetyl CoA**. Or Stored as lipids in fat cells (adipose tissue.



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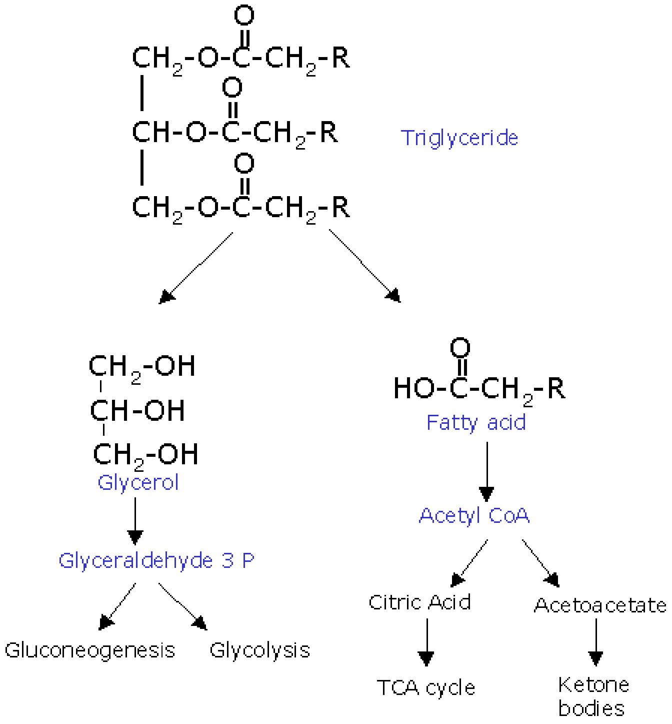
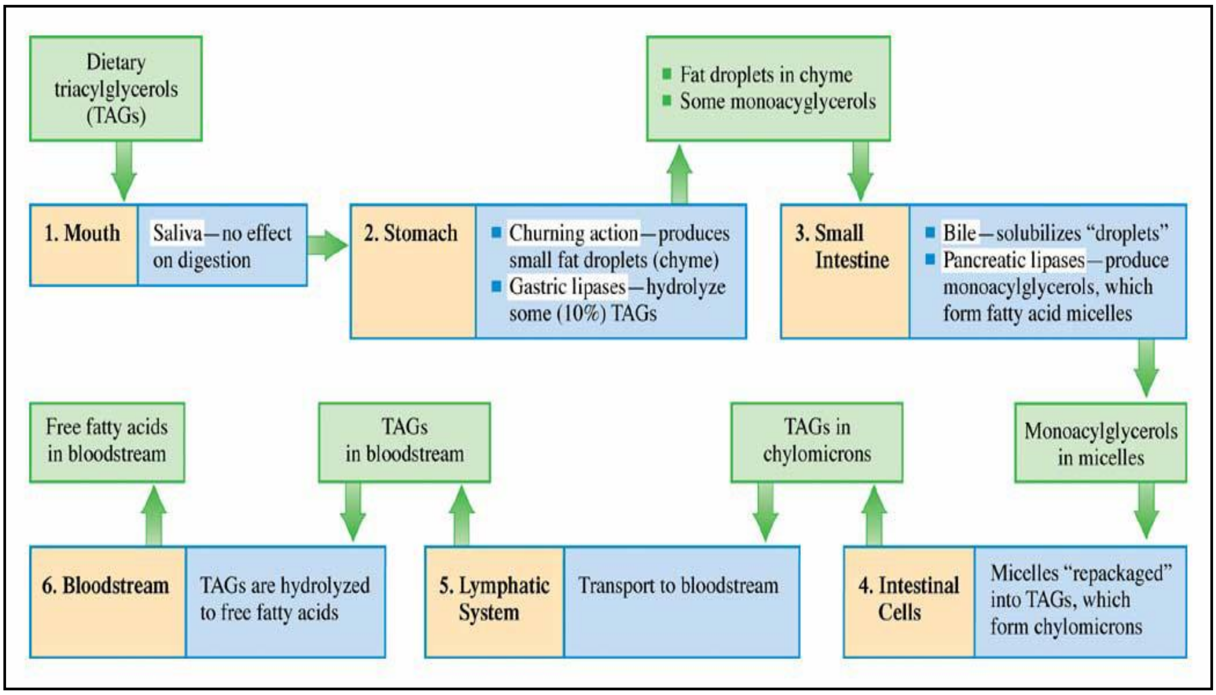
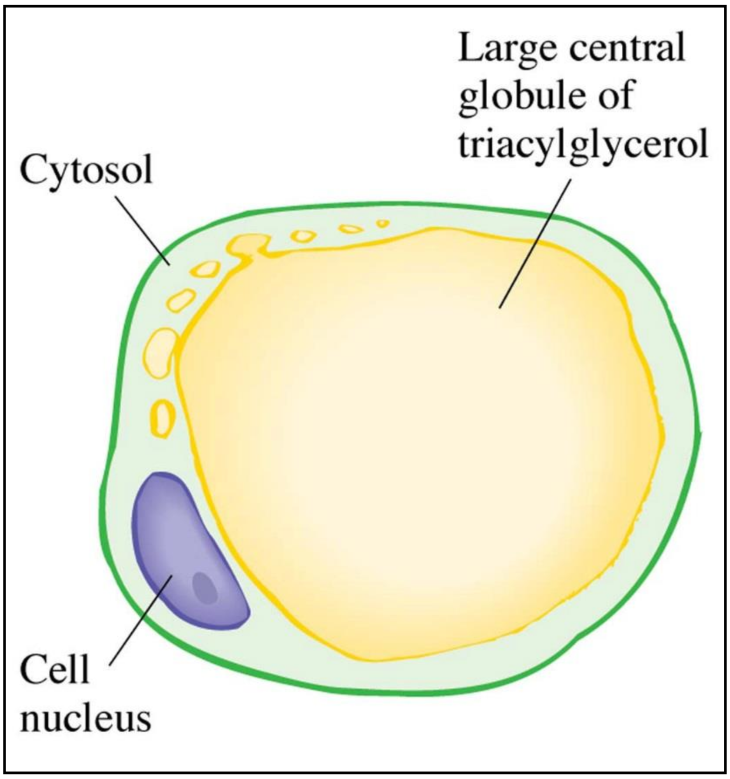


Summary of events that must occur before triacyglycerols (TAGs) can reach the bloodstream through the digestive process.



Triglyceride Storage & Mobilization

Storage of triacylglycerol is in **adipocytes** Fatty acids stored primarily as triacylglycerol.Triacylglycerol is **hydrolyzed** to release **fatty acids** when needed.



Hormonal control of lipolysis

The breakdown of triglycerides by lipases is under hormonal control.

Hormones involved are:

Epinephrine, glucagon, and insulin.

Epinephrine & glucagon:

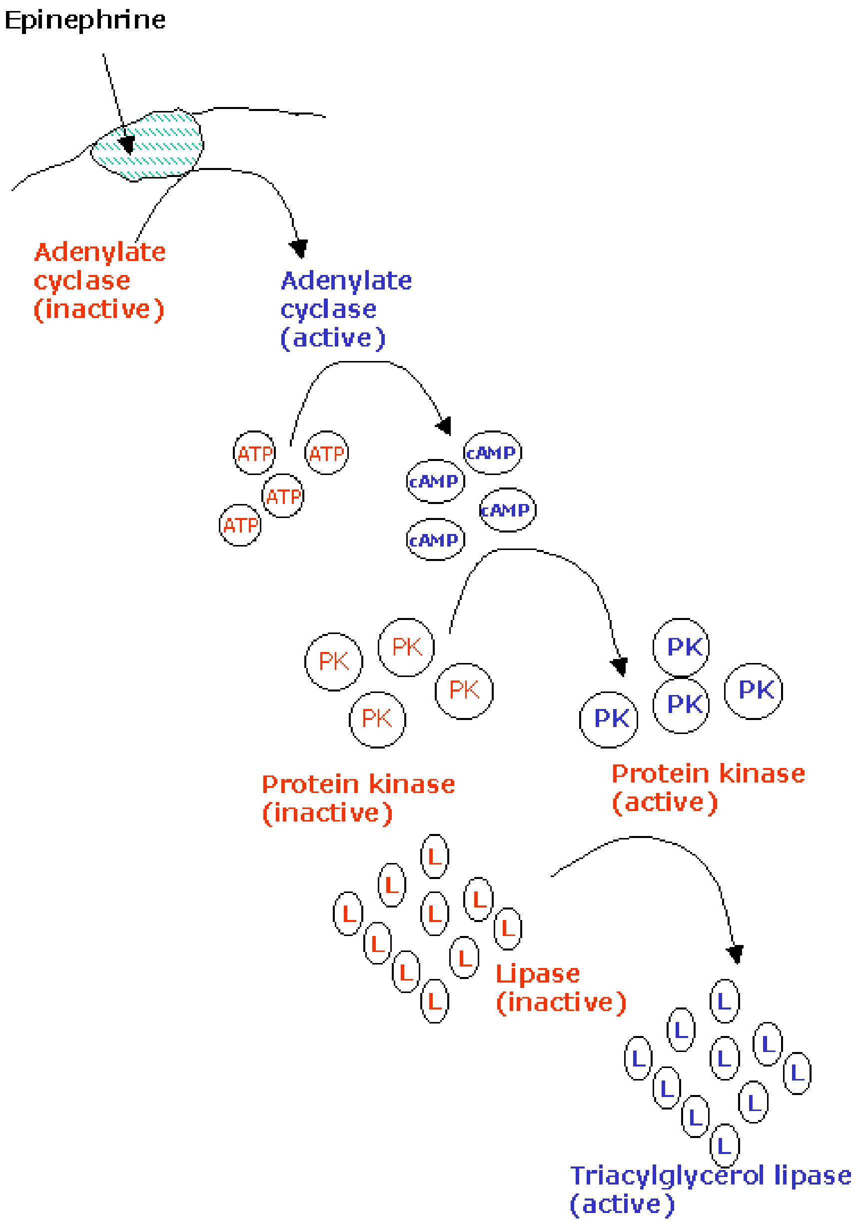
promote breakdown of fat (lipolysis)

Insulin:

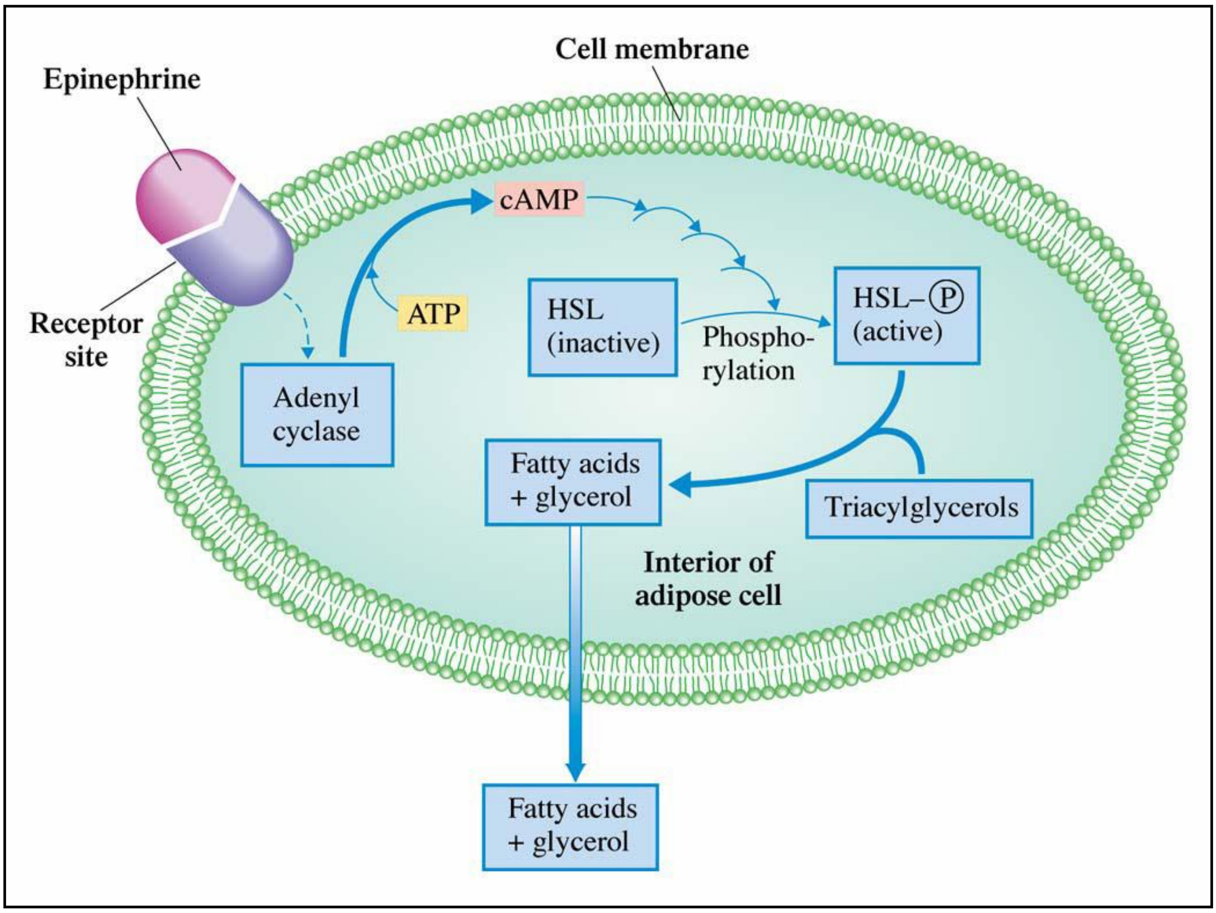
inhibits lipolysis.

Triacylglycerol Mobilization:

Hydrolyzing lipid reserves in adipose tissue for **energy**.Triggered by hormones~10% TAGs replaced in adipose tissue daily as they get used up for energy.



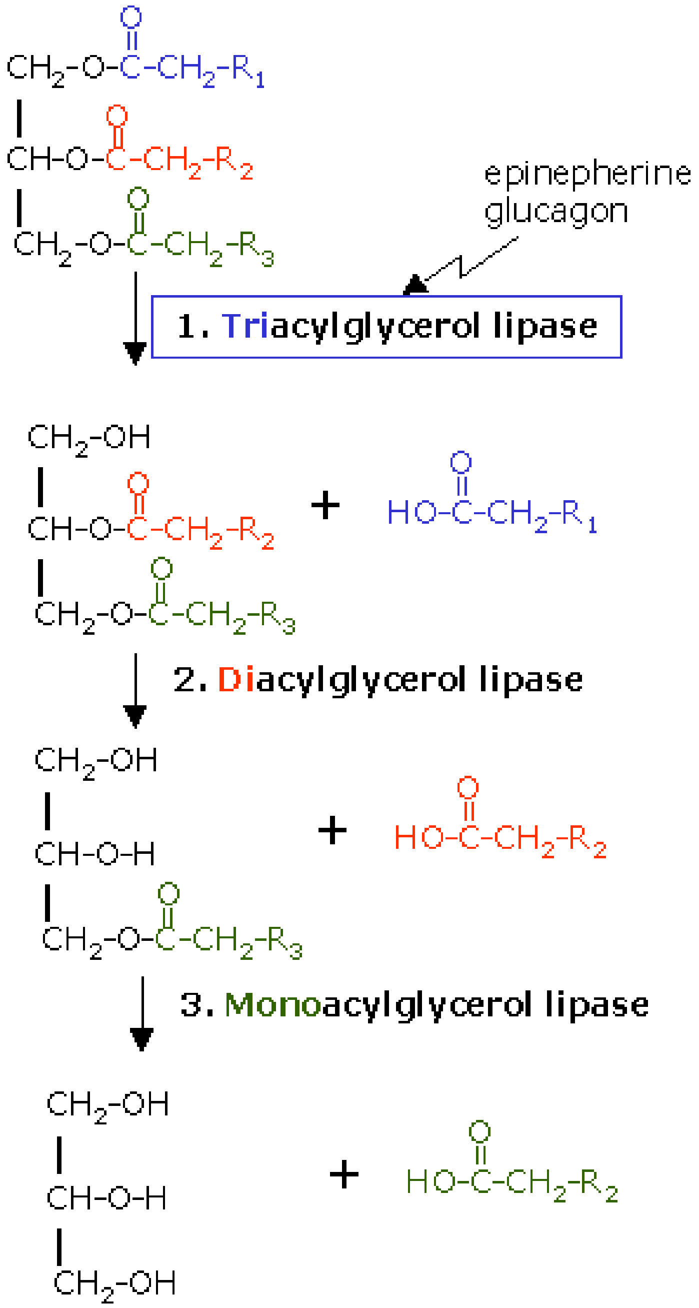
Hydrolysis of stored triacylglycerols in adipose tissue is triggered by hormones that stimulate cAMP production within adipose cells.



Third time is a charm! TAGs hydrolyzed a 3rd time to form fatty acids.

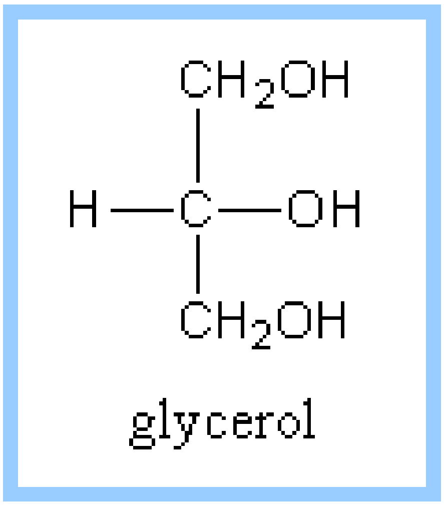
Triacylglycerol lipase **Di**acyclglycerol lipase **Mono**acylglycerol lipase

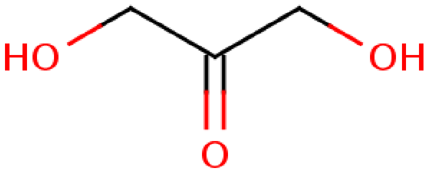
Only triacylglycerol lipase is activated by epinephrine.



One glycerol formed for each TAG hydrolyzed. Enter bloodstream & go to liver or kidneys for processing. Converted in 2 steps to

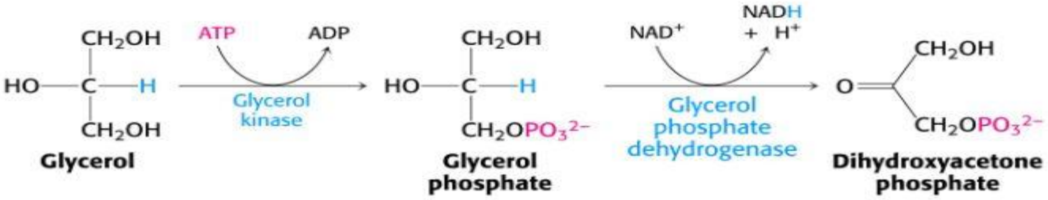
Dihydroxyacetone phosphate





Where will the phosphate be attached?

Uses up one ATP.Reduces one NAD$^+$ to NADH



Primary hydroxyl group is phosphorylated
Dihydroxyacetone phosphate
is an intermediate for both

Glycolysis:
converted to Pyruvate, then to Acetyl CoA, & eventually to CO$_2$,

releasing its energy.

Gluconeogenesis:

creates Glucose from **non-carbohydrate** source

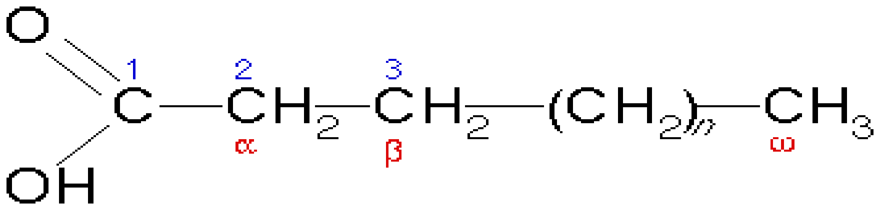
Lipid metabolism & carbohydrate metabolism

are connected.

Fatty acids can also be broken down for energy. What kind of reaction is needed?

Oxidation!

Quick review first on fatty acid numbers & letters:



Fatty acid numbering system

Review Important fatty acids:

Name	# Carbons: (saturation)
Palmitate	16:0
Stearate	18:0
Palmitoleate	16:1 - cis at C9
Oleate	18:1 - cis at C9
Linoleate	18:2 - cis at C9 and C12
Linolenate	18:3 - cis at C9, C12 & C15

Lipid Metabolism

Lipid nomenclature

- Oxidation of Fatty acids
- β-oxidation
- Ketone Bodies

Lipid nomenclature

Fatty acids

- triacylglycerols: know structure
- phospholipids
- waxes
- sphingolipids
- Glycosphingolipids
- Isoprenoids
- Steriods
- Nomenclature
- saturated: palmitate, stearate, no double bonds
- unsaturated: palmitoleate, Oleate: double bond at cis9 position
- polyunsaturated
- Melting points: saturated vsunsaturated

Oxidation of Fatty acids

- Know equation for palmitate: $C_{16}H_{32}O + O_2 \text{ ---> } CO_2 + H_2O$
- Comparison of glucose with palmitatefor ATP production and energy yield
- Mobilization of Triacylglycerols from adipose tissue

–hormonal control: glucagon, epinephrine

–lipases

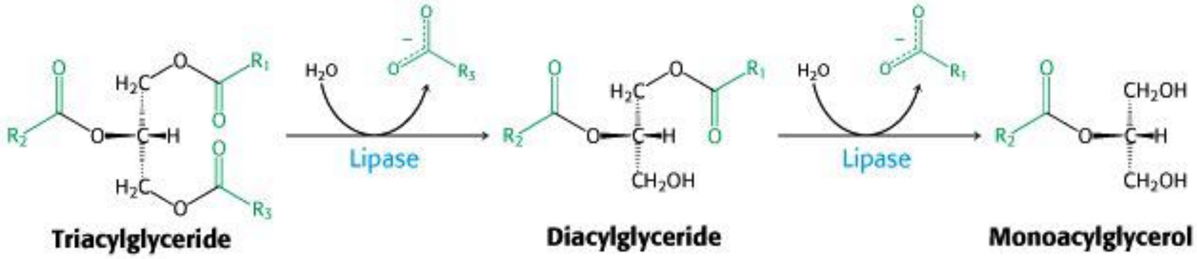
–transport by lipoproteins

–fate of glycerol

•transport into cytoplasm of cell

Digestion of lipid in diet

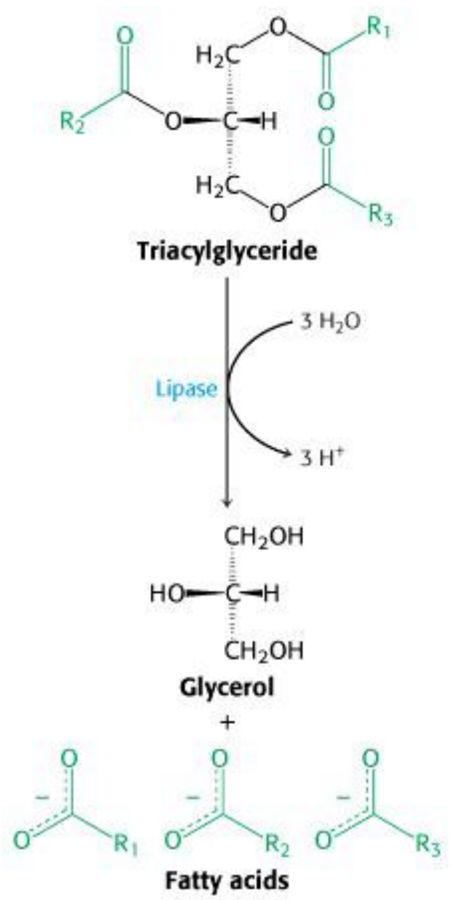
- Triacylglycerolsfrom diet
- broken down in small intestine
- lipases
- bile salts
- transport to adipose tissue

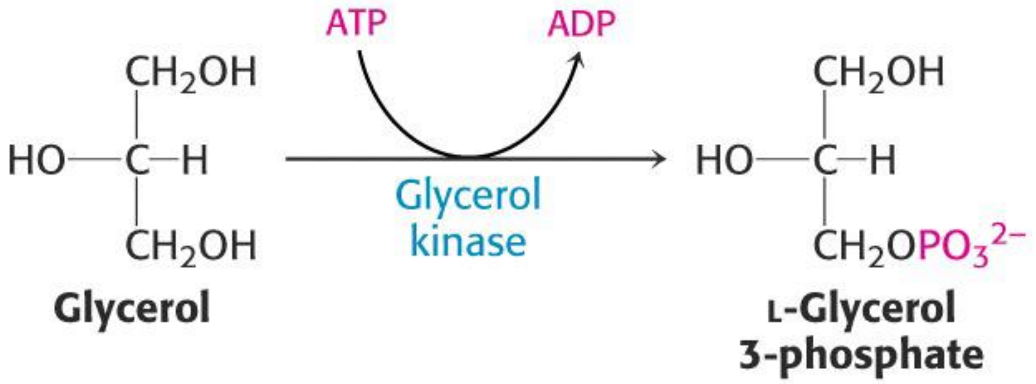


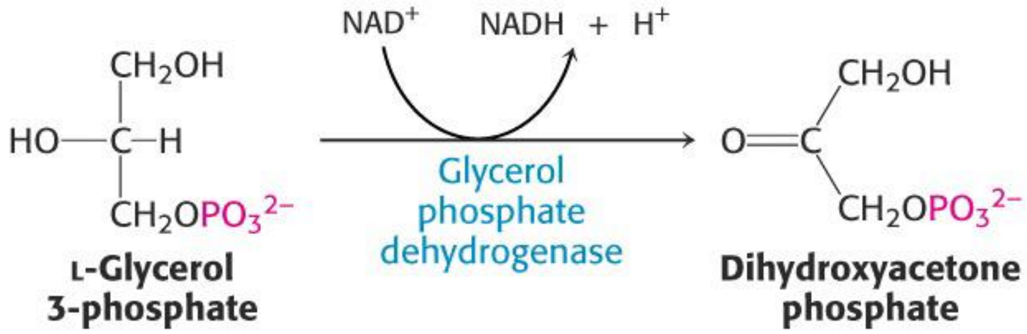
Mobilization of Triacylglycerols

–hormonal control of lipolysis: glucagon, epinephrine
–lipases
–transport by lipoproteins
–transport into cytoplasm of cell
–Insulin inhibits lipolysis

Breakdown of triacylglycerides



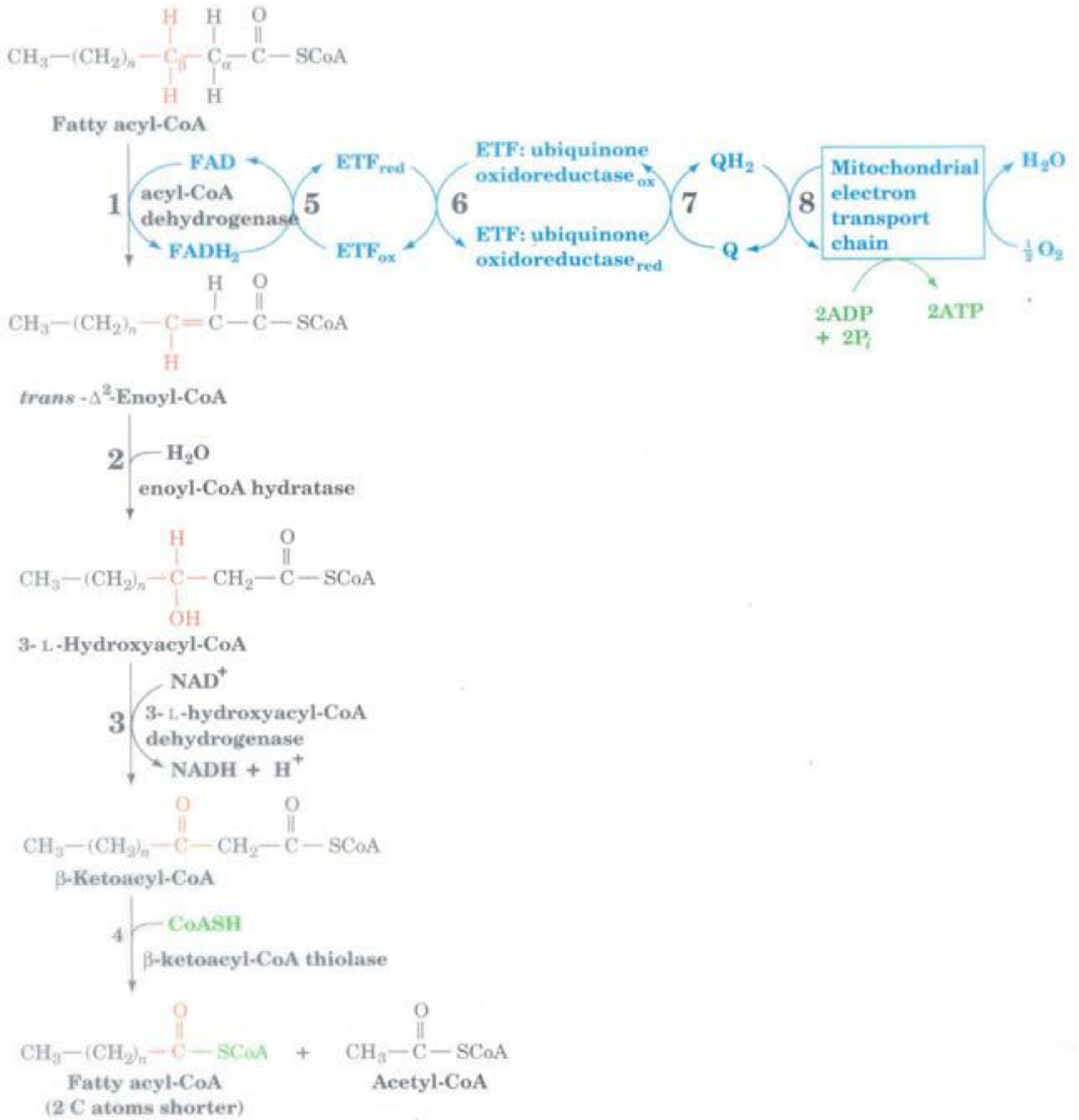




fate of glycerol

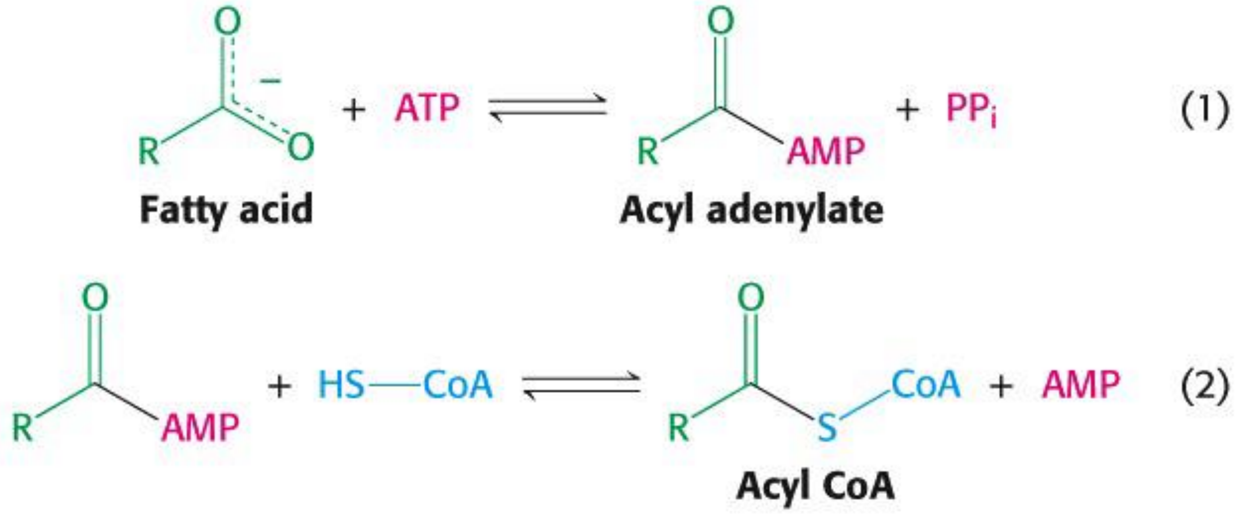
β-oxidation

- occurs in mitochondria
- uses FAD and NAD
- produces acetyl CoA



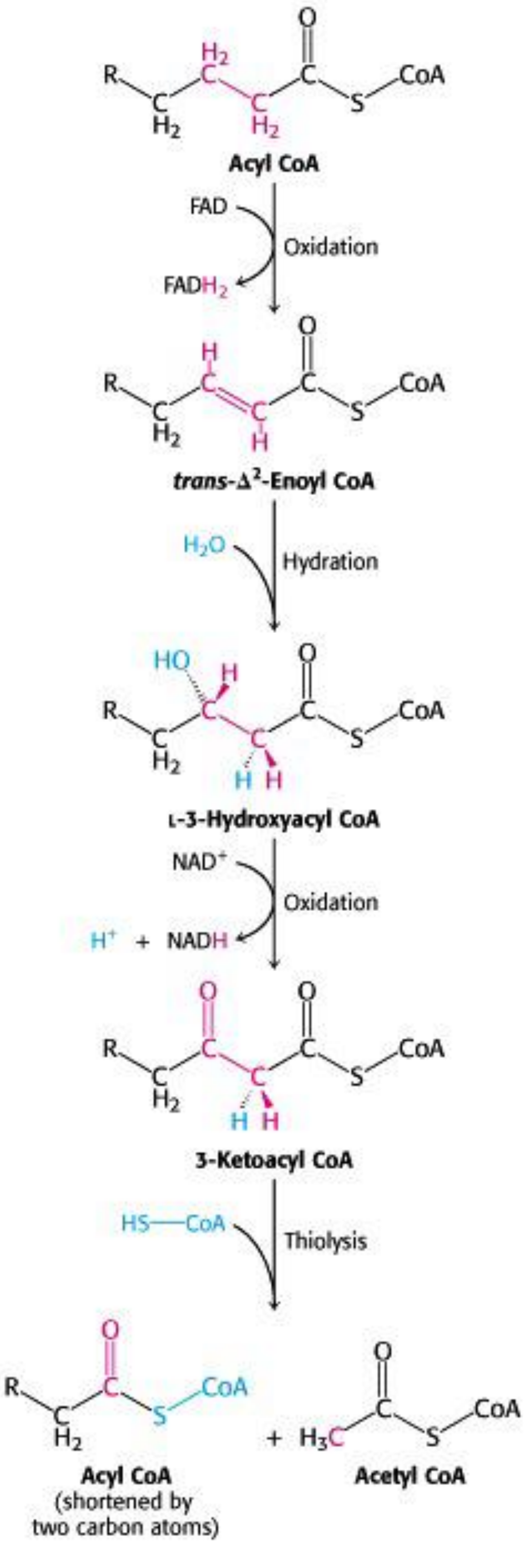
acylCoA synthetase

- two step reaction
- ATP + FA ---> AMP-FA
- AMP-FA + CoASH------> FA-CoA + AMP



β-oxidation

AcylCoA dehydrogenase
- enoyl-CoA hydratase
- L-hydroxyacyldehydrogenase
- ketoacyl-CoA thiolase
- Repeat steps



Summary of Reactions

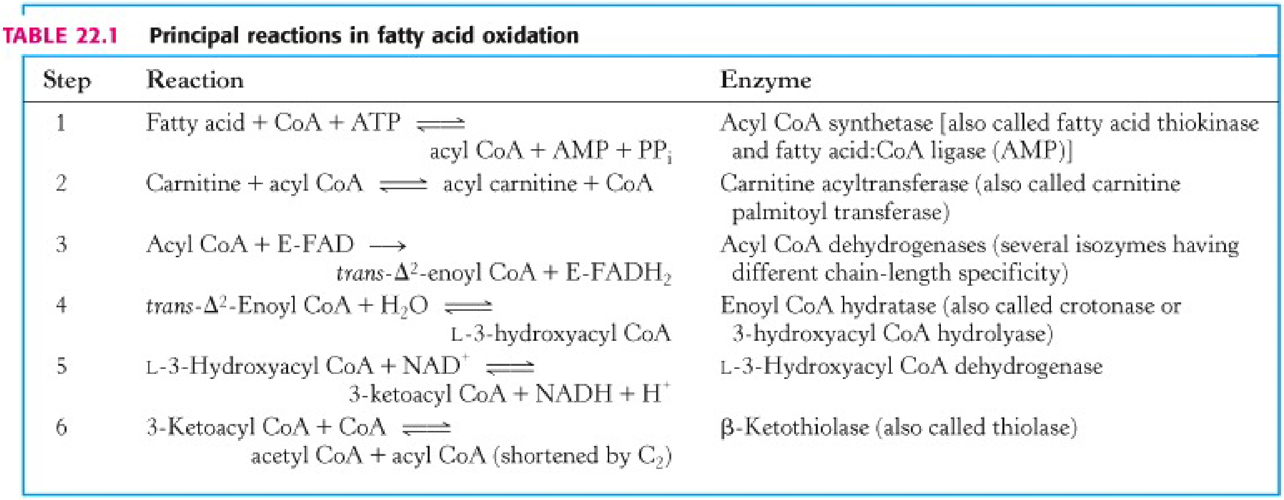


TABLE 22.1 **Principal reactions in fatty acid oxidation**

Step	Reaction	Enzyme
1	Fatty acid + CoA + ATP $\rightleftharpoons$ acyl CoA + AMP + PP_i	Acyl CoA synthetase [also called fatty acid thiokinase and fatty acid:CoA ligase (AMP)]
2	Carnitine + acyl CoA $\rightleftharpoons$ acyl carnitine + CoA	Carnitine acyltransferase (also called carnitine palmitoyl transferase)
3	Acyl CoA + E-FAD $\rightarrow$ *trans*-Δ^2-enoyl CoA + E-$FADH_2$	Acyl CoA dehydrogenases (several isozymes having different chain-length specificity)
4	*trans*-Δ^2-Enoyl CoA + H_2O $\rightleftharpoons$ L-3-hydroxyacyl CoA	Enoyl CoA hydratase (also called crotonase or 3-hydroxyacyl CoA hydrolyase)
5	L-3-Hydroxyacyl CoA + NAD^+ $\rightleftharpoons$ 3-ketoacyl CoA + NADH + H^+	L-3-Hydroxyacyl CoA dehydrogenase
6	3-Ketoacyl CoA + CoA $\rightleftharpoons$ acetyl CoA + acyl CoA (shortened by C_2)	β-Ketothiolase (also called thiolase)

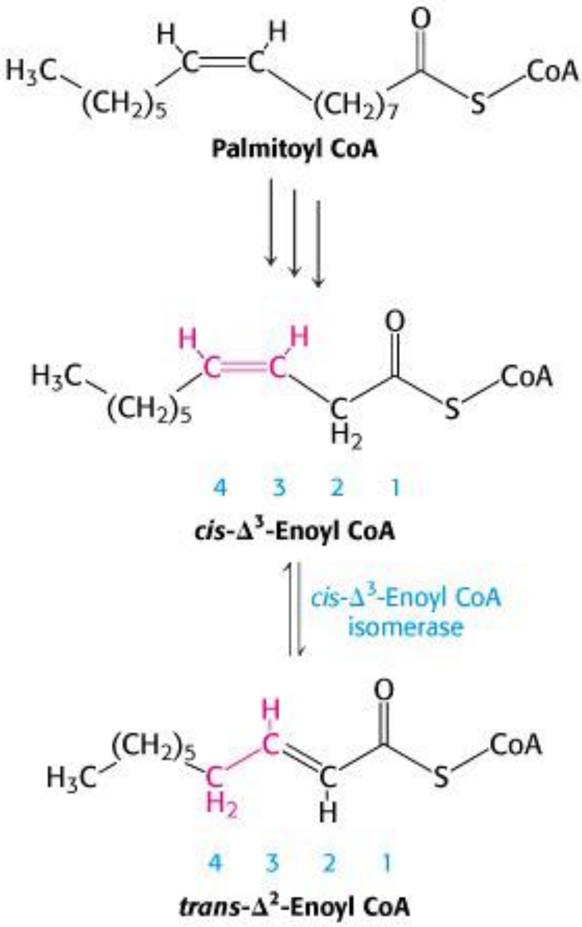
Energy production

•NADH and FADH from B-oxidation

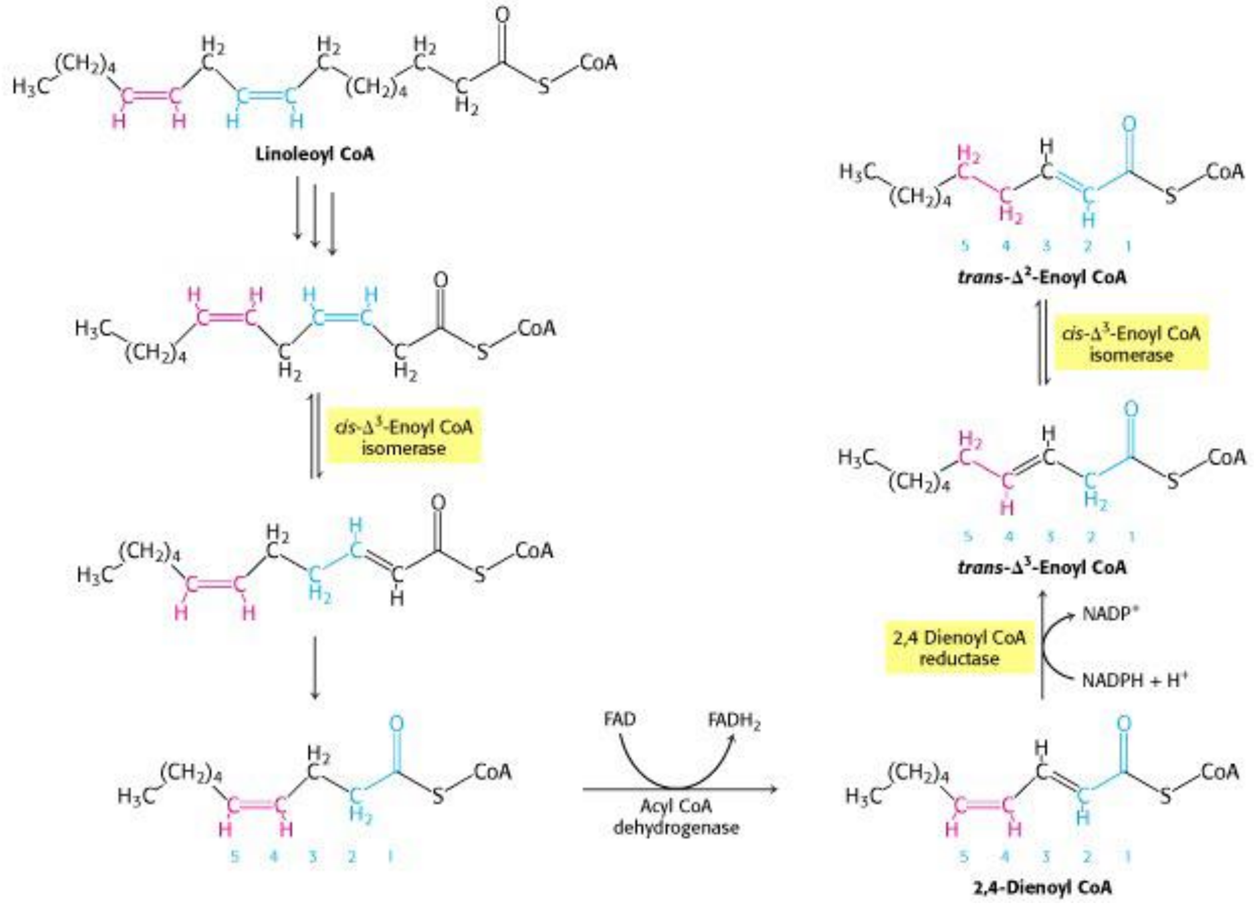
•TCA cycle from acetyl CoA

•Total net yield is minus 2 ATP from activation

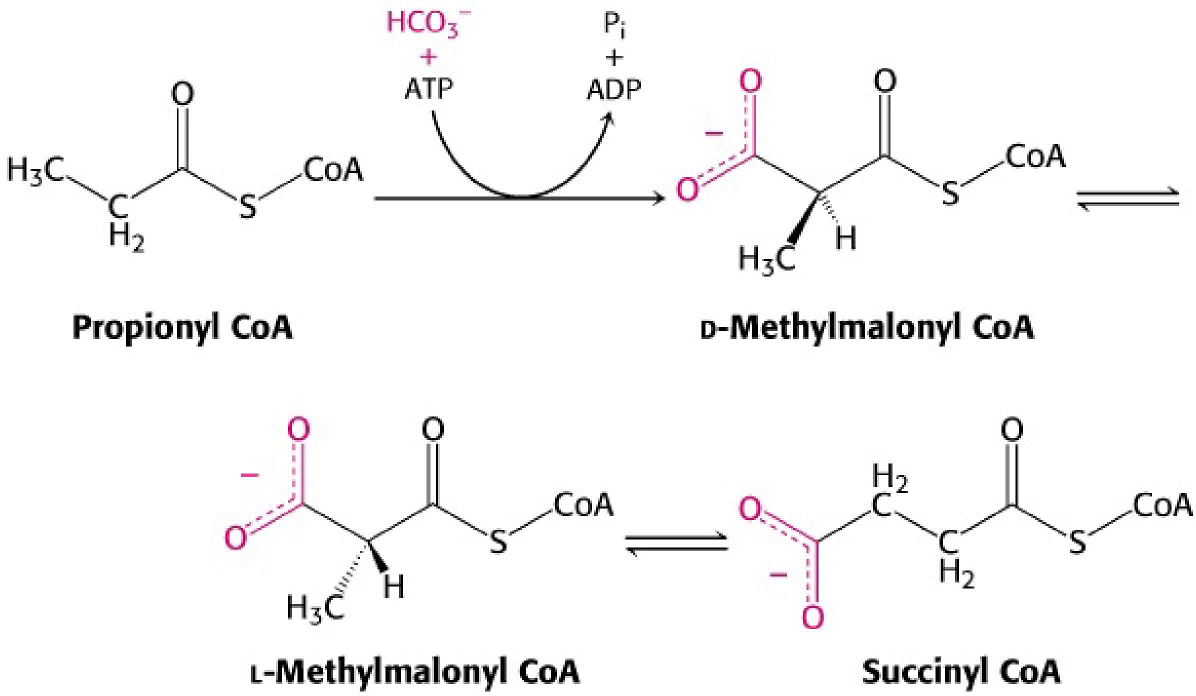
Oxidation of Unsaturated Fatty acids



Unsaturated Fatty acids

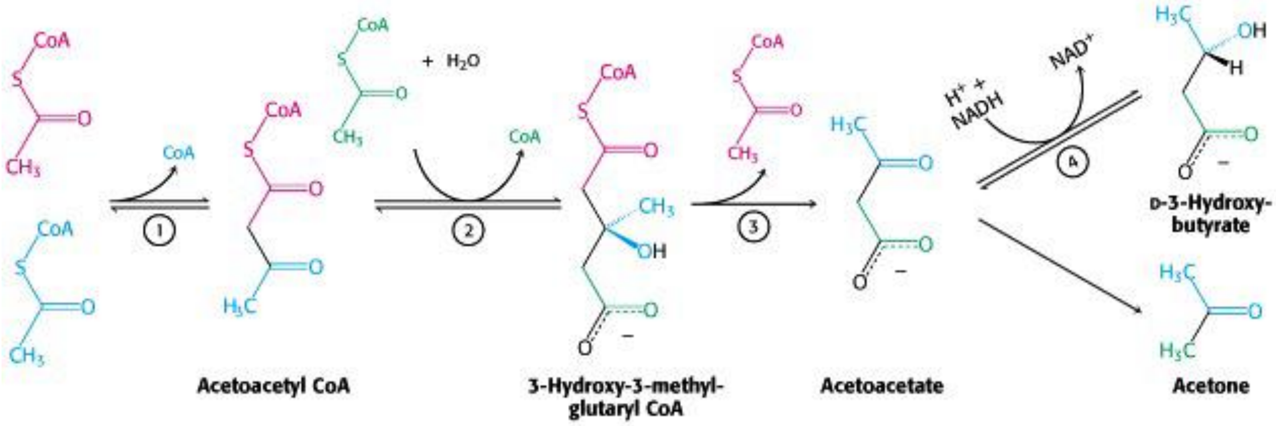


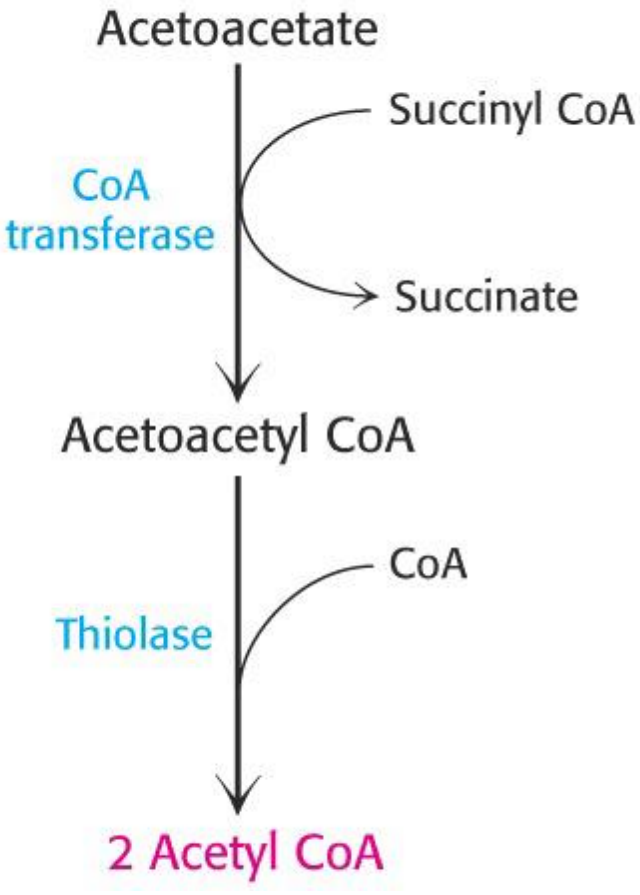
Oxidation of odd chain fatty acids



- form propionylCoA
- produce succinylCoA

Ketone Bodies





- Acetoacetate
- Acetone
- B-hyroxybutyrate
- HMG CoA synthase

Referances

Available online
1-BIOCHEMISTRY IN PERSPECTIVE

2-METABOLISM OF CARBOHYDRATES, LIPIDS, PROTEINS AND NUCLEIC ACIDS, Course Team

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Organic and Inorganic Chemistry

Part 2: Inorganic Chemistry

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References:

1- Vogel's Textbook of Quantitative Chemical Analysis, Arthur Vogel and John Mendham, Pearson, 6th Edition, 1 January 2000.

2- Principles of Inorganic Chemistry, Brian W. Pfennig, Wiley, 2015.

INORGANIC CHEMISTRY

THE MAIN GROUP ELEMENTS

Introduction:

Inorganic chemistry has often been said to comprise a vast collection of untreatable facts. It deals with many compounds formed by many elements. It involves the study of the chemistry of more liquids or solids whose reactions may be or may have to be studied at very low or very high temperatures.

Although various concepts help to bring order and system into inorganic chemistry, the oldest and still the most meaningful relies on the periodic table of the elements. It depends on the electron structures of the gaseous atoms of different elements, where a pattern of electronic structures of the elements was built by successively adding electrons to the available energy levels. However, the periodic table can also be based entirely on the chemical properties of the elements and so it gives us a good knowledge for chemical facts.

The nature and types of the elements :

It is self evident that the chemical properties of an element must depend on the electronic structure of the atom.

This determines not only how the elements can bind to other elements but also to their selves thus hydrogen (l s) can clearly only from a diatomic molecule. Briefly, elements divided into:

Monatomic elements : e.g. , noble gases (He , Ne, Ar,Kre, Xe ,Rn) and vapor mercury.

Diatomic molecules: H_2, N_2, O_2, F_2, Cl_2, Br_2 , I_2 for single electron-pair bond in a diatomic molecule completes the octet. For nitrogen $2S^2$ $2P^2$ $2P^3$

and oxygen $2S^2$ $2P^4$ multiple bonding can give simple diatomic molecule. Also P_2 and S_2 are stable at elevated temperatures, but not at 25Cº.

<u>Polyatomic molecules</u>: P_4, Sn,Se_8, in which the P-P bonding of the type found in N_2 and O_2 is less effective. White phosphorus has tetrahedral molecules. Sulfur has a profusion of allotropes; these contain multy atom sulfur rings. The largest ring known is S_{20}, but the most stable form is orthorhombic sulfur.

With respect to certain properties elements are divided into metals and nonmetals.

<u>Metals</u>:

The majority of the elements are metals. These have many physical properties different from other solids: notably

1- high reflectivity.

2- high electrical conductance decrease with increasing temperature.

3- high thermal conductance.

4- mechanical properties such as strength and ductility.

There are three basic metal structures: cubic hexagonal close packed and body-centered cubic

With respect to chemical properties we see that metals are highly electropositive (giving positive ions), consequently they have basic character and can be used as reducing agents.

<u>Nonmetals</u> :

Elements have tendency to accept electrons and form negative ions are known as nonmetals. They have acidic character and can be used as oxidizing agents.

Elements which have properties between those of metals and nonmetals are known as semimetals or metalloids.

According to the electronic configuration of the atoms of the elements, they are divided into:

(a)<u>Non-transition elements</u>: which form the main group elements and we will discuss in details.

(b)<u>Transition elements</u>: which may be strictly defined as elements have partly filled d or f shells. We adopt a broader definition and include also elements that have partly filled d or f shells in compounds. So we treat the metals Cu, Ag and Au as transition metals. Since Cu (II) has a $3d^9$ configuration, Ag (II) has a $4d^9$ configuration, and Au (III) has a $5d^8$ configuration. This group of elements will be discussed in details in separate course.

<u>The chemistry of the main group elements in relation to their position in the periodic table:</u>

Now we can proceed to more detailed commentary on the chemical reactivity and types of compounds formed by the elements. The periodic table forms the basic for the discussion, starting with the simplest chemistry, namely that of hydrogen, and proceeding to the heaviest elements.

Hydrogen $1S^1$

Its chemistry depends on three electronic processes:

(1) Loss of the 1S valence electron to form the Proton H^+. The proton never exists as such except in gaseous ion beams. It is associated with other atoms or molecules and it found in water as H_3O^+ or $H(H_2O)_n^+$.

(2) Acquisition of an electron: The H atom can acquire an electron forming the hydride ion H^+ with the He; $1S^2$ structure. This on exists only in hydrides (The compounds produced as a result of combination of H^+ ion with electropositive metals are called hydrides, e.g. NaH, CaH_2).

(3) Formation of covalent bonds with nonmetals and even many metals, e.g. NH_3 , BH_3.

Helium $1S^2$ and the noble gases n S^2 np^6

It has the closed 1S shell. The physical properties of the other noble gases very systematically with size. Although the first ionization energies are high because of their inert character; the values decrease as the size of the atom increases and consequently the ability to inter into chemical combination with other atoms should increase.

Elements of the first short period :

The seven elements Li to F constitute the first members of the groups of elements. Li (z=3) has the structure $1S^2$,2S. With increasing z, electrons enter the 2S and 2P levels until the closed shell configuration $1S^2$ $2S^2$ $2P^6$ on neon is reached. These elements are in common with the elements of their respective groups in view of the similarity in the outer electronic structures of the gaseous atoms. The increase in nuclear charge and consequent changes in the extranculear structure result in extremes of physical and chemical properties: Li has low ionization enthalpy according to the facile loss of an electron to form Li^+ ion. This leads to high reactivity of Lithium toward oxygen nitrogen, water and many other elements. For Be, the first and second ionization enthalpies are high and

so the Be^{+2} ion does not occur, (in BeF^2 the Be-F bonds have covalent character) B ($2S^2$, $2P^1$) is bound covalently in all its compounds.

Anion formation first appears for carbon, which forms C^{2-}_2 and some other polyatomic ions. The existence of C^{4-} is uncertain. Carbon is a true nonmetal It can form single, double and triple bounds, and also it is able to form chains of carbon-carbon bonds.

Nitrogen compounds are covalent. With electro-repetitive elements, ionic nitrides containing N^{3-} may be formed .

Oxygen molecule has two unpaired electrons, and so it is very reactive. It forms covalent bond with many compounds (CO, SO_3,). Oxygenated ions O^{2-}, O_2^- , O^{2-}_2 are also exist.

Fluorine is extremely reactive due largely to the low bond energy in F_2. It forms ionic compounds containing F^- ions and covalent compounds, owing to the high electron negativity of fluorine.

The second short period

The elements Na, Mg, Al and Si ,P, S and Cl constitute the second short period. Their outer most shells are similar to those of the first short period, but the chemistries differ. In particular, the chemistries of Si , P , S and Cl. The main reason for this is; the heavier atoms would encounter large repulsive forces due to overlapping of their filled inner shells, whereas the small compact inner shell of the first-row elements, that is, just $1S^2$, does not produc this repulsion.

However, the second row elements give a better guide to the chemistries of the heavier elements in their respective groups than do the first row members.

Remainder of no transition elements

Group I : (Li , Na , K , Rb , Cs and Fr).

All the elements are highly electropositive giving +1 ions. These metals show most clearly the effect of increasing size ad mass on chemical properties. Thus as examples , the following decrease from Li to Cs:

(a) melting points and heat of sublimation of the metals.

(b) hydration energies.

(c) strength of covalent bonds in M_2 molecules.

Group II : Be, Mg, Ca, Sr, Ba and Ra

Calcium, Sr, Ba and Ra are also highly electropositive forming +2 ions. Systematic group trends are shown, for example, by increasing:

(a) hydration tendencies.

(b) insolubilities of sulfates.

(c) thermal stabilities of carbonates and nitrates.

Group III: B, Al, Ca, In and T1

Al has a considerable tendency to covalent bond formation, and the mainly ionic nature of the heavier elements. Gallium, In and T1 like Al are borderline between ionic and covalent in compounds, even thought the metals are quite electropositive and they form M^{+3} ions.

Group IV: C, Si, Ge, Sn and Pb

Carbon is nonmetallic; silicon is also nonmetallic but little of the chemistry of Si can be inferred from that of C. Germanium is much like silicon, although it shows more metallic-type behavior in its chemistry. Tin and lead are metals, and both have some metal lime chemistry especially in the divalent state.

The main chemistry in the IV oxidation state for all the elements is essentially one that involves covalent bonds and molecular compounds (e.g. Ge Cl_4 and Pb Et_4). There is a decrease in he tendency to catenation in the order C> S1 > Ge~ Sn ~ Pb. The strengths of covalent bonds to other atoms decrease in going from C to Pb. The divalent state is also found in compounds like carbines (e.g., : CF_2) and those for the other group IV elements can be regarded as carbon like.

Group V: P, As, Sb and Bi

Like nitrogen, phosphorus is essentially covalent in all its chemistry but arsenic, antimony and bismuth show increasing tendencies to cationic behavior. Although electron gain to achieve the electronic structure of the next noble gas is conceivable (as in N^{-3}) considerable energies are involved so that the anionic compounds are rare. Similarly, loss of valence electrons is difficult because of high ionization energies. There are no + 5 ions and even the + 3 ions are not simple, being SbO^+ and BiO^+, BiF_3 seems predominantly ionic. The increasing metallic character is shown by the oxides that changes from acidic for phosphorus to basic for bismuth, and by halides that have increasing ionic character.

Group VI: S, Se, Te and Po

These atoms can achieve the configuration of the noble gas by forming :

(1) The M^{-2} ions, in salts of highly electropositive elements.

(2) Two electron pair bonds as in H_2S or $SeCl_2$.

(3) Anionic species with one bond as in HS^-.

(4) Three bonds and one positive charge as in Sulfonium ions R_3S^+

There are also compounds in formal oxidation states IV and VI with 4,5, or 6 covalent bonds, (e.g., $SeCl_4$, SeF_5^-, and TeF_6).

Except Po there is no cationic behavior. There are gradual changes in properties with increasing size and decreasing electro negativity.

a) Decreasing stability of the hydrides H_2X.

b) Increasing metallic character.

c) Increasing tendency toward forming anionic complexes, such as $(SeBr_6)^{-2}$, $(TeBr_6)^{-2}$, $(PoI_6)^{-2}$

Group VII:

The halogen atoms are only one electron short of the noble gas configuration and the elements form the anion X^- or a single covalent bond.

Their chemistries are completely nonmetallic. The change in behavior with increasing size are progressive, and there are closer similarities within the group.

The halogens can form compounds in higher formal oxidation states, mainly in halogen fluorides such as ClF_3, ClF_5.

HYDROGEN

Hydrogen, the first element in the periodic table. It has the simplest atomic structure of all elements, and consists of a nucleus of charge +1 and one orbital electron. Hydrogen has little tendency to lose this electron and great tendency to pair the electron and form covalent bond. Also hydrogen can gain an electron and form negative ions in reactions with highly electropositive metals. Since its properties differ from those of both group I and group VII elements, it could well be put in a group of its own.

Isotopes of hydrogen:

If atoms of the same element have different mass numbers, they are called isotopes. Three isotopes of hydrogen are known: 'H hydrogen "H", ^{2}H deuterium (D) and ^{3}H tritium (T).

Since these isotopes have the same electronic configuration, they have the same chemical properties, but the difference in mass makes them show much greater differences in physical properties. The only differences in chemical properties are equilibrium constants and the rates of reactions.

Deuterium is found in the ordinary hydrogen, and it can be separated by electrolysis. D_2O may be obtained by repeating electrolysis of H_2O several times. Tritium is radioactive and has a half life time of 12.26 years.

$$^{3}_{1}T \longrightarrow {}^{3}_{2}He + B^{-}$$

It is produced in nuclear transformations.

$$^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{12}_{6}C + {}^{3}_{1}T$$

Ortho and Para hydrogen:

The hydrogen molecule H_2 exists in two different forms known as ortho and para hydrogen. If the nuclear spins of the two atoms in the molecule are in the same direction, it gives ortho hydrogen, and if the nuclear spins of the two atoms in the molecule are in opposite directions, it gives para hydrogen.

(ortho) (para)

At absolute zero, hydrogen is 100% in the para form, but as temperature is raised, the proportion of ortho hydrogen increases up to a limiting mixture containing 75 % ortho hydrogen .

<u>Properties of molecular hydrogen</u>

Hydrogen is the lightest gas known, and is colorless, and almost insoluble in water. It is found in many compounds such as water, carbohydrates and organic compounds, ammonia and acids, but as molecular hydrogen's , its abundance is very small .

It can be prepared according to the following methods :

(1) Electrolysis of water or sodium hydroxide.

(2) From hydrocarbons.

$$CH_4 + H_2O \xrightarrow[\text{Ni catalyst}]{\text{high temp.}} Co + H_2$$

(3) From coal also, but this method is too expensive

$$C + H_2O \xrightarrow{\text{red hot}} CO + H_2 \xrightarrow[450^oC/Fe_2O_3]{+H_2O} 2H_2 + CO_2$$

CO_2 is removed by dissolving in water under pressure, or reacting with K_2CO_3 solution, giving $KHCO_3$.

(4) Hydrogen can be prepared by the reaction of salt like hydrides with water.

$$LiH + H_2O \longrightarrow LiOH + H_2$$

(5) In the laboratory, the usual method is the reaction of dilute acids on metals.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

1- Hydrogen burns in air, but it is not very reactive and under certain conditions, it explodes with oxygen and halogens.

2- It is used in the production of ammonia.

$$N_2 + 3\ H_2 \longrightarrow 2\ NH_3$$

and this reaction is favored by high pressure, low temperature and the presence of suitable catalyst.

3- Hydrogen is also used to reduce metal oxides to meals.

4- It is useful in hydrogenation processes. Hydrogen molecule is very stable.

$$H_2 \longrightarrow 2\ H \qquad \Delta H = 431\ kg\ mol^{-1}$$

S-Block Elements

Group I- Alkali Metals

Table (1) :

Element	Symbol	Electronic structure	
Lilthium	Li	(Ne)	$2S^1$
Sodium	Na	(Ne)	$3S^1$
Potassium	K	(Ar)	$4S^1$
Rubidium	Rb	(Kr)	$5S^1$
Caesium	Cs	(Xe)	$6S^1$
Francium	Fr	(Rn)	$7S^1$

Electronic structure:

As we mentioned in the last chapter, the elements of group I all have one electron in their outer orbital an S-electron in a spherical orbital. There are similarities in the electronic structures of the outer most shells of these elements (Table1); accordingly, many similarities in chemical behavior would be expected. The elements are typically soft, highly reactive, univalent metals, and form colorless ionic compounds Li shows considerable differences from the rest of the group.

General properties:

The atoms are the largest in their corresponding period in the periodic table, and when the outer electron is removed to give a positive ion, the positive charge on the nucleus is greater than the number of electrons so that the electrons are attracted towards the nucleus, and the ion is smaller than the corresponding atom. Even so, the ions are very large, and increase in size from Li to Fr where shells of electrons are added.

These elements have low density because of their large size.

They have low ionization energies, because the outer orbital electrons are a long way from the nucleus and they are relatively easy to remove, and as the size of the atom increases, the electrons are further away from the nucleus and are less strongly held, so the ionization energy decreases. (Table 2).

Electro negativity values for this group elements are very low. Thus when they react with other elements to form compounds, ionic bonds are formed.

$$Na + 1/2\ Cl_2 = \longrightarrow Na^+\ Cl^-$$

Table (2)

Element	atomic radius (A°)	ionic radius (A°)	density (g/cc)	ionization energy kJ mol^{-1}	Electro-negativity	M.p. C°
Li	1.23	0.60	0.54	520	1.0	181
Na	1.57	0.95	0.97	496	0.9	99
K	2.03	1.33	0.86	419	0.8	63
Rb	2.16	1.48	1.53	403	0.8	39
Cs	2.35	1.69	1.87	373	0.7	29

Since there is only one valiancy electron in this group have a low cohesive energy and are soft. The cohesive energy decreases and softness increase (Li → Cs), because the increase in size of atoms in this direction is followed by increasing repulsion from the nonbonding electrons. According to the low values of cohesive energy and its decrease (Li → Cs), the values of melting and boiling points are low and decrease as size increases.

The melting point of lithium is different from the other element of the group .

Sodium is found in NaCl, and potassium occurs as KCl in sea water. Francium is radioactive and has a short half-life period of 21 minutes.

The metal ions all have inert gas configuration, thus all electrons are paired and consequently they are diamagnetic and colorless.

<u>Chemical properties:</u>

(1) Chemically these elements are very reactive, and tarn rapidly in air to form the oxide; and the nitride in the case of lithium (Li_3N) but not other elements.

(2) These elements react with water and liberating hydrogen to form hydroxides, which are the strongest bases.

$$2\ Na + 2\ H_2O \longrightarrow 2\ Na\ OH + H_2$$

The reaction increase from Li to Cs.

(3) Mono oxides, peroxides, and super oxides are formed when metals are burnt in air (e.g., Li_2O, Na_2O_2, and KO_2). They are prepared by dissolving the metal in liquid ammonia and casing it to react with the appropriate amount of oxygen. M_2O oxides are basic oxides because they react with water and forming strong bases. They are all very soluble in water (except for LiOH). M_2O_2 and NO_2 oxides are oxidizing agents because they react with water and acid giving H_2O_2 and O_2.

$$Li_2O + H_2O \longrightarrow 2\ Li\ OH$$

$$Na_2O_2 + 2H_2O \longrightarrow 2\ NaOH + H_2O_2$$

$$KO_2 + 2H_2O \longrightarrow KOH + H_2O_2 + 1/2\ O_2$$

(4) The metals all react with sulphur forming sulphides and polysulphides.

$$2\ Na + S \longrightarrow Na_2S$$

$$2\ Na + nS \longrightarrow Na_2S_n \quad (n=2,3,4,5, \text{ or } 6)$$

The reaction takes place in ammonia solution as solvent.

(5) The metals react with hydrogen forming hydrides, which contain the H-ion (as indicated from electrolysis, where the hydrogen liberated at the anode). These hydrides react with water liberating hydrogen.

$$Li + 1/2\ H_2 \longrightarrow Li\ H$$

$$LiH + H_2O \longrightarrow LiOH + H_2$$

$Li(AlH_4)$ is a useful reducing agent in organic chemistry. It is prepared as shown in the following equation:

$$4\ LiH + Al\ Cl_3 \xrightarrow{ether} Li\ (Al\ H_4) + 3LiCl$$

As the size of atoms increase (Li → Cs), reaction with hydrogen becomes less easy.

Solubility and hydration :

All the simple salts are soluble in water, and conductivity measurements give results in the order, $Cs^+ > Rb^+ > K^+ > Na^+ > Li+$ in aqueous solution. This is due to the ions being hydrated in water or in solution. Li^+ is heavily hydrated, hence it moves slowly, and Cs^+, the least hydrated moves faster. (Table 3).

The primary shell of water molecules which hydrate a metal ion is forming a complex. A secondary layer of water molecules further hydrates the ions, though these are only held by weak ion dipole attractive forces. The strength of such forces is inversely proportional to the distance, that is to the size of the metal ion. Thus the secondary hydration decreases from Li → Cs. The size of the hydrated ions affect the passage of these ions through water and this explains why hydrated

Li^+ are attached less strongly, and hence eluted first from action exchange columns.

Table (3)

Element	**atomic radius (A^o)**	**ionicmobility at infinite dilution**	**Approx. radius of hydrated ion (A^o)**	**Approx. hydration number**
Li^+	**0.60**	**33.5**	**3.40**	**25.3**
Na^+	**0.95**	**43.5**	**2.76**	**16.6**
K^+	**1.33**	**64.5**	**2.32**	**10.5**
Rb^+	**1.45**	**67.5**	**2.28**	**10.0**
Cs^+	**1.69**	**68.0**	**2.28**	**9.9**

As we said before, simple salts of group I elements are all soluble in water. The solubility of most of the salts in water decrease on descending the group. For a substance to dissolve, the hydration energy must exceed the lattice energy.

All the metals of Group I dissolve directly in very high concentration in liquid ammonia, and these solutions conduct electricity better than any salt in any liquid. The metals are also soluble in other amines and act as powerful reducing agents.

Oxy salts (carbonate, bicarbonate and nitrate) of Group I metals:

Because of the highly electropositive or basic nature of these metals, their oxy salts are uite stable. The carbonates are remarkably stable, and decompose into oxides at temperatures over 1000^{o}C Li_2CO_3 is less stable and decomposes more readily.

Group I metals also form solid bicarbonates. Except NH_4HCO_3, these are the only solid bicarbonates known. They decompose to carbonates on gently heating liberating CO_2

$$2\ NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

Note that Li does not form a solid bicarbonate but it can exist in solution.

All carbonates, and bicarbonates are soluble in water, and Na_2CO_3 is used as washing soda but Na_2HCO_3 is used as baking powder.

The nitrates are all very soluble in water, and $LiNO_3$ and $NaNO_3$ are deliquescent. KNO_3 is used in gun powder. The solid nitrates are very stable, but decompose on strong heating into nitrites.

$$Na\ NO_3 \longrightarrow Na\ NO_2 + 1/2\ O_2$$

$LiNO_3$ decomposes forming the oxide:

$$2Li\ NO_3 \longrightarrow Li_2O + 2\ NO_2 + 1/2\ O_2$$

Halides of Group I elements:

Li form hydrated halides of the type $LiX._3H_2O$ (X = Cl or Br or I) because of the small size of its ion. The other alkali metal halides form anhydrous crystals, which have NaCl structure with coordination number 8.

Alkali metal halides react with halogens and inter halogen compounds forming ionic plyhalide compounds.

$$KI + I_2 \longrightarrow KI_3$$

$$KBr + ICl \longrightarrow K(BrICl)$$

$$KF + BrF_3 \longrightarrow K(BrF_4)$$

Extraction of the metals:

Sodium is obtained by the Downs process i.e. electrolysis of NaCl with $CaCl_2$ added to lower the operating temp. from 803°C (m.p. of NaCl) to 505°C (m.p. of $NaCl/CaCl_2$ mixture).

Also sodium may be obtained by Castner process in which fused NaOH is electrolyzed .

$$4\ NaOH \longrightarrow 4Na + 2\ H_2O + O_2$$

But that method has low current efficiency and is absolete.

The modern method to obtain potassium is to pass sodium vapor over molten KCl in a large fractionating tower.

$$Na + KCl \longrightarrow K + NaCl$$

<u>Compounds with carbon:</u>

Metals of group I elements react with acetylene forming carbides.

$$Na + C_2H_2 \longrightarrow NaHO_2 \longrightarrow Na_2C_2$$

which on hydrolysis give acetylene.

$$Na_2C_2 + H_2O \longrightarrow 2\ NaOH + C_2H_2$$

Li forms carbide by direct reaction with carbon

$2Li + 2C \longrightarrow Li_2C_2$. Also these metals replace hydrogen in organic acids forming salts.

$$Na + CH_3COOH \longrightarrow CH_3COONa + H$$

$$K + C_6H_5COOH \longrightarrow C_6H_5COOK + H$$

Differences between Li and the other group I elements:

Lithium is a typical of group I elements, but shows slight similarity with group. II elements, particularly Mg. This is due to the polarizing power $\frac{\text{(ionic charge)}}{\text{(ionic radius)}^2}$ being similar.

The following points illustrate the common properties of lithium and the diagonal relationship.

(1) The melting point and boiling point of Li are compara-tively high.

(2) Lithium is much harder than the other group I metals.

(3) Lithium reacts the least readily with oxygen forming the normal oxide, but the higher oxides being unstable.

(4) Li is much less electropositive, and therefore many of its compounds are less stable (Li_2CO, $LiNO_3$ and LiOH) all form oxide on gentle heating, and no solid bicarbonate is known.

(5) The ion and its compounds are more heavily hydrated than those of the rest of the group.

(6) Unlike the other group I elements, Li reacts directly with C to form carbide.

(7) Li has a greater tendency to form complexes because of the small size of its ion.

Group II

Alkaline Earth Metals

Table (4)

Element	Symbol	Electronic	Structure
Beryllium	Be	(He)	$2S^2$
Magnesium	Mg	(NE)	$3S^2$
Calcium	Ca	(Ar)	$4S^2$
Strontium	Sr	(Kr)	$52S^2$
Barium	Ba	(Xe)	$6S^2$
Radium	Ra	(Rn)	$7S^2$

Electronic structure:

All group I elements have two S electrons in their outer orbital as shown in the above table. They are typically divalent. These metals are highly reactive, but less basic than group I. Beryllium shows some differences from the rest of the group.

General properties:

The size of atoms is large, but is smaller than the corresponding group I elements, since the extra charge on the nucleus draws the orbital electrons in. Similarly, the size of ions is large, but is smaller than the corresponding group I elements, since the removal of two outer electrons increases the effective unclear charge.

The number of bonding electrons in the metals is now two, so that these have higher melting and boiling points and densities than group I metals. Also the two valence electrons participate in metallic bonding, make these elements harder than group I.

The metals of group II are electropositive with high chemical reactivates.

The ionization energies are higher than those of group I atoms. The total energy required to produce divalent ions for group II elements is over four times greater than the amount needed to ionize group I metals; also the hydration energies of group II ions are greater than for group I elements, because of the small size and increased charge of nucleus of group II ions. As the size of ions increase down the group I, the hydration energy decrease. (Table 5).

Since the divalent ions have the inert gas structure with no unpaired electrons, the compounds of group II element are always divalent, ionic, diamagnetic and odorless, unless the acid radical is colored.

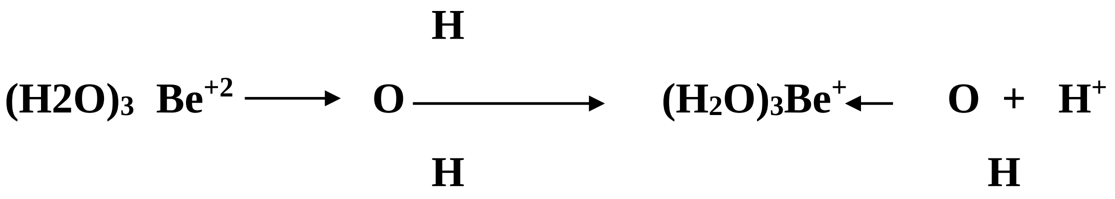
Table (5)

Element	**atomic radius (A^o)**	**ionic radius M^{+2} (A^o)**	**Ionization energy Kg mol^{-1} 1st**	**2nd**	**Melting point C^o**	**Electro negativity**
Be	**0.89**	**0.31**	**899**	**1757**	**1277**	**1.5**
Mg	**1.37**	**0.65**	**737**	**1450**	**650**	**1.2**
Ca	**1.74**	**0.99**	**590**	**1145**	**838**	**1.0**
Sr	**1.91**	**1.13**	**549**	**1064**	**768**	**1.0**
Ba	**1.98**	**1.35**	**503**	**965**	**714**	**0.9**
Ra	**-**	**1.50**	**509**	**979**	**700**	**-**

Behavior of Beryllium:

Beryllium differs from the rest of the group partly because it is extremely small and partly because of its comparatively high electro negativity; so that it forms two covalent bonds in its anhydrous compounds. Its ions in solution have the form $(Be(H_2O)_4)^{2+}$. This increases the effective size of the beryllium ion, and stable ionic salts $((Be(H_2O)_4))\ SO_4$, $(Be(H_2O)_4)\ (NO_3)_2$.)) are known.

In pure water beryllium salts are acidic. This is due to the strength of Be-O bond which weakens the O-H bonds, hence there is a tendency to lose protons.



$$(H2O)_3\ Be^{+2} \longrightarrow \overset{H}{\underset{H}{O}} \longrightarrow (H_2O)_3Be^{+} \longleftarrow \underset{H}{O} + H^{+}$$

Solubility and hydration energy:

The solubility of most salts decreases with increased atomic weight. The hydration energy also decreases as the metal ions become larger.

Fluorides and hydroxides increase in solubility on desc-ending the group. This is because the lattice energy decreases more rapidly than the hydration energy, and this favors increased solubility since a substance to dissolve, the hydration energy must exceed the lattice energy.

Chemical properties:

(1) The electro positively of the metals is less than that in group I.

(2) The metals still react with water to form hydrogen and metal hydroxides.

$$M + 2\ H_2O \longrightarrow M(OH)_2 + H_2$$

Beryllium is not typical. It reacts with steam to form the oxide BeO or fails to react at all. Magnesium reacts slowly with hot water. The other metals react with cold water.

(3) The basic strength of group II hydroxides increase with increasing the atomic weight of metals. Beryllium hydroxide $Be(OH)_2$ is amphoteric.

$$Be(OH)_2 + 2\ HCl \longrightarrow BeCl_2 + 2H_2O$$

$$H_2BeO + KOH \longrightarrow K\ H\ BeO_2 + H_2O$$

$Mg(OH)_2$ is weakly base, $Ca(OH)_2$ is moderately strong base, while $Sr(OH)_2$ and $Ba(OH)_2$ strong base. Calcium hydroxide is used as lime water to detect CO_2. The effect of excess CO_2 on these is to produce soluble bicarbonates, thus removing the turbidity.

$$Ca(OH)_2+CO_2 \rightarrow H_2O+CaCO_3 \text{ (insoluble white ppt.)}$$

$$CaCO + CO_2\text{(excess)} \rightleftharpoons Ca(HCO_3)_2 \quad \text{(soluble).}$$

These bicarbonates are stable in solution only, and decom-pose to carbonates.

(4) Oxides of group II elements have the form MO. They are usually prepared by thermal decomposition Of MCO_3, $N(NO_3)_2$, MSO_4 and $M(OH)_2$. Also when this group elements burin in oxygen, MO oxides are produced. Beryllium oxide is covalent, but all the other oxides are ionic. Beryllium oxide is insoluble in water. It dissolves in acids to give salts, and in alkalis to give beryllates. That means, this oxide is amphoteric. Magnesium oxide reacts with water forming magnesium hydroxide.

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

CaO reacts very readily with water, and $Ca(OH)_2$ is produced, and also but more readily the reaction of Sr and Ba with water.

$$CaO + H_2O \longrightarrow Ca(OH)_2 + 1500\ Cal$$

Calcium oxide is prepared on a large scale by heating $CaCO_3$ in lime kilns. It is used in the manufacture of Na_2CO_3, NaOH, CaC_2, bleaching powder, glass and cement.

Also group II elements form peroxides and the case with which the peroxides are formed increases with increasing size. No peroxide of beryllium is known. Crude magnesium peroxide has been made using hydrogen peroxide. Calcium peroxide can be made as the hydrate by treating $Ca(OH)_2$ with H_2O_2 and then dehydrating the product. Strontium peroxide can be formed by passing air over SrO at high pressure and temperature. Barium peroxide BaO_2 is formed by passing air over BaO at 500°C.

The peroxides are white ionic solids containing, $(O\text{-}O)^{-2}$ ion. On treatment with acid, H_2O_2 is formed .

(5) The sulphates are soluble in water but the solubility decreases down the group, Be > Mg>>Ca > Sr>Ba and $CaSO_4$ is almost insoluble. Sulphates decompose on heating, giving oxides.

$$Mg\ SO_4 \xrightarrow{heat} MgO + SO_3$$

With respect to carbonates, the stability of the salt increases with increasing basicity. For nitrates; all nitrates can be prepared in solution and as hydrated salts by the reaction of HNO_3 on carbonates, oxides, or hydroxides to the oxides. Anhydrous nitrates can be prepared using liquid dinitrogen tetroxide.

$$Mg\ Cl_2 + N_2O_4 \longrightarrow Mg(NO_3)_2 + 2\ N_2O_4$$

$$Mg\ (NO3)_2\ 2N_2O_4 \xrightarrow[\text{Under vacuum}]{\text{warm } 50^oC} Mg(NO_3)_2$$

Beryllium is unusual in that it forms a basic nitrated in addition to the normal salt.

$Be(NO_3)_2 \xrightarrow{120^oC} Be_4O(NO_3)_6$ basic beryllium nitrate.

(6) All the elements except beryllium form hydrides of type MH_2 by direct combination, and impure beryllium hydride has been made by reducing $BeCl_2$ with $LiAlH_4$. All group II hydrides are reducing agents, which react with water and liberate hydrogen. Calcium, strontium and barium hydrides are ionic, and contain the hydride ion H^-. Beryllium and magnesium hydrides are covalent and polymeric $(BeH_2)n$.

H H H
Be Be Be Be
H H H

(7) All metals are forming halides (MX_2) by direct comb-ination with the halogen or by the action of acid halogen on the metal or carbonate. Beryllium halide are covalent, hygroscopic and fume in air due to hydrolysis. They sublime, and they do not conduct electricity. Anhydrous beryllium halides are polymeric $(BeX_2)_n$ and like $(Be\ H_2)_n$

Cl Cl Cl
Be Be Be Be
Cl Cl Cl

The fluorides MF_2 are almost insoluble. The other metal halides are ionic and readily soluble in water. The halides are hygroscopic and form hydrates. $CaCl_2$ is a well known drying agent.

(8) By contrast with elements in group I the alkaline earth elements burn in nitrogen and form nitrides M_3N_2. The beryllium nitride is rather volatile, the others are not. All nitrides are colorless crystalline solids.

They decompose on heating and react with water to liberate ammonia and form metal oxide or hydroxide .

$$Mg_2\ N_3 + 3H_2O \longrightarrow 2NH_3 + 3MgO$$

(9) Group II elements form ionic carbides MC_2 by heating the metals Mg to Ba or by heating their oxides with carbon. Calcium carbide is the best known; it reacts with water, liberates acetylene and is thus called an acetylide.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

(10) All the metals react with acids and liberate hydrogen, although beryllium reacts slowly. Sodium hydroxide also gives hydrogen when treated with beryllium, but has no effect on the other metals. This illustrates the increase in basic properties from amphoteric to basic on descending the group.

(11) By treating magnesium with an alkyl or aryl halide (Cl^-, Br^- or I^-) in an absolutely dry organic solvent such as diethyl ether, magnesium forms Grignard reagents, which are probably the most versatile reagents in organic chemistry.

$$Mg + RBr \longrightarrow RMgBr \quad \text{(Grignard reagent)}$$

$$RMgBr + CO_2 \xrightarrow{\text{acid}} RCOOH$$

$$RMgBr + I_2 \longrightarrow RI$$

(12) Group II metals are not noted for their ability to form complexes, since complex formation is favored by small highly charged ion with suitable empty orbital's. Thus Be form many $M_2\ (BeF_4)^{-2}$ complexes and Ba very few.

Extraction of the metals :

The metals of this group are not easy to produce by chemical reaction because they are strong reducing agents and they form carbides. They are strongly electropositive and so aqueous solutions cannot be used for displacing one metal by another, or for electrolysis because of the reaction of the metal with water.

All the metals can be obtained by electrolysis of the fused chloride, with the addition of NaCl to lower the m. point, although Sr and Ba tend to form colloida suspension.

Beryllium is obtained by reducing BeF_2 with Mg. Magnesium is now prepared commercially by the Pigeon process by reduction of magnesium oxide with ferrosilicon and aluminum. The MgO is obtained by treating sea water, which contains Mg^{+2} ions, with $MgCa(CO_3)_2$. $Mg(OH)_2$ is obtained, and can filtered off and heated to give the oxide.

Calcium is obtained by heating $CaCO_3$ to give the oxide CaO, treating with NH_4Cl and water to give $CaCl_2$, followed by electrolysis of the fused chloride.

Strontium and Barium are obtained from their oxides by reduction with aluminum.

Differences between Beryllium and the other Group II Elements:

Beryllium is anomalous in many of its properties and show a diagonal relationship to aluminum in group III:

(1) Be is very small and has a high charge density, so it should have a strong tendency to covalence. The melting point of its compounds is lower.

(2) Be forms many complexes–not typical of group I and II.

(3) Be like Al is rendered passive by nitric acid.

(4) Be is amphoteric, liberating M_2 with NaOH and forming beryllates. Al forms aluminates.

(5) Be $(OH)_2$ like $Al(OH)_3$ is amphoteric.

(6) Be salts are among the most soluble known.

P - BLOCK ELEMENTS

Group III The Boron Group

Table (6)

Element		Electronic Configuration	Oxidation state
Boron	B (He)	$2S^2 2P^1$	III
Aluminium	Al (Ne)	$3S^2 3P^1$	(1) III
Gallium	Ga (Ar)	$3d^{10} 4S^2 4P^1$	1 III
Indium	In (Kr)	$4d^{10} 5S^2 5P^1$	1 III
Thallium	Tl (Xw)	$4F^{14} 5d^{10} 6S^2 6P^1$	1 III

General properties :

In this group the first element boron is nonmetal, but the other elements are fairly reactive metals.

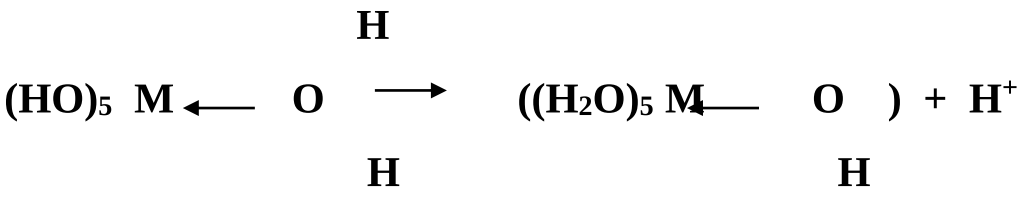
The most important are of aluminum is bauxite $AL_2O_3.H_2O$. Boron occurs in earth's crust as borax $Na_2B_4O_7.10.H_2O$. Gallium, indium and thallium are found as traces in zinc and lead sulphides ores.

All the elements show oxidation state, III, unlike the S block elements, some of the elements of this group show lower valence states in addition to the group. Valence the heavier elements show an increased tendency to form univalent compounds, and in fact univalent thallium, compounds are the most stable. Mono valence is explained by the S electrons in the outer shell remaining paired, and not participating in bonding because the energy to unpair them is too great. This occurs particularly among heavy elements in the p-block and is called the inert pair effect. Gallium is apparently divalent in a few compounds such as

$GaCl_2$, but the structure has been shown to be $Ga^+(GaCl_4)^-$ which contains Ga(+1) and Ga(+III) (Table 6).

The small size of the ions, their high charge and the large values for the sum of the first the ionization energies suggest that the elements are largely covalent.

In solution, the large amount of hydration energy evolved off sets the high ionization energy an all metal ions exist in a hydrated state. The hydrated metal ions have six molecules of water which are held strongly giving an octahedral structure. The strength of the metal oxygen bond weakens the O-H bonds. Some hydrolysis occurs, and protons are released thus giving acidic solutions.



$$(HO)_5\ M \longleftarrow \overset{H}{\underset{H}{O}} \longrightarrow ((H_2O)_5\ M \longleftarrow \underset{H}{O}\ ) + H^+$$

The covalent radial of the atoms (Table 7) do not increase in a completely regular way from B to Ti as was found on descending Group I and II.

This is because the inner electronic configuration of Ga In and Ti contains ten d-electrons. These shield the nuclear charge less efficiently than the S and P electrons, so the outer electrons are more firmly held by the nucleus. (Shielding decreases S > P > d > f). Thus atoms with a d^{10} inner shell are smaller and consequently have higher ionization energies than would other wise be expected. In a similar way the inclusion of fourteen even more poorly shielding f electrons further affects the size and ionization energy of T1.

Table (7)

Element	covalent radius	Ionic radius	Ionization Energy $M \longrightarrow M^{+3}$	electro-negativity
B	0.50	0.20	6764	2.0
Al	1.25	0.52	5114	1.5
Ga	1.25	0.60	5500	1.6
In	1.50	0.81	5066	1.7
Th	1.55	0.91	5413	1.8

The finely divided amorphous boron is usually impure and burns in air to form the oxide and nitride, and in the halogens to form tri-halides. It reduces nitric and sulphuric acids and liberates hydrogen with NaOH.

Pure crystalline boron is, in contrast, un-reactive except at very high temperatures or with reagents such as hot concentrated ulphuric acid or Na_2O_2.

Aluminum is stable in air because it develops an oxide film which protects the metal from further attack.

Gallium and indium are stable in air and are not attacked by water except when free oxygen is present.

Thallium is a little more reactive and is superficially oxidized in air.

The electropositive or metallic nature of the elements increases from B to Al according to the increase in size and because they follow immediately after the S block elements. From Al to T1 the electropositive deceases because these elements follow after the d-block elements. These extra d-electrons do not shield the nuclear charge very effectively, so that the orbital electrons are more firmly held and the metals are less electropositive. This is illustrated by the increase in ionization energy

between Al and Ga even though the larger atom would be expected to have a lower values. (Table 7).

Group III oxides:

(a) Boron sesquioxide and the borates :

Sesquioxide M_2O_3 of all the elements can be made by heating the elements in oxygen. B_2O_3 is more usually made by dehydrating boric acid.

$$H_3BO_3 \xrightarrow{100^oC} HBO_2 \xrightarrow{red\ heat} B_2O_2$$

Ortho boric acid   metal boric acid

B_2O_3 is acidic in its properties ad is the anhydride of ortho boric acid.

On heating with metal oxides it gives meta borates which indicate its acidic properties.

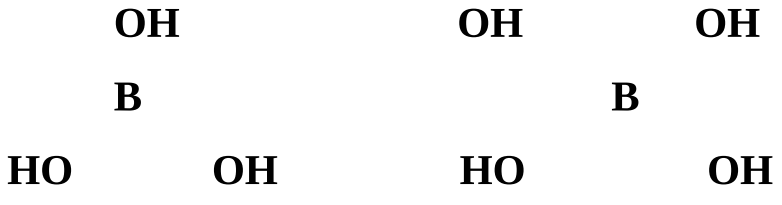
$$COO + B_2O_3 \longrightarrow CO(BO_7)_2$$

Boron sesquioxide can react with very strongly acidic oxides such as phosphorus pent oxide, and forming a phosphate. In these reactions it is being forced to behave as a base.

$$B_2O_3 + P_2O_5 \longrightarrow 2\ BPO_4$$

Ortho boric acid H_3BO_3 behaves as a weak mono basic acid.

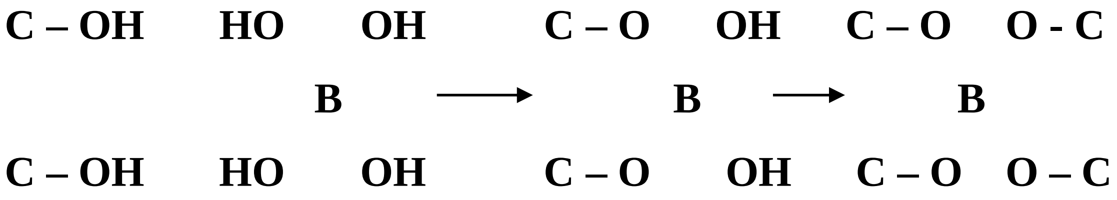
$$H_3BO_3 + H_2O \rightleftharpoons H^+ + (B(OH_4)^- \qquad pK=9$$



On titration with NaOH:

$$H_3BO_3 + NaOH \longrightarrow \begin{array}{l} Na(B(OH)_4) \\ \\ NaBO_2 + 2\,H_2O \end{array}$$

The ortho boric acid can be converted into a strong mono basic acid by the addition of certain organic polyhydroxy compounds such as glycerol, manitol or sugars. The added compound must have OH groups on adjacent atoms in the cis configuration. The increase in acid strength occurs because the cis diol forms complexes and effectively removes $(B(OH)_4)^-$ from solution, thus upsetting the balance of the reversible reaction, hence all the H_3BO_3 ionizes and the maximum number of H^+ are produced.



$$\begin{array}{l} C-OH \\ \\ C-OH \end{array} \quad \begin{array}{ccc} HO & & OH \\ & B & \\ HO & & OH \end{array} \longrightarrow \begin{array}{ccc} C-O & & OH \\ & B & \\ C-O & & OH \end{array} \longrightarrow \begin{array}{ccc} C-O & & O-C \\ & B & \\ C-O & & O-C \end{array}$$

The most important metoborat is borax

$$Na_2\,B_4O_7.\ 10H_2O + 2\,HCl \longrightarrow 2NaCl + 4\,H_3BO_3 + 5\,H_2O$$

Sodium per borate is produced in a large amounts. It is used as a brightener in washing powders.

$$NaBO_2 + H_2O_2 \longrightarrow NaBO_3.\ 4\,H_2O$$

(b) The other group III oxides:

Alumina Al_2O_3 can be made by dehydrating $AL(OH)_3$. Aluminum has a very strong affinity for oxygen, and this is used in the thermite reduction of metal oxides.

$$3\,Mn_3O_4 + 8\,Al \longrightarrow 4\,Al_2O_3 + 9\,Mn$$

Aluminum hydroxide is amphoteric, thought it acts as a base principally, giving salts that contain the $(Al(H_2O)_6)^{+3}$ ion.

$$Al(OH)_3 \longrightarrow Al^{+3} + 3\,OH^-$$

Aluminum hydroxide exhibits acidic properties when it reacts with NaOH forming sodium aluminates which is often formulated Na AlO_2. $2H_2O$.

Gallium, like aluminum, forms an amphoteric oxide and hydroxide. Indium sesquioxide is completely basic. Thallous hydroxide TlOH is a strong base, and is soluble in water, thus differing from the trivalent hydroxides. If an element can exist in more than one valence state there is a general tendency for the lower valence state to be the most basic.

Hydrides of group III elements:

None of the group III elements react directly with hydrogen, but a number of interesting hydrides are known.

Boron hydrides are called boranes. There are seven well characterized boranes.

$B_n H_{n+4}$		$B_n H_{n+6}$	
B_2H_6	diborane	B_4H_{10}	tetraborane
B_5H_9	pentaborane-9	B_5H_{11}	pentaborane - 11
$B_{10}H_{14}$	decaborane-14	B_9H_{15}	nomaborane
		$B_{10}H_{16}$	decaborane - 16

==

Diborane has been studied more than the other boranes. It may be prepared by a variety of methods.

1- $Mg_3B_2 + H_3PO_4 \longrightarrow$ **mix. of boranes** $\xrightarrow{heat} B_2H_6$

2- $2BCl_4 + 6\,H_2 \xrightarrow[\text{electric charge}]{\text{silent}} B_2H_6 + 6\,HCl$

3- $4BCl + 3\,LiAl\,H_4 \longrightarrow 2B_2H_6 + 3\,AlCl_3 + 3LiCl$

In diborane there are twelve valence electrons, three from each boron atom and six from the hydrogen's. Electron diffraction results indicate the structure.

H H H

B B

H H H

All the boranes react with ammonia, but the products depend on the condition

$B_2H_6 + NH_3 \xrightarrow[\text{Low. temp.}]{\text{excess } NH_3} B_2\,H_6.\,2NH_3$

$\xrightarrow[\text{Higher temp.}]{\text{Excess } NH_3} (BN)_x$ boron nitride

$\xrightarrow[\text{high temp.}]{\text{ration } 2NH_3:1B_2H_6} B_3N_3H_6$ borazole.

In addition to the boranes, rather more stable complex borohydrides containing the group $(BH_4)^-$ are known. Sodium borohydride can be made.

$4\,NaH + B\,(OCH_3)_3 \longrightarrow Na(BH_4)\ 3\,NaOCH_3$

Methyl borate

The borohydride ion is tetrahedral and reacts with water with varying ease. Li (BH_4) reacts violently with water.

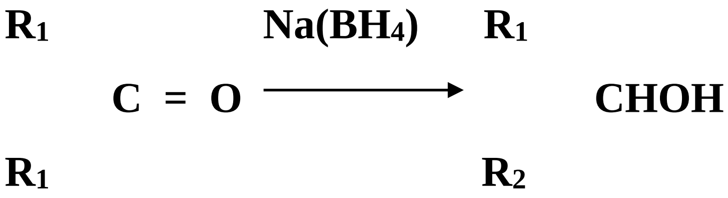
$$Li(BH_4) + H_2O \longrightarrow Li\,BO_2 + 4\,H_2$$

Na(BH_4) may be re crystallized from cold water.

K(BH_4) is quite stable.

The stability of Na(BH_4) in alcoholic and aqueous solutions makes it a useful reagent in the reduction of aldehydes to primary alcohol, and ketones to secondary alcohols.

$$R.CHO \quad Na(BH_4) \quad R.CH_2OH$$



$$\begin{matrix} R_1 & & R_1 \\ & C = O \xrightarrow{Na(BH_4)} & CHOH \\ R_1 & & R_2 \end{matrix}$$

The other elements in the group also form electron deficient hydrides.

(AlH_3)$_n$ can be made from LiH and $AlCl_3$

$$LiH + AlCl_3 \longrightarrow (Al\,H_3)_n$$

with excess LiH, Li(AlH_4) is formed

$$\text{excess } LiH + AlCl_3 \longrightarrow Li(Al\,H_4)$$

Li(AlH_4) is a most useful organic reducing agent.

Gallium forms Li(GaH_4)

Indium forms ($In\,H_3$)$_n$

There is a doubt the existence of a hydride of thallium.

Hydroboration:

An important reaction occurs between B_2H_6 and olefins and acetylene.

$$B_2H_6 + RCH = CHR \longrightarrow B(CH_2\text{-}CH_2R)_3$$

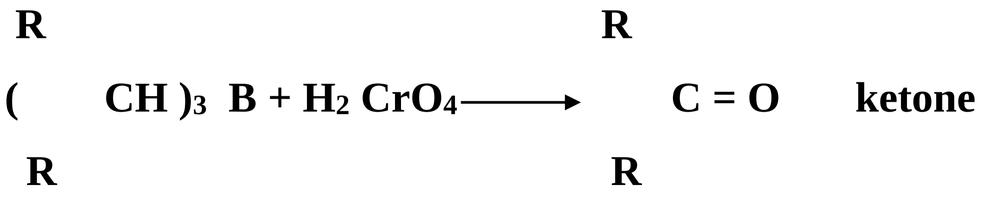
$$B_2H_6 + RC = CHR \longrightarrow B(RC = CHR)_3$$

The reactions are carried out in dry ether and under an atmosphere of nitrogen because H_2H_6 and the products are very reactive. The alkyl borane products are not usually isolated, but may be converted to hydrocarbons by treatment with carboxylic acids, to alcohols by reaction with alkaline H_2O_2 and to ketones or carboxylic acids by oxidation with chromic acid.

$$BR_3 + 3\,CH_3COOH \longrightarrow 3RH + B(CH_3COO)_3$$

Hydrocarbon

$$B(CH_2 - CH_2R)_3 + 3H_2O_2 \longrightarrow 3RCH_2CH_2OH + H_3BO_3$$



$$\left(\begin{matrix}R & \\ & CH\\ R & \end{matrix}\right)_3 B + H_2\,CrO_4 \longrightarrow \begin{matrix}R & \\ & C = O\\ R & \end{matrix} \quad \text{ketone}$$

$$(CH_3 - CH_2)_3\ B + H_2\,CrO_4 \longrightarrow CH_3COOH$$

Carboxylic acid

Hydroboration is a simple and useful process because of the mild conditions required for the initial hydride addition and the variety of products which can be produced using different reagent to break to B-C bond.

Halides of Group III elements:

a) Tri halides

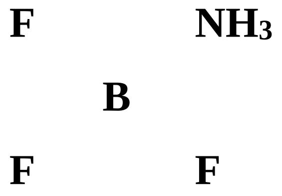
All the elements from tri halides. The boron halides BX3 are covalent and gaseous. They are all hydrolyzed by water, the fluoride forming fluoro borates and the other halides giving boric acid.

$$BF_3 + H_2O \longrightarrow H_3BO_3 + HF$$

$$BF_3 + HF \longrightarrow H^+ + (BF_4)^-$$

The B atom in the BX_3 molecule can accept alone pair of electrons from a donor atom such as

O , N , P , or S ;

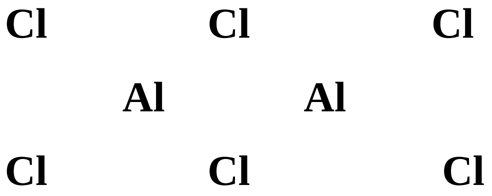


$$\begin{array}{ccc} F & & NH_3 \\ & B & \\ F & & F \end{array}$$

This makes BF_3 a useful organic catalyst for Friedel - Crafts reactions such as alkylations, acylation and esterifications. BF_3 is produced in the U.S.A by the reaction.

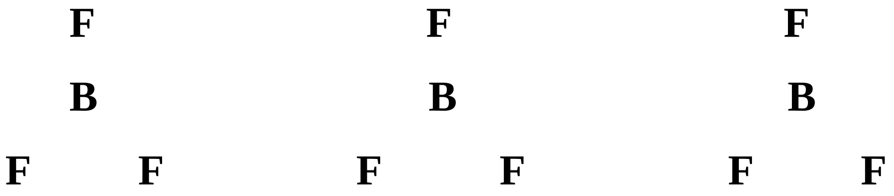
$$B_2O_3 + 6HF + 3H_2SO_4 \longrightarrow 2BF_3 + 3H_2SO_4.H_2O$$

Fluorides of Al, Ga In and Tl are ionic and have high melting points. The other halides are largely covalent when anhydrous. $AlCl_3$, $AlBr_3$ and $GaCl_3$ exists as dimmers, thus attaining an octet of electrons.



$$\begin{array}{ccccc} Cl & & Cl & & Cl \\ & Al & & Al & \\ Cl & & Cl & & Cl \end{array}$$

A group III element has only three valence electrons, and when it forms three covalent bonds it has a share in only six electrons and is therefore electron deficient. The BX_3 halides attain an octet by bonding, but the other elements are larger, and cannot get effective overlap, so they polymerize to remedy the electron deficiency.



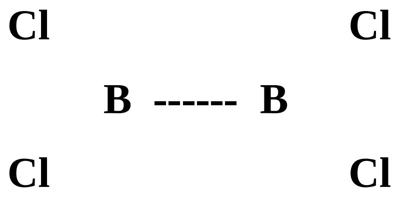
$$\begin{array}{ccccccccc} & F & & & F & & & F & \\ & B & & & B & & & B & \\ F & & F & F & & F & F & & F \end{array}$$

(b) Di halides:

In addition to the tri halides, boron forms halides of formula B_2X_4. These decompose slowly at room temper-ature. B_2Cl_4 can be made:

$$2\ BCl_3 + 2Hg \xrightarrow[\text{Low pressure}]{\text{electric discharge}} B_2Cl_4 + Hg_2Cl_2$$

The structure is:



$$\begin{array}{ccc} Cl & & Cl \\ & B\ \text{------}\ B & \\ Cl & & Cl \end{array}$$

Gallium and indium form di halides:

$$GaCl_3 + Ga \longrightarrow GaCl$$

$$In + HCl\ \text{gas} \longrightarrow InCl_2$$

These are more properly written $Ga^+(GaCl_4)^-$ and contain M(I) and M(III) rather than divalent Ga and In.

Thallium forms univalent thallous halides which are more stable than the tri halides.

(c) Mono halides:

All group III elements form mono halides M in the gas phase at elevated temperature

$$Al\ Cl_3 + 2\ Al \xrightarrow[\text{temp.}]{\text{high}} 3\ AlCl$$

These compounds are not very stable. They are covalent except for Tl^+F^- which is ionic. Boron form a number of stable polymeric mono halides $(Bx)_n$

$$H_2Cl_4 \xrightarrow{\text{mercury discharge}} B_4Cl_4$$

$$\text{Slow} \searrow$$

Decomposition $B_8Cl_8, B_9Cl_9, B_{10}Cl_{10}, B_1Cl_{11}, B_{12}Cl_{12}$

Complexes:

Group III elements form complexes much more readily than the S block elements on account of their smaller size and increased charge. Many complexes are known such as tetrahedral hydride and halide complexes $Li(AlH_4)$ and $H(B\ F_4)$. Also octahedral complexes are important, for example, $(GaCl_6)^{-3}$, $(In\ Cl_6)^{-3}$ and $(TlCl_6)^{-3}$. Complexes with chelate groups are useful in gravimetric determination such as 8 hydroxy quinoline complex.

8- hydroxy quinoline complex

Organometallic compounds:

In addition to carboranes and the alkylboranes, all the Group III tri halides will react with Grignard reagents and organo lithium reagents forming tri alkyl or tri aryl compound.

$FB_3 + 3\ C_2H_5MgI \qquad B(C_2H_5)_3$

$AlCl + 3\ CH_3MHI \qquad Al(CH_3)_3$

$GaCl_3 + 3C_2H_5Li \qquad Ga(C_2H_5)_3$

$InBr_3 + 3C_6H_5Li \qquad In(C_6H_5)_3$

The use of aluminum alkyls in producing poly thene alcohols and isoprene is of considerable industrial importance.

Extraction of the elements :

Boron is obtained by the reduction of B_2O_3 with magnesium or sodium.

$$Na_2B_4O_7.10H_2 \xrightarrow{\text{acid}} H_3BO_3 \xrightarrow{\text{heat}} B_2O_3 \xrightarrow{\text{Na or Mg}} B$$

Boron obtained in this way is amorphous, and may contain 5 % impurities. Pure crystalline boron may be obtained in small quantities by the reduction of BCl_3 with H_2, or the pyrolysis of BI_3.

$$2BCl_3 + 3H_2 \xrightarrow{\text{red hot filament}} B_2 + 3HCl$$

$$3BI_3 \xrightarrow[\text{W or Ta}]{\text{red hot filament}} 2\,B + 3\,I_2$$

Boron is used to increase the harden ability of steels.

Aluminum is obtained from the ore , bauxite $Al_2O_3.H_2O$ by the addition of NaOH, forming sodium aluminate which dissolves, thus separating Al from iron oxide. Aluminum is produced on a large scale and is used widely in alloys, paint and coking utensils.

Gallium, indium and thallium occur only in minute quantities and are usually obtained by electrolyzing aqueous solution of their salts.

The large differences between boron (non metal always covalent, acidic, high melting point) and aluminum are to be expected since Al^{3+} is 2.5 times the size of B^{+3}.

Group IV The Carbon Group

Table (8)

Element			Electronic Configuration	Oxidn number	
Carbon	C	(He)	$2S^2 2P^2$		IV
Silicon	Si	(Ne)	$3S^2 3P^1$	II	IV
Germanium	Ga	(Ar)	$3d^{10} 4S^2 4P^2$	II	IV
Sn	Sn	(Kr)	$4d^{10} 5S^2 5P^2$	II	IV
Lead	Pb	(Xe)	$4F^{14} 5d^{10} 6S^2 6P^2$	II	IV

Metallic and nonmetallic character:

The change from nonmetal to metal with increase atomic number is well illustrated in group IV. Carbon and silicon are nonmetals, germanium he some metallic properties, and tin and lead are metal. This can be illustrated from the structures (Table 8).

Differences between carbon silicon and the remaining elements:

Carbon differs from the other elements in its limitation to a coordination number of four (because there are no orbital's in the second shell), its unique ability to form multiple bonds such as C=C, C=C , C=O and C=N and in its ability to form chains (catenation). The tendency to catenation is related to the strength of the bond.

Carbon and silicon have only S and P electrons, but the other elements follow a completed transition series with ten d electrons. Thus some differences are expected, and carbon and silicon differ both from one another and from the rest of the group, while germanium, tin and lead form a graded series.

General properties:

The covalent radial increase down the group, but the difference in size between Si land Ge is less than might be otherwise expected because the filling of the 3d shell increase the nuclear charge and provides only poorly shielding d electrons. In a similar way the small difference in size between Sn and Pb is because of the filling of the 4f shell.

The ionization energies decrease from C to Si, but then change in an irregular way because of l the effects of filling the d and f shells. The large amount of energy required to form M^{4+} ions suggests that simple ionic compounds will be very rare, and occur only with highly electronegative elements such as F and O. The compounds SnF_4, SnO_2, PbF_4 and PbO_2 are ionic.

The elements of this group form covalent compounds with four covalent bonds, by promotion of electrons from the ground state to an excited state; and SP^3 hybridization of the orbital's, results in a tetrahedral structure.

Electronic structure of carbon atom :

Ground state : 1S 2S 2P

Two unpaired electrons from two covalent bonds

excited state:

four unpaired electrons from four covalent bonds and SP^3 hybridization results in a tetrahedral structure .

The elements in this group are relatively un reactive, but reactivity increases down the group. They are generally attacked by acid alkalis, and the halogens: graphite by F, Si by HF, Ge by H_2SO_4 and HNO_3 and Sn and Pb by a number of acids.

Inert pair effect:

The inert pair effect shows itself increasingly in the heavier members of the group. On descending the group, there is a decrease in stability of + IV oxidation and an increase in stability of (+II) state.

Formation of complexes:

The ability to form complex is favored by a high charge, small size, and availability of empty orbital's of the right energy. Carbon has a maximum of eight electrons in its outer shell. In four covalent compounds of carbon, the second shell contains the maximum of eight electrons. Because this structure resembles that of an inert gas, these compounds are stable, and carbon does not form complexes. Four covalent compounds of the subsequent elements can form complexes due to the availability of d orbital's, with coordination number six.

Formation of hydrides:

Al the elements form covalent hydrides, but differ in the number of formed and the ease with which they formed. Carbon forms a vast number of chain and ring compounds including the alkenes, alkenes, alkenes (C_nH_{2n+2}) C_nH_{2n}, and C_nH_{2n-2}, respectively), and aromatic compounds. The strong tendency to catenation has been related to the strenergth of C-C bond.

Silicon forms a limited number of saturated hydrides Si_nH_{2n+2}, called silanes and exist as straight chains or branched chains.

Germanium hydrides are similar to silanes, but are less inflammable, and less readily hydrolyzed. SnH_4 is less stable and more difficult to prepare. pbH_4 is even less stable and even more difficult to prepare.

Formation of halides:

All the tetra halides are known except PbI_4. They are all very volatile and covalent, except SnF_4 and PbF_4 which are ionic. CF_4 is un reactive and very stable, and used solvent and insulator. Mixed chloro fluro hydro-carbons such as $CFCl_3$ and CF_2Cl_2 are known as freons, and used as refrigeration fluids. SiF_4 is readily hydrolyzed by alkali

$$SiF_4 + 8\ OH^- \longrightarrow SiO_4^{-4} + 4F^- + 4H_2O$$

Silicon halides are rapidly hydrolyzed by water to give silicic acid.

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

$CeCl_4$ and $GeBr_4$ are hydrolyzed less readily. $SnCl_4$ and $PbCl_4$ hydrolyze in dilute solutions, but hydrolysis can be repressed by the addition of halogen acid.

$$Sn(OH)_4 \underset{H_2O}{\overset{HCl}{\rightleftarrows}} Sn\ Cl_4 \underset{H_2O}{\overset{HCl}{\rightleftarrows}} (Sn\ Cl_6)^{-2}$$

Oxides formation:

Five oxides of carbon are known, CO, CO_2,C_3O_2 , C_5C_2, and $C_{12}O_9$, though only the first two are known. CO is a poisonous gas, sparingly soluble in ater. It is formed when carbon is burned in a limited amount of air. It is prepared by dehydrating formic acid with concentrated sulphuric acid.

$$H.COOH + H_2SO_4 \longrightarrow CO + H_2O$$

It is an important fuel because it burns in air and a considerable amount of heat evolves.

$$2CO + O_2 \longrightarrow 2CO_2 + 565\ Kg\ mol^{-1}$$

CO is a good reducing agent and can reduce many metal oxides.

$$Fe_2O_3 + 3\,CO \xrightarrow{\text{blast furnace}} 2\,Fe + 3CO_2$$

$$Cu + CO \rightarrow Cu + 2CO_2$$

Also carbon monoxide is an important ligand which can donate a share in a lone pair of electrons, and can form a coordinate bond with many transition metals and form carbonyl compounds (e.g. $Ni(CO)_4$).

C O or : C : O : (electronic structure of (CO)).

CO_2 is obtained by the action of dilute acid on carbonate, by burring carbon in excess of air and on an industrial scale by heating $CaCO_3$. Solid CO_2 sublimes directly to the vapor state. The gas is detected by its action on lime water.

$$\begin{tikzcd}
Ca(OH)_2 + CO_2 \arrow[r] & CaCO_3 + H_2O \arrow[d, "+ CO_2"] \\
& Ca(HCO_3)_2
\end{tikzcd}$$

CO_2 is acidic oxide and it is the anhydride of H_2CO_3 acid .

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

The acid is unstable and has never been isolated, but it gives arise to two series of salts, carbonates and bicarbonates .

$$\begin{tikzcd}
& NaHCO_3 \quad \text{(acid salt)} \\
NaOH + H_2CO_3 \arrow[ur] \arrow[dr] & \\
& Na_2CO_3 \quad \text{(normal salt)}
\end{tikzcd}$$

The structure of CO_2 is :

$$O = C = O \longleftrightarrow O^{+}\ C - O \longleftrightarrow O - C\ O^{+}$$

and the structure of carbonic acid:

H - O

C = O

H - O

Silicon have the oxides SiO and SiO_2. Germanium, tin and lead have the dioxides: GeO SnO_2 and PbO_2, and mono oxides GeO, SnO and PbO. Monoxides are slightly more basic and ionic than the corresponding higher oxides.

Lead forms also a mixed oxide Pb_3O_4 (red lead) which may be represented as $2PbO.PbO_2$ and used in paint.

<u>Occurrence and extraction of the elements</u>:

Carbon occurs mainly as coal and in crude oil and also as carbonates in rocks such as $CaCO_3$ and $MgCO_3$.

Germanium is found as traces in some silver and zinc ores, and in some coals.

Tin is mined as SnO_2, and lead is found as the ore galena PbS.

SiO_2, GeO_2 and SnO_2 may be reduced by carbon to the element. PbS may be roasted in air to give PbO

$$3\ PbS \xrightarrow{heat/air} PbS + PbO \longrightarrow Pb + SO_4$$

Group V The Nitrogen Group

Table (9)

Element		Electronic structure	Oxidation state
Nitrogen	N)	$2S^2 2P^3$	- III – II – I O I II III IV V
Phosphorus	P	$3S^2 3P^3$	III V
Arsenic	As	$3d^{10} 4S^2 4P^3$	III V
Antimony	Sb	$4d^{10} 5S^2 5P^3$	III V
Bismuth	Bi	$4F^{14} 5d^{10} 6S^2 6P^3$	III V

Electronic structure and oxidation states:

All the elements of the group have five electrons in their outer shell. They exhibit a maximum oxidation state of five towards oxygen by using all five outer electrons in forming bonds. Valencies of 3 and 5 are shown according to the inert pair effect of 5 electrons Table (9).

In case of nitrogen, a very wide range of oxidation states exists:

(-III) in ammonia NH_3

(-II) in hydrazine N_2H_4

(-I) in hydroxylamine NH_2OH .

(O) in nitrogen N_2 .

(+ I) in nitrouns oxide N_2O .

(+ II) in nitric oxide NO .

(+III) in nitrous acid HNO_2 .

(+IV) in nitrogen dioxide NO_2 .

(+V) in nitric acid HNO_3 .

Metallicl and nonmetallic character:

Within the group there is an increase in electro-positive (metallic) character. M and P are nonmetals. As and Sb are metalloids which show many metallic proporties, and Bi is a true metal. This is shown in the properties of their oxides. Normal oxides of N and P are strongly acidic, whilst As and Sb are amphoteric and Bi is largly basic.

Bond type:

The ionization energy required to produce M^{+5} is so high that it never occurs .

The sum of the first three ionization energies for Sb and Bi are just low enough for them to form M^{+3} ions, such as SbF and BiF_3. The M^{+3} ions are rapidly hydrolyzed in water to SbO^+ and BiO^+, but this change is reversed by adding 5M HCl .

$$Bi^{3+} \underset{HCl}{\overset{H_2O}{\rightleftharpoons}} BiO^+$$

Nitrogen can gain three electrons and form N^{-3} ion.This require higher energy. Generally in these elements, the bonds l are convalent.

Hydrides:

Elements of this group form volatile hydrides of formula MH_3. The ease of replacing the hydrigens by other grops decreases from MH_3 to BiH_3.

Ammonia is prepared in the labortory by heating an ammonium salt with sodium hydroxide.

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_3 + H_2$$

As the stability of hydrides decreases on descending the group, the hydrides of the other elements may be obtained in small amounts only.

The ammonia forms ammonium NH_4 salts very readily and utilizes the lone pair of electrons to form a coordinate bond as shown.

Electronic structure of 1S 2S 2P
nitrogen atom-ground state
Nitrogen having gaind a
share in three electrons
from three hydrogen
atoms in NH_3 molecule

SP^3 hybridization tetrah dral
with one position occupied
by a lone pair.

The structure of ammonia is tetrahydral with one position occupied by a lone pair.

Thus ammonia forms coordination complexes with metal ions from the Co, Ni, Cu and Zn groups which accords with its strong donor properties.

Ammonia is a weak base, and is hydrogen bonded in the liquid state. Hydrides of other elements are much weaker and not form hydrogen bonds. Hydrides of Nitrogen are:

Ammonia	NH_3	**(-III)**
Hydrazine	N_2H_4	**(- II)**
Hydroxylamine	NH_2OH	**(- I)**

Hydrazine is manufactured by oxidizing ammonia by sodium hypochlorite in dilute aqueous solution .

$$NH_3 + NaCl \rightleftharpoons NH_2\,Cl + NaOH$$

$$2NH_3 + Na_2Cl \rightleftharpoons NH_2 - NH_2 + NH_4Cl$$

Side reactions may occur are

$$N_2H_4 + 2NH_2Cl \longrightarrow N_2 + 2NH_4Cl$$

$$2NH_3 + 3NH_2 \longrightarrow N_2 + NH_4\,Cl$$

These side reactions are inhibited by using dilute solution and adding gelatin.

Hydrazine is covalent liquid and have strong reducing properties. It is basic and form two series of salts.

$$N_2H_4 + HX \longrightarrow N_2H_5^{+} + X^{-}$$

$$N_2H_4 + 2HX \longrightarrow N_2H_6^{2+} + 2X^{-}$$

The structure of hydrazine is similar to that of hydrogen peroxide.

H H

N N $\qquad$ **H – O – O – H**

H H

Hydrazine is powerful reducing agent only in alkaline solution but in acidic or neutral is only mild agent.

$$N_2H_4 + 2\ I_2 \longrightarrow 4\,HI + N_2$$

$$N_2H_4 + 2O_2 \longrightarrow 2H_2O_2 + N_2$$

When there are powerful reducing agent in acidic solution it is forced to react as an oxidizing agent .

$$N_2H_4 + Z_n + 2HCl \longrightarrow 2NH_3 + Z_n\,Cl_Z$$

The nitrogen atoms of hydrazine have a lone pair of electrons, which can form coordinate bonds to metal ions such as Ni^{+2} and Co^{2+}.

Hydroxyl amine, like hydrazine, is a weaker base than ammonia.

$$NH_2\,OH + HCl \longrightarrow (NH_3OH)\ Cl$$

$$NH_2\,HO + H_2SO_4 \longrightarrow (NH_3OH)\ HSO_4$$

Hydroxyl amine is mild reducing agent, but it can as an oxidizing agent. It can form coordinate bonds and complexes with metals.

Hydrazoic acid and azides:

Hydrazoic acid HN_3 is exploxidve when pure, but stable in aqueous solution.

It reacts with metals forming salts called azides, and nitrogen is evolved.

$$6\ HN_3 = 4\,Li \longrightarrow \underset{\text{Lithium azide}}{4LiN_3} + 2NH_3 + 2N_2$$

Sodium azide can be made by reaction between nitrous oxide and sodamid under anhydrous condition.

$$N_2O + NaNH_2 \longrightarrow NaN_3$$

For the N_3^- ion three resonance structures may be drawn .

$$:\overset{..}{N} = \overset{+}{N} = N: \qquad {}^{2-}:\overset{..}{N} \leftarrow \overset{+}{N} = N: \qquad :N = N \rightarrow N:^{-2}$$

For the acid MH_3, the resoaance structures allowed are:

$$\underset{H}{N} = N^{+} \rightleftarrows N:^{-} \qquad \underset{H}{N} \leftarrow N^{+} = N:$$

Halides:

For nitrogen; halides derived from HN_3 acid are:

FN_3, ClN_3, BrN_3 and IN_3. They are extremely unstable and explosive.

Trihalides: NF_3 is stable, but NCl_3 is explosive NBr_3 and NI_3 are unstable.

All trihalides are hydrolyzed with water;

$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3\ HOCl$$

But NF_3 is stable towards towards hydrolysis, unless sparked with water vapour:

$$NF_3 + 3H_2O \longrightarrow 6HF + N_2O_3$$

For the other elements of group V, all the possible trihalides are known, (phosphine PH_3 form salts with HCl while the other not).

Oxides and oxyacids of nitrogen:

Nitrogen forms a very wide range of oxides :

N_2O	Nitrous oxide
NO	Nitric oxide
N_2O_2	Nitrogen sesqui oxide
NO_2 , N_2O_4	Nitrogen dioxide
N_2O_5	Dinitrogen pentaoxide
NO_3 , N_2O_6	Nitrogen trioxide

(very unstable)

Nitrous oxide: It is stablel and relatively, unreactive gas. It prepared by heating NH_4NO_3 gently.

$$NH_4\,NO_3 \longrightarrow N_2O + 2\,H_2O$$

It is used in the preparation of azides.

$$N_2O + NaNH_2 \longrightarrow NaN_3 + H_2O$$

The N_2O molecules is linear, and there is resonance between two extreme structures:

$$:N \qquad N \qquad O: \longrightarrow \; :N \qquad N \rightarrow \qquad O:$$

Nlitrous oxide is anutral oxide and does not form hyponitrous acid with water ($H_2N_2O_2$).

<u>Nitric oxide</u>: it is colourless gas. It is used in preparing nitric acid by oxiding ammonia.

It is prepared in laboratory by the reduction of dilute nitric acid with copper, or nitrous acid with iodide ions.

$$3Cu + 8HNO_3 \longrightarrow 2NO + 3Cu(NO_3)_2 + 4H_2O$$

$$2HNO_2 + I^- + 2H^+ \longrightarrow 2NO + I_2 + 2H_2O$$

NO gas is paramagnetic since there is an odd electron in molecule. However, the liquid and solid states are diama-gnetic because dimers are formed and unpaired electrons cancels out.

N O
O . . . . N

<u>Nitrogen sesquioxide</u>: It is unstable gas and can be obtained by condensing NO and NO_2 together.

$$NO + NO_2 \xrightarrow{\text{condensation}} N_2O_3$$

It is an acdic oxide and is the anhydride of mitrous acid.

$$N_2O_3 + H_2O \rightleftharpoons 2HNO_2$$

The structure of N_2O_3 is not known, but the nitrite ion NO_2^- has a plane triangular structure, in which one position is occupoied by a lone pair.

O $\qquad\qquad$ O^-

$:N \longleftrightarrow N$

O^- O

Nitrous acid is unstable, and both HNO_2 and nitrites act as oxidizing agents with formation of N_2O or NO. But in the presence of powerful oxidizing agent they acts as reducing agents.

Nitrogen dioxide: is a red brown poisonous gas. It is produced by oxidizing NO in manufacture of nitric acid.

In laboratory, it prepared by heating lead nitrate.

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

The gas becomes dimers on condensation to the colorless dinitrogen tetra oxide .

$$2NO_2 \rightleftharpoons N_2O_4$$

NO_2 is an odd electron molecule, but the resonance energy is unsufficient to prevent dimerization. The dimer has no unpaired electrons, and the solid has been shown to have a planar structure.

O O

N N

O O

N_2O_4 reacts with water to give nitric and nitrous acids.

$$N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2$$

and HNO_2 decomposes into NO and NO_2

$$2HNO_2 \longrightarrow NO + NO_2 + H_2O$$

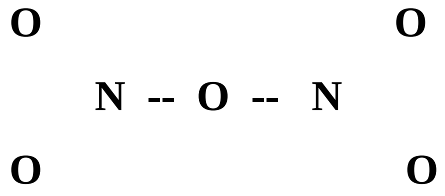
The NO_2 -N_2O_4 system is an oxidizing agent .

Dinitrogen pentaoxide :

It is the anhydride of HNO_3. It is prepared by dehydr-ating HNO_3 with P_2O_5.

$$2H\,NO_3 \xrightarrow{P_2O_5} H_2O + N_2O_5$$

It has the structure :



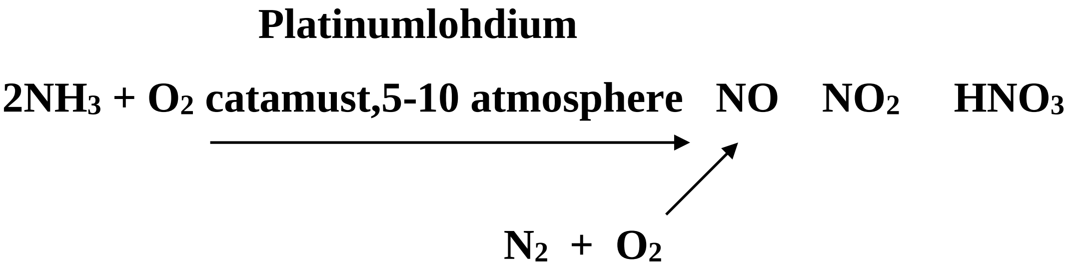
$$\begin{matrix} O & & & & O \\ & N & -- O -- & N & \\ O & & & & O \end{matrix}$$

HNO_3 is an exellent oxidizing agent when not and concentrated.

It is produced by the Haber-Bosch process.

$$N_2 + 3H_2 \xrightarrow{200\ \text{atoms}\ 500^oC} 2\,NH_3$$

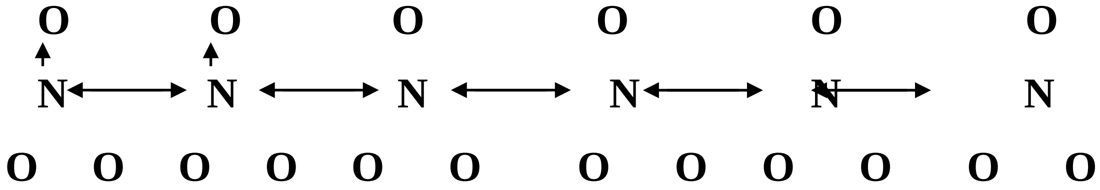
Haber – Bosch



$$2NH_3 + O_2 \xrightarrow[\text{catamust,5-10 atmosphere}]{\text{Platinumlohdium}} NO \quad NO_2 \quad HNO_3$$

$$N_2 + O_2 \nearrow NO$$

The nitrate ion is planar and may be represented as a resonance hybrid.



$$\overset{O}{\overset{\uparrow}{N}} \longleftrightarrow \overset{O}{\overset{\uparrow}{N}} \longleftrightarrow \overset{O}{N} \longleftrightarrow \overset{O}{N} \longleftrightarrow \overset{O}{N} \longleftrightarrow \overset{O}{N}$$

$$O \quad O \quad O \quad O \quad O \quad O \quad O \quad O \quad O \quad O \quad O \quad O$$

Reduction of nitrates in acid solution gives either NO_2 or NO, but in alkaline solutions ammonia is produced.

$$3Cu + HNO_3 \xrightarrow{\text{cold dilute } (<lM)} NO + Cu(NO_3)_2 + 4HO$$

$$Cu + 3HNO_3 \xrightarrow{\text{stronger acid}} NO_2 + Cu(NO_3)_2 + H_2O$$

$$Cu/Al/Zn\ (\text{alloy}) + NaOH \longrightarrow H$$

$$NO_3^- + H \longrightarrow NH_3$$

Oxides of Phosphorus , Arsenic and Bismuth

The oxides of the rest of the group are listed in the following table:

P_4O_6III	As_4O_6III	Sb_4O_6 III	BI_2O_3III
P_4O_7III V		$(SbO2)_n$III V	
P_4O_8			
P_4O_9			
P_4O_{10}	As_4O_{10} V	SbO_{10} V	

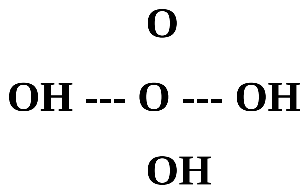
==

Fewer oxides are formed than are with nitrogen because of the inability of these elements to form double bonds.

<u>Oxyacids of phosphorous</u> :

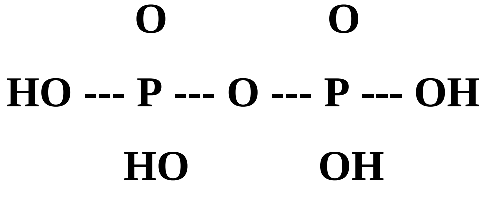
1)<u>Phosphoric acids</u>: (p is (+v) oxidation state, and compounds have oxidizing properties).

<u>Ortho phosphoric acid</u> : H_3PO_4



$$\begin{array}{c} \mathrm{O} \\ \mathrm{OH\ ---\ O\ ---\ OH} \\ \mathrm{OH} \end{array}$$

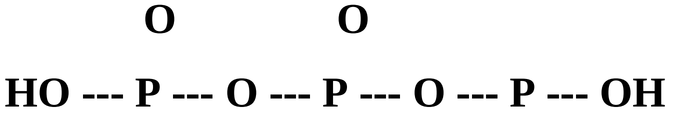
A very large number of phosphoric acids and their slats the phosphates arise by sharing oxygen atoms at 1 or 2 corners f PO_4, such as:



$$\begin{array}{ccccc} & \mathrm{O} & & \mathrm{O} & \\ \mathrm{HO\ ---} & \mathrm{P} & \mathrm{---\ O\ ---} & \mathrm{P} & \mathrm{---\ OH} \\ & \mathrm{HO} & & \mathrm{OH} & \end{array}$$

Pyro phosphoric acid

$H_4P_2O_7$



$$\begin{array}{ccccccc} & \mathrm{O} & & \mathrm{O} & & & \\ \mathrm{HO\ ---} & \mathrm{P} & \mathrm{---\ O\ ---} & \mathrm{P} & \mathrm{---\ O\ ---} & \mathrm{P} & \mathrm{---\ OH} \end{array}$$

tripoly phosphoric acid

OH OH $H_5P_3O_{10}$

H_3PO_4 is prepared from phosphate rock.

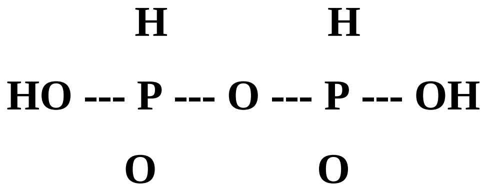
$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 2H_3PO_4 + 3CaSO_4$$

Also, by hydrolysis of P_4O_{10} or by the action of HNO_3 on phosphorous.

$$\left.\begin{array}{l} P_4O_{10}+H_2O \\ P + HNO_3 \end{array}\right. \quad H_3PO_4 \xrightarrow[\text{heat}]{\text{gentle}} \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7} \xrightarrow[\text{heat}]{\text{strong}} \underset{\text{meta phosphoric acid}}{(HPO_3)_n}$$

2)Phosphorous Acids:(P is (+III) oxidation state and have reducing properties).

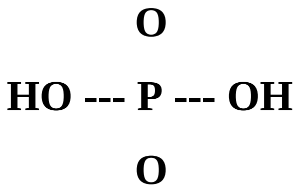
They are less well known and are basic:



$$\underset{O}{\overset{H}{HO - P}} - O - \underset{O}{\overset{H}{P - OH}}$$

Pyro phosphorous acid

$H_4P_2O_5$



$$HO - \underset{O}{\overset{O}{P}} - OH$$

ortho phosphoric acid

H_3PO_3

Phosphates are used as fertilizers (ammonium phosphate) super phosphate, and triple super phosphate.

$Ca_3(PO_4)_2 + H_2SO_4$ $[Ca_2H_2(PO_4)_2 + CaSO_4]$

Super phosphate

$Ca_3(PO_4)_2 + H_3SO_4$ $[Ca_2H_2(PO_4)_2]$ **triple**

Super phosphate

Occurrence and extraction :

Nitrogen comprises 78% of the earth's atmosphere and it also occurs as Nitrates ($NaNO_3$ is the most common).

It is obtained commercially by the fractional distill-ation of liquid air (N_2 b.pt.- 196°C).

In laboratory it is made by warming ammonium nitrite or by oxidizing ammonia with sodium or calcium hypo chlorite.

$$NH_4Cl + NaNO_2 \longrightarrow NaCl + NH_4NO_2 \longrightarrow N_2 + H_2O$$

$$4NH_3 + 3Ca(OCl)_2 \longrightarrow 3CaCl_2 + 6\,H_2O + 2N_2$$

Phosphorous is obtained by reduction of calcium phosphate with C or SiO_2 at 1300°C.

$$Ca_3PO_4 + SiO_2 \longrightarrow CaSiO_3 + P_4O_{10}$$

$$P_4O_{10} + C \longrightarrow P + CO$$

As Sb and Bi are obtained as metallurgical byproducts.

Group VI The Oxygen Group

Table (10)

Element		Electronic structure	Oxidation state
Oxygen	O	$2S^2 2P^3$	(- III),(– I)
Sulphur	S	$3S^2 3P^3$	(-II) (II),(IV),(VI)
Selenium	Se	$3d^{10} 4S^2 4P^3$	(-II) (II),(IV),(VI)
Tellurium	Te	$4d^{10} 5S^2 5P^3$	(II),(IV),(VI)
Polonium	Po	$4F^{14} 5d^{10} 6S^2 6P^3$	(II),(IV)

Metallic and Nonmetallic Character:

The first four elements are nonmetallic in character and the nonmetallic character is strongest in O and S, weaker in Se and Te, whilst Po, which is radioactive is markedly metallic.

Electronic structure and oxidations states:

The elements all have the electronic structure S^2P^4 and tend to attain an inert gas configuration by gaining two electrons forming M^{-2} ions, or by sharing two electrons thus forming two covalent bonds Table (10). Most metal oxides are ionic and contain O^{2-} ions because oxygen is highly electronegative. S^{-2}, Se^{-2}, and T^{2-} ions are less probable and compounds formed with S, Se and Te are 50 % ionic.

Also the elements form covalent compounds such as H_2O, Cl_2O, H_2S. Cl_2S .

Oxygen is never more than divalent because the second shell is limited to eight electrons and it requires too much energy to excite an electron into a higher shell.

Other elements S, Se, Te and Po have empty d orbital's which may be used for bonding and they can form four or six bonds by unpairing electrons.

S P d

Ground state

two unpaired electrons can form two bonds

Excited state

four unpaired electrons can form four bonds

Further
Excited state

six unpaired electrons can form six bonds

<u>Differences between oxygen and other element</u> :

1-Oxygen is more electronegative and more ionic in its compounds.

2-Hydrogen bonding is very important for oxygen compounds.

3-There is no higher valence states for oxygen because of the limitation of the second shell to eight electrons, whereas the other elements can use d orbital's and have higher valence states.

<u>Abundance and extraction:</u>

Oxygen is manufactured by the fractional distillation of liquid air.

It is prepared in the laboratory:

(1) by thermal decomposition of $KClO_4$ (with MO_2 as catalyst) .

$$KClO_4 \xrightarrow[MnO_2 \text{ catalyst}]{\text{heat}} KCl + O_2$$

(2) by the catalytic decomposition of hypo chlorites

$$2\,HOCl \xrightarrow{Co^{2+}} 2\,HCl \quad O_2$$

(3) by electrolysis of water acidified with trace of H_2SO_4

Large amounts of sulpher are obtained from oil refineries and natural gas plants.

H_2S is oxidized in air to give SO_2 which is subsequently reacted with H_2S giving S.

$$2H_2S \quad 3O_2 \longrightarrow 2SO_2 \quad 2H_2O$$

$$SO_2 \quad 2H_2S \longrightarrow 2H_2O \quad 3S$$

Se and Te occur among sulphide ore .

Molecular structure:

Oxygen is gas stable as a diatomic molecule, S, Se, Te and Po are solids at normal temperature and have complex structure. If oxygen molecule had two covalent bonds:

O = O : O : : O :

then all electrons would be paired and the molecule should be diamagnetic. Oxygen is paramagnetic and there for contains unpaired electrons.

The other form of oxygen is ozone O_3. Ozone decomposes slowly to oxygen. Pure liquid O_3 may be explosive because its decomposition into oxygen is exothermic.

$$2O_3 \longrightarrow 3O_2 \qquad H = 284 \text{ Kg/mole.}$$

Therefore oxygen needs energy to be changed to ozone. This energy could be obtained in many forms:

(i)Thermal energy: by heating oxygen to high temperatures in the electric are oven.

(ii)Photo energy: by the action of ultraviolet rays.

(iii)Electricenergy: by passing a silent electric discharge through oxygen gas.

(iv)Chemical energy: by decomposition of water with fluorine.

$$F_2 \quad H_2O \xrightarrow{\qquad} H_2F_2 + O + heat$$

$$3\ O \quad heat \xrightarrow{\qquad} O_3$$

The ozone molecule is diamagnetic and has an angular structure. Both O to O bonds have the same length (1.27A°) which is intermediate between the double bond distance(1.1 A°) and the single bond distance (1.4 A°). The molecule may be represented as a resonance hybrid

O +

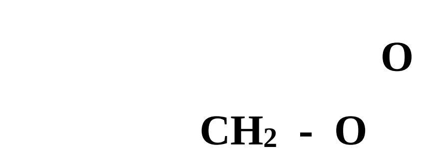
- O :O: ↔ O :O: -

O +

Ozone is highly reactive. Its higher reactive in compare-ison to oxygen is consistent with the higher energy content of ozone. It is a powerful oxidizing agent ($O_3 \rightarrow O_2 + O$)

$$2\ KIO_3 \quad H_2O \xrightarrow{\qquad} 2KOH + I_2 + O_2$$ **(detection Ozone).**

Ozone reacts with unsaturated organic compounds to form explosive compounds called ozonides; the latter are broken up with water giving interesting compounds H_2O_2 is evolved in most of the cases.



$$CH_2 = CH_2 + O_3 \xrightarrow{\qquad} \begin{array}{l} CH_2 - O \\ \qquad\quad O \\ CH_2 - O \end{array} \xrightarrow{H2O} H_2O_2 + 2HCHO$$

Hydrides:

The elements all form volatile bivalent hydrides H_2O, H_2S, H_2Se, H_2Te and H_2Po. These can be made from the elements, but normally H_2S

and H_2Te are obtained by the action of acids on metal sulphides selenides and telluride's.

$$FeS + H_2SO_4 \longrightarrow H_2S + FeSO_4$$

Hydrogen polonide has only been obtained in trace amounts from a mixture of Mg, Po and dilute acid.

The hydrides decrease in stability from H_2O to H_2Te, because the overlap with hydrogen become less favorably.

The H-O-H bond angle of 105 in water is in accordance with SP^3 hybridization of the oxygen atom, with slight distortion due to the two lone pairs of electrons.

In H_2Se and H_2Te the bond angles becomes close to 90° suggesting that almost pure p orbital's on Se and Te are used for bonding to hydrogen.

Volatility usually decreases as the atoms become larger and heavier. This trend is shown by the boiling points of H_2Se, H_2Te and H_2Po.

	Bond angle	Boiling point
H_2O	H-O-H = 105o	100
H_2S	H-S-H = 92o	-60
H_2Se	H-Se-H = 191o	-42
H_2Te		-2.3

==

Water has an abnormally low volatility because it is associated by means of hydrogen bonds in the solid and liquid states.

Oxygen and hydrogen also react to form hydrogen peroxide, H_2O_2, which is also obtained by the addition of an acid to a peroxide salt.

$$BaO_2 + H_2SO_4 \qquad BaSO_4 + H_2O_2$$

H_2O_2 can be commercially obtained by electrolysis of H_2SO_4 here by the resulted peroxy sulfuric acid reacts with water to give H_2O_2

$$2H_2SOP_4 \rightleftharpoons 2H^+ + 2HSO_4^-$$

$$2H^+ + 2e^- \xrightarrow{\text{cathode}} H_2$$

$$2HSO_4 \xrightarrow{\text{anode}} H_2S_2O_8 + 2e^-$$

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$$

$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H2O_2$$

H_2O_2 is a colorless liquid. It is a weak diprotic acid in water solution; one or two hydrogen's can be neutralized by NaOH to give sodium hydro peroxide $NaHO_2$ or sodium peroxide NaO_2 respectively. H_2O_2 could function either as oxidizing agent ($H_2O_2 \rightarrow H_2O + O$).

$$pbS + 4H_2O_2 \longrightarrow pbSO_4 + 4H_2O$$

$2KI + H_2O_2 + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O + I_2$ (detection of H_2O_2)

or as a reducing agent ($H_2O_2 + O \rightarrow H_2O + O_2$), $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$ and this reaction is used for quantitative determination of H_2O_2. H_2O_2 is sold under the name "perhydrol" and is used as a bleaching agent (soda bleach, NaOH + H_2O_2) for bleaching silk, wool and hair. It is also used as antiseptic in medicine for washing wounds, ears and teeth, as oxidizing agent, for restoring color of blackened lead paintings, as a preservative, as a fuel or propellant in submarine and rockets and as a source of oxygen for the combustion of liquid fuel.

Strength of H_2O_2 solution:

The strength of H_2O_2 solution is stated in terms of the volume of oxygen evolved on heating

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

The commercial preparations are "10,20,30 or 100 volumes" according as it gives off 10.,20,.30 or 100 times its volume of oxygen respectively. A" 10 volume "Solution would be or ugly 3% in strength. Exact calculation may be done as follows:

A"10volume"solution should give oxygen=10x 10 =100 ml.

As per equation: $2H_2O_2 \longrightarrow 2H_2O + O_2$, 68 g. H_2O_2 gives 22,400 ml of oxygen at N.T.P.

Wt of H_2O_2 that giving 100 ml oxygen at N.T.P.

would be $\frac{68}{22400} \times 100 = 0.03$ g i.e. the solution

would be 3.03 % .

Also we could find out that a "10 volume" H_2O_2 is 1.786 N H_2O_2. Also in H_2O_2 solution is "5.6 volume H_2O_2" solution.

Halides:

Compounds of oxygen and halogens will be described in group VII under halogen oxides.

Fluorine forms SF_6, SeF_6, and TeF_6. They are all colorless gases. SF_6 is inert and SeF_6 is slightly more reactive and TeF_6 is hydrolyzed by water.

$$TeF_6 + 6H_2O \longrightarrow 6HF + H_6TeO_6$$

Many tetra halides are known. In contrast to the relatively stable hexa fluorides, the tetra halides are very water sensitive.

$$SF_4 + H_2O \longrightarrow SOF_2 + 2HF$$

SCl_2 is the best known di halide.

Dimeric mono halides such as S_2F_2, Se_2Cl_2 and Se_2Br_2 are known.

Oxides:

Element	MO2	MO3	other	oxides
S	SO_2	SO_3	S_2O	S_2O_3
Se	SeO_2	SeO_3		TeO
Te	TeO_2	TeO_3		PoO
Po	PoO_2			

Dioxides MO_2 :

O:

So_2 is gas and its structure is :S

O:

SeO_2 is solid at room temperature. The gas has the same structure as SO_2, but solid forms infinite chains which are not planar.

O O O O

Se

Se Se

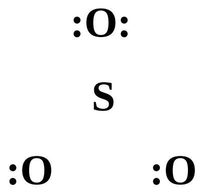
SO_2 dissolves in water and H_2SO_3 acid cannot be isolated SO_2 is important in the manufacture of sulphuric acid and for bleaching. It also acts as a mild reducing agent in acidic solution and as a strong reducing agent in alkaline solution. It has also been used as a non-aqueous solvent, but there is considerable doubt its postulated self ionization.

$$2\ SO_2 \rightarrow SO^{2+} + SO_3^{2-}$$

Trioxides MO_3:

SO_3 is the only important trioxide. It is manufactured by direct reaction of O_2 on SO_2. SO_3 reacts with water and forms H_2SO_4. Also SO_3

dissolves in H_2SO_4 to give fuming sulphuric acid. SO_3 gas has the structure:



$$\underset{:O\qquad :O}{\overset{:O:}{S}}$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

Other oxides :

S_2O it very reactive. It attacks metals and KOH It is formed when S and SO_2 are subjected to a silent electric discharge.

Oxy acids of sulphur:

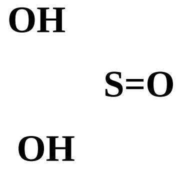
The oxy acids of sulphur are more numerous and important than those of Se and Te. Many of them are not exist as free acids, but are known as salts. These acids have S in the oxidation state (IV) or (VI). The acids are listed in five groups according to structural similarities.

(1) Sulphoxylic acid :

H_2SO_2 sulphoxylic acid

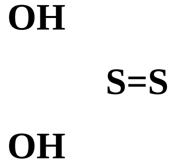
(2) Sulphurous acid series

H_2SO_3 sulphurous acid



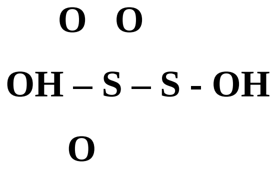
$$\underset{OH}{\overset{OH}{S=O}}$$

$H_2S_2O_2$ sulphurous acid



$$\underset{OH}{\overset{OH}{S=S}}$$

$H_2S_2O_5$ dior pyrosulporous acid



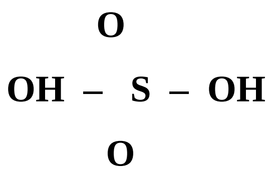
$$OH-\underset{O}{\overset{O}{S}}-\overset{O}{S}-OH$$

O O

$H_2O_2O_4$ dithionous acid $HO - S - S - OH$

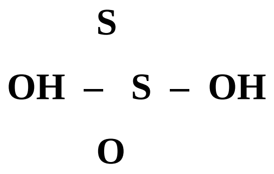
(3) Sulphuric acid series:

H_2SO_4 sulphuric acid



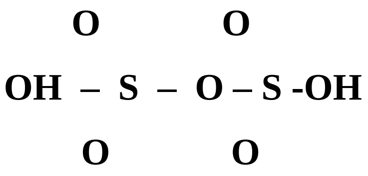
$$OH - \overset{O}{\underset{O}{S}} - OH$$

$H_2S_2O_3$ thio sulphuric acid



$$OH - \overset{S}{\underset{O}{S}} - OH$$

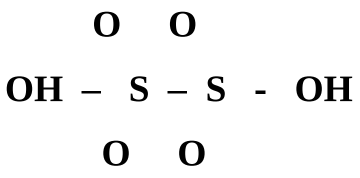
$H_2S_2O_7$ dior pyro sulphoric acid



$$OH - \overset{O}{\underset{O}{S}} - O - \overset{O}{\underset{O}{S}} - OH$$

(4) Thionic acid series:

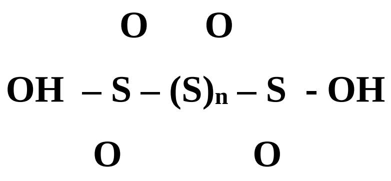
$H_2S_2O_6$ dithionic acid



$$OH - \overset{O}{\underset{O}{S}} - \overset{O}{\underset{O}{S}} - OH$$

$H_2S_nO_6$ poly thionic acid

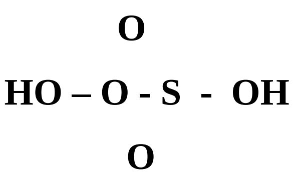
(n=1 – 12)



$$OH - \overset{O}{\underset{O}{S}} - (S)_n - \overset{O}{\underset{O}{S}} - OH$$

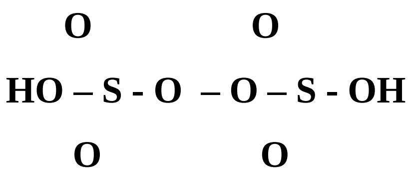
(5) Paroxo acid series:

H_2SO_5 peroxomono sulphuric acid



$$HO - O - \overset{O}{\underset{O}{S}} - OH$$

$H_2S_2O_6$ peroxodisulphuric



$$HO - \overset{O}{\underset{O}{S}} - O - O - \overset{O}{\underset{O}{S}} - OH$$

Oxidation-Reduction Reactions:

The term oxidation was originally applied to reactions in which substances combined with oxygen, and reduction was defined as the removal of oxygen from an oxygen-containing compound. Now oxidation and reduction are the processes in which an atom undergoes an algebraic increase or decrease in oxidation number respectively. On this bases, oxidation-reduction is involved in thereaction ,

$$S^{o} + O_2^{o} \longrightarrow SO^{2-}_2$$

i.e. sulfur is oxidized and oxygen is reduced. It is clear that neither oxidation nor reduction can occur alone; each process must occur to the same extent in a given reaction; and again, the sum of the oxidation numbers of any chemical species equals the charges on that species (zero if the entire compound is considered). In any reaction, the sum of the reactant species must equal the sum of the charges of the product species (zero for reactions involving only molecules).

Since one substance cannot be reduced unless another is simultaneously oxidized, the material that is reduced is responsible for the oxidation; therefore it is called the oxidizing agent or oxidant. The material that is itself oxidized is called the reducing agent or reluctant. Therefore,

S^{o} (oxidized, reducing agent)+O^{o}_2 (reduced, oxidizing agent)

$$\longrightarrow \quad S^{4+} O^{2-}_2$$

There are two methods, commonly used to balance oxidation-reduction equations:

(a) <u>The oxidation-number method</u>:

The unbalanced expression for the reaction of HNO_3 with H_2S is :

$$HNO_3 + H_2S \longrightarrow NO + S + H_2O$$

1- Oxidation numbers of the atoms in the equation are determined, thus:

$$H\overset{+5}{N}O_3 \quad H_2S^{2-} \longrightarrow \overset{2+}{N}O + S^{o} + H_2O$$

2- Coefficients are placed before the appropriate formulas so that the total decrease in oxidation number equals the total increase in that number, i.e. Nitrogen is reduced (5+ to 2+ , a decreases of 3) and sulfur is oxidized (2- to O, an increase of 2). Thus it is necessary that 2 molecules of HNO_3 and 2 molecules of NO, as well as 3 molecules of H_2S and 3 atoms of S , be indicated. Thus the total increase in oxidation number will be 6 and will equal the total decrease of 6.

$$2\,HNO_3 + 3H_2S \longrightarrow 2\,NO + 3S + H_2O$$

3- Balancing is completed by inspection. Now 8 hydrogen atoms on the left, therefore $4H_2O$ molecules must be indicated on the right.

$$2\,HNO_3 + 3\,H_2S \longrightarrow 2\,NO + 3S + 4H_2O$$

Finally, balanced equation should be checked to ensure that there are as many atoms of each element on the left as there are on the right.

The method may be used to balance Net Ionic Equations, in which only ions and molecules that actually take past in the reaction are shown. e.g. K^+ ion does not take part in the reaction of $KClO_3$ with I_2 and is not shown in the equation. The steps in balancing are:

1- $H_2O + \overset{0+}{I_2} + \overset{5+}{Cl}O_3^- \longrightarrow \overset{+5}{I}0_3^- + \overset{-1}{Cl} + H^+$

2- Each iodine atom undergoes an increase of 5 (from 0 to 5). The increase in oxidation number is 10 (two iodine atoms). Chlorine undergoes a decease of 6 (from 5 to -1).

The lowest common multiple of 6 and 10 is 30. Therefore $3I_2$, molecules must be indicated (a Total increase of 30) and $5ClO_3^-$ ions are needed (a total decrease of 30). The coefficients of the products, 10^{-3} and Cl^-, fellow from this assignment.

$$H_2O + 3I_2 + 5ClO_3^- \longrightarrow 6\,IO^-_3 + 5Cl^- + H^+$$

If H_2O is ignored, there are now 15 oxygen atoms on the left and 18 oxygen atoms on the right. To make up 3 oxygen atoms on the left, we must indicate $3H_2O$ molecules, thus the coefficients of H^+ must be 6 to balance the hydrogen's of the H_2O molecules.

$$3H_2 + 3I_2 + 5ClO^-_3 \longrightarrow 6lO_3^- + 5Cl^- + 6H^+$$

An ionic equation must indicate charge balance as well as mass balance. Since the algebraic sum right (5-), the equation is balanced. Electron transfer reactions are examples of oxidation-reduction e.g. the reaction of Na and Cl_2, a Na atom loses it valence electron to a Cl^-atom.

$$2\,\overset{o}{Na} + \overset{o}{Cl_2} \longrightarrow 2\,\overset{I+}{Na} + 2\,\overset{-1}{Cl^-}$$

Hence, electron loss represents a type of oxidation and electron gain a type of reduction. This equation can be divided into two partial equations that represent half reaction.

Oxidation : $2\,Na \longrightarrow 2\,Na + 2e^-$

Reduction : $2e^- + Cl_2 \longrightarrow 2Cl^-$

(b)The ion-electron method of balancing oxidation Reduction Equations :

These employ partial equations and only ions that are involved in the reaction are shown: Unionized (or slightly ionized) species and

insoluble substances that take parting the reaction are written in molecular form. The steps of the method can be illustrated using the reaction between $Cr_2O_7^-$ ion and Cl^- ion.

1- Two skeleton partial equations for the half reactions are written with the central element of each partial equation balanced.

$$Cr_2O_7^{2-} \longrightarrow 2\,Cr^{3+} \quad \& \quad 2Cl \longrightarrow Cl_2$$

2- The hydrogen and oxygen atoms are then balanced. Since this reaction occurs in acid medium, H^+ and H_2O can be added where needed. For each O-atom that is needed, one H_2O molecules is added to the side of the partial equation that is deficient. The hydrogen is then brought into balance by the addition of $2H^+$ to the opposite side. Thus 7 oxygen must be added to the right side of the partial equation, the second partial equation is already in material balance.

$$Cr_2O^{2-}{}_7 + 14\,H^+ \longrightarrow 2Cr^{3+} + 7H_2O \ \& \ 2Cl^- \longrightarrow Cl_2$$

3- The partial equations are then electrically balanced. In the first equation the net charge is 12+ on the left side of the equation (14+ and 2-) and 6+ on the right side. Six electrons must be added to the left. The second equation is balanced electrically be the addition of 2 electrons to the right.

$$Cr_2O^{2-}{}_7 + 14\,H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \ \& \ 2Cl \longrightarrow Cl_2 + 2e^-$$

4- The number of electrons lost must equal the number of electrons gained, therefore, the oxidation equation is multiplied by 3.

$$Cr_2O^{2-}{}_7 + 14\,H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \ \& \ 6Cl \longrightarrow Cl_2 + 6e^-$$

5- Addition of the two partial equations gives the final equation.

$$Cr_2O^{2-}{}_7 + 14\,H^+ + 6e^- \longrightarrow 2Cr^{3+} + 3C^- + 7H_2O$$

These steps are illustrated for the reaction in which As_4O_6 reacts with MnO^-_4 to produce H_3AsO_4 and Mn^{2+}.

1- $MnO^-_4 \longrightarrow Mn^{2+}$ & $As_4O_6 \longrightarrow 4H_3AsO_4$

2- To the first equation $4H_2O$ are added to the right side and $8H^+$ to the left side. In the second equation, 10 H_2O must be added to the left side to make up the needed 10 oxygen (16-6=10)., In the second equation we have now 20 hydrogen atoms on the left (10 x 2 = 20) and 12 (4 x 3 = 12) on the right, therefore $8H^+$ must be added to the right side of equation 2.

$$MnO^-_4 + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

$$As_4O_6 + 10H_2O \longrightarrow 4H_3AsO_4 + 8H^+$$

3- To balance the net charges, electrons are added.

$$MnO^-_4 + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$As_4O_6 + 10H_2O \longrightarrow 4H_3AsO_4 + 8H^+ + 8e^-$$

4- Now the first equation must be multiplied through by 8 and the second by 5.

$$8\,MnO^-_4 + 64H^+ + 40e- \longrightarrow 8Mn^{2+} + 32H_2O$$

$$As_4O_6 + 50H_2O \longrightarrow 20H_3AsO_4 + 40H^+ + 40e^-$$

5- When these two partial equations are added, water molecules and hydrogen ions must be cancelled as well as electrons.

$$8\,MnO^-_4 + 5As_4O_6 + 24H^+ + 18H_2O \longrightarrow 9Mn^{2+} + 20H_3AsO_4$$

In alkaline medium, equations are balanced in a manner slightly different from those that occur in acidic solution. All the steps are the same except the second one; H^+ cannot be used to balance equations for alkaline reactions. e.g., the reaction between MnO^-_4 and N_2H_4 in alkaline solution.

1- $MnO^-_4 \longrightarrow MnO_2$ & $N_2H_4 \longrightarrow N_2$

2- For reactions occurring in alkaline solution, OH^- and H_2O are used to balance oxygen and hydrogen added to the side of the equation that is deficient and one H_2O molecule is added to the opposite side. For each hydrogen that is needed, one H_2O molecule is added to the side that is deficient, and one OH^- ion is added to the opposite side.

In the first equation, the right side is deficient by 2 oxygen atoms, we add, therefore, 4 OH^- to the right side and $2H_2O$ to the left.

$$MnO_4^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$$

In the second equation, we must add 4 hydrogen atoms to the right side. For each H-atom needed we add one H_2O to the side deficient in hydrogen and one OH^- to the opposite side. In the present case, we add $4H_2O$ to the right side and $4OH^-$ to the left side to make up the 4 hydrogen atoms needed on the right.

$$N_2H_4 + 4OH^- \longrightarrow N_2 + 4H_2O$$

3- Electrons are added to effect charge balance.

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

$$N_2O_4 + 4OH^- \longrightarrow N_2 + 4H_2O + 4e^-$$

The lowest common multiple of 3 and 4 is 2. Therefore,

4- The first equation is multiplied by through by 4 and the second by 3 so that the number of electrons gained equals the number lost.

$$MnO_4^- + SH_2O + 12e^- \longrightarrow 4MnO_2 + 16OH^-$$

$$3N_2H_4 + 12OH^- \longrightarrow 3N_2 + 12H_2O + 12e^-$$

5- Addition of partial equations, with cancellation of OH^- ions and H_2O molecules as well as electrons, gives the final equation.

$$4MNO_4^- + 3N_2H_4 \longrightarrow MnO_2 + 4H_2O + 4OH^- + 3N_2$$

As a final example, consider the following skeleton equation for a reaction in alkaline solution .

$$Br_2 \longrightarrow BrO^-_3 + Br^-$$

In this reaction the same substance, Br_2 is both oxidized and reduced. Such reactions are called disprop-ortionateness or auto-oxidation-reduction reactions.

1- $Br_2 \longrightarrow 2\,BrO_3^-$

$Br_2 \longrightarrow 2Br^-$

2- $Br_2 + 12\ OH^- \longrightarrow 2BrO_3^- + 6H_2O$

$Br_2 \longrightarrow 2Br^-$

3- $Br_2 + 12\ OH^- \longrightarrow 2BrO_3^- + 6H_2O + 10e^-$

$Br_2 + 2e^- \longrightarrow 2\,Br^-$

4- $Br_2 + 12\ OH^- \longrightarrow 2BrO_3^- + 6H_2O + 10e^-$

$5Br_2 + 10e^- \longrightarrow 10\,Br^-$

5- $6Br_2 + 12\,OH^- \longrightarrow 2BrO_3^- + 10Br^- + 6H_2O$

However most oxidation–reduction reactions may be balanced by the ion electron method which is especially convenient for electrochemical reactions and reactions of ions in water solution. Half reactions cannot occur alone and partial equations do not represent complete chemical changes. Even ion the electrochemical cells, where the two half reactions take place at different electrodes, the two half reactions always occur simultaneously.

Group VII The Halogens

Table (11):

Element		**Electronic configuration**	**Oxidation states**
Fluorine	**F**	$2S^22P^5$	**-I**
Chlorine	**Cl**	$3S^23P^5$	**-I,+I,III,+IV,+V,VI,+VII**
Bromine	**Br**	$3d^{10}4S^24P^5$	**-I,+I,+III,IV,+V,IV**
Iodine	**I**	$4d^{10}5S^25P^5$	**-I,+I,III,+IV,+V,VI,+VII**
Astatine	**At**	$4F^{14}5d^{10}6S^26P^5$	

Electronic structure and oxidation states:

The halogens show very close group similarities. The elements all have seven electrons in their outer shell, and they either gain an electron and form (X^- ion) or form covalent bond in order to complete their octet.

Fluorine is always univalent and has the oxidation number (-1). It is the most electronegative element. Other elements have oxidation number (+I), (+III), (+V) and (+VII). Table (11).

General properties:

*** The melting and boiling points are increased with increased atomic number for these elements.**

*** Fluorine and chlorine are gases, bromine is liquid and iodine is solid.**

*** The elements all form diatomic molecules.**

*** The ionization energies of the halogens are all very high, because of the little tendency to lose the electrons. The value for F is the highest, and for I is the lowest.**

*** The halogen molecules are all colored. F_2 gas is yellow, and I_2 gas is violet.**

*** Halogens act as oxidizing agents, since they have tendency to gain electrons. The oxidizing power decreases on descending the group. F_2 is so strong as an oxidizing agent that it oxidizes water to oxygen.**

$$F_2 + H_2O \longrightarrow 2H^+ + 2F^- + 1/2\ O_2$$

The reaction is exothermic and spontaneous. For Cl_2 the following reaction occurs.

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

I_2 is very weak oxidizing agent

$$I_2 + H_2O \rightleftharpoons 2H^+ + 2I^- + 1/2\ O_2$$

The reaction is endothermic and the reverse process occurs and oxygen oxidizes iodide ions to iodine.

Reactivity of the elements :

Fluorine is the most reactive of the elements in the periodic table. It reacts with all elements except the noble gases He, Ne, and Ar.

The reactivity of the halogens decrease with increasing atomic number.

Chlorine and bromine react with most of the elements, though less vigorously. Iodine is less reactive and does not combine with some elements such as S and Se.

The great reactivity of fluorine is due to the low energy of the F-F bond, (the extremely high oxidizing power, the small size of the atoms or ions and the high electro negativity).

Hydrogen halides:

The halogens all react with hydrogen and form HX hydrides. Whilst the reaction of hydrogen with fluorine is quite violent, the reaction with iodine is slow at room temperature.

HF and HCl are usually prepared by treatment of salts with strong sulphuric acid.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

In the gaseous state, the hydrides are essentially covalent, but in aqueous solutions they ionize and HCl, HBr and HI function as strong acids.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

Liquid HF has been used as a non-aqueous solvent It undergoes self ionization.

$$2HF \rightleftharpoons H_2F^+ + F^-$$

Halogen oxides:

Most of the halogen oxides are unstable. The iodine oxides are the most stable, then chlorine oxides and the bromine oxides all decompose below room temperature. The higher oxidation states are more stable than the lower states. The bonds are largely covalent because of the small difference in electro negativity between the halogens and oxygen fluorine form binary compounds (fluorides of oxygen) because fluorine is more electronegative than oxygen. Compounds of the halogens with oxygen are shown in the following table.

	MX_2	M_2X_2	M_2X	Others
Fluorides	OF_2	O_2F_2		O_4F_2
	Cl_2O		ClO_2	Cl_2O_6 , Cl_2O_7
Oxides	Br_2O		BrO_2	BrO_3

I_2O_4 , I_4O_9 , I_2O_5

==

Oxyacids:

Chlorine, bromine and iodine form four series with formulae :

HOX	**hypohalous acids**
HXO_2	**halous acids**
HXO_3	**halic acids**
HXO_4	**perhalic acids**

Hlous acids: HOX

The hypogalous cids HOCl, HOBr and HOI are all weak acids and only exist in aqueous solutions. Hypochlorous acid is the most stable and its sodium salt NaOCl (sodium hypochlorite) is used for bleaching cotton fabric.

Halous acids : HXO_2

The only halous acid known is $HCLO_2$ (chlorous acid). It exists only in solution. It is a strong acid than HOCl.

Halic acids: HXO_3

$HClO_3$ and $HBrO_3$ are known in solution, but HIO_3 exists as white solid. The acids all are strong oxidizing agents and strong acids.

Chlorates may be made by the action of Cl_2 on NaOH

$$6HaOH + 3Cl_2 \xrightarrow{heat} NaClO_3 + 5NaCl + 3H_2O$$

Perhalic acids: HXO_4

$HClO_4$ and HIO_4 and their salts are well known; perbromates (BrO_4^-) have only recently been prepared.

$HClO_4$ is one of the strongest acids, and is a powerful oxidizing agent. It can be made from NH_4ClO_4 and dilute nitric acid or from $NaClO_4$ and concentrated hydrochloric acid.

$NaClO_4$ is made by electrolysing aqueous $NaClO_3$, using smooth platinum electrodes to give a high oxygen over potential to prevent the electrolysis of water.

$$NaClO_3 + H_2O \xrightarrow{\text{electrolysis}} NaClO_4 + H_2O$$

Group VIII The Noble Gases

The outstanding characteristics of the noble gases is their low order of chemical reactivity. Until 1962, no true compounds of these elements were known and hence they were called "inert gases". Since 1962, approximately 25 compounds of the heavier elements of this group have been prepared.

The noble gases or zero group of the periodic table consists of six elements, helium, neon, argon exception of radon, which is obtained from radioactive disintegration, are contained in atmosphere, thought only in very minute quantities, and therefore called the rare gases of the atmosphere.

Table (12) : Some properties of Noble gases :

Element	Symbol	Electronic structure	First I.P. v.	M.P °C	B.P. °C
Helium	He		24.6	-268.9	
Neon	Ne	$[He]2S^22P^6$	21.6	-248.6	-246.0
Argon	Ar	$[Ne]3S^23P^6$	15.7	-189.4	-185.9
Krypton	Kr	$[Ar]3d^{10}4S^24P^6$	14.0	-157.2	-153.2
Xenon	Xe	$[Kre]4d^{10}5S_25P^6$	1201	-111.9	-108.1
Radon	Rn	$[Xe]4f^{14}5d^{10}6S^22P^6$	10.8	- 71.0	- 62.0

Electronic structure and general properties :

The two electrons of He form a complete shell, and all the other inert gases have an octet of electrons in their outer shell. The electronic configuration is related to their chemical in activity. These atoms have an electron affinity near to zero and have ionization potentials than any other elements. Consequently they do not gain or lose electrons under normal conditions and do not form many bonds. Thus they exist as single atoms (mono atomic molecules. The only forces between these atoms are very weak Van der Waals forces and so the melting points and boiling points are very low, (table 12). With increasing atomic number, the atomic size increase and the outer electrons become slightly less tightly held. Therefore, the ionization potential decreases regularly from He to Rn. This factor (i.e. increasing size of electron cloud), also accounts for increasing strength of Van der Waals forces, and consequently the increasing melting point and boiling point from He to Rn. However, He, has the lowest boiling point of any known substance, this is because there are no strong interatomic forces; only the weakest Van der Waals forces operate which hold atoms together.

Compounds of the Noble Gases:

Considerable efforts have been made to find evidence for compounds formation by the noble gases.

(1) Under excited conditions:

$$\overset{1S^2}{\text{He-ground state}} \quad (\text{ 460 Kcal }) \rightarrow \overset{1S^1 \quad 2S^1}{\text{He-excited state}}$$

These high energy conditions are only realized spectra-scopically under conditions of electrical discharge, or electron bombardment. In a discharge tube He^{+2} , HeH and HeH^{2+} have been observed, but only survive momentarily. Metal electrodes in discharge tubes absorb inert gases to form Pt_3 He, FeHe and FeAr, perhaps as interstitial compounds.

(2) By coordination:

Noble gas atoms may donate an electron pair to suitable acceptor. Thermal analysis of Ar with BF_3 was said to give peaks in the freezing point curves corresponding to 1Ar: 1, 2,3,6,8 and16 BF_3 (i.e. Ar: → BF_3), but this work was not repeatable by other workers.

(3) By dipole/induced dipole attractions :

The noble gas atoms may be polarized by a strong dipole on other molecules and thus possess a weak induced dipole of their own. The solubility of the noble gases in water is high and increases with increased size. This is probably because the larger atoms are more easily polarized by the surrounding water molecules. Certain derivatives of phenol, Kr $(phenol)_2$, Xe $(phenol)_2$ and Rn $(phenol)_2$ may have this sort of attraction.

(4) Clathrate compounds:

Until recently, the only well-established "compounds" of the noble gases were those in which the gases are trapped in cavities in the crystal lattice of other compounds. If quinol (1,4 di hydroxy benzene, HO OH) is crystallized in the presence of the heavier noble gases under a pressure of 10-40 atmospheres, the gas becomes trapped in cavities of about 4A^{o} diameter in the ß-quinol structure. When the clatherate is dissolved, e.g. in ethanol, the hydrogen bonded arrangement of ß-quinol breaks down and the inert gas escapes. Other small molecules such as O_2, SO_2, MeCN and CH_3OH form clathrates as well as Ar, Kr and Ke. The absence of He and Ne compounds occurs because they are too small and can escape

from the cavities. The composition of these compounds corresponds to 3 quinol trapped molecule, though normally all the cavities are not filled.

The gases Ar, Kr and Xe may be trapped in cavities in a similar way when water solidifies in the presence of these noble gases. The So-called inert gas hydrates have formula approximating to $6H_2O$: a gas atom.

Clathrates are useful in the separation of noble gases, e.g. Ne can be separated from Ar, Kr and Xe, because Ne is the only gases that doest from a clathcate with quinol. Kr-85 chathrate provides a safe and useful source of ß-radiations while Xe-133 clathrates provides a compact source for ß-radiations. In addition, clathrates are a convenient from of handling, processing and shipping of rare gas isotopes.

However, the first chemical reaction of a noble gas to be observed, the reaction of Xe with PtF_6 was reported by Bartlett in 1962. P_tF_6 is a powerful oxidizing agent, it reacts with oxygen to give oxygen to give oxygen hexafloroplatinate (V)$[O^+_2]$ $[P_tF_6]^-$. Since the first ionization potential of molecular O_2 is 12.2eV is close to that of Xe (12.1 eV), Bartlett, reasoned that Xe should react with PtF_6 giving the red crystalline solid consisting of xenon haxafluroplatinate (V) $[Xe^+]$ $[P_tF_6^-]$ and other compounds.

The best characterized noble-gas compounds are the xenon fluorides, XeF_2, XeF_4 and XeF_4 with oxidation states +2, +4, and +6 respectively. These are prepared by direct reaction of Xe and Fe using suitable proportion of Xe and F_2.

$$Xe + F_2 \longrightarrow XeF_2$$

$$XeF_2 + F_2 \longrightarrow XeF_4$$

$$XeF_4 + F_2 \longrightarrow XeF_6$$

There are unconfirmed reports of XeF_8. The fluorides react quantitatively with hydrogen:

$$XeF_2 + H_2 \longrightarrow Xe + 2HF$$

$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF$$

$$XeF_6 + 3H_2 \longrightarrow Xe + 6HF$$

Oxygen-containing compounds of Xe are produced by reactions of xenon fluorides with water. Partial hydrolysis of XeF_6 yields xenon oxytetrafluride $XeOF_4$, a colorless liquid.

$$XeF_{6(S)} + H_2O \longrightarrow XeOF_{4(L)} + 2HF_{(g)}$$

Complete hydrolysis of XeF_6 or hydrolysis of $XeOF_4$ produces a solution that yields XeO_3 upon evaporation.

$$XeF_{O(S)} + 3H_2O \longrightarrow XeO_{3(aq)} + 6HF_{(g)}$$

$$XeOF_{4(L)} + 2H_2O \longrightarrow XeO_{3(aq)} + 4HF_{(aq)}$$

Also, XeO_4 and also sodium xenate $Na_4XeO_6.8H_2O$ with oxidation number of Xe as 8 are known.

The order of decreasing reactivity of the group elements (increasing I.P.) is Rn > Xe > Kr > Ar > Ne > He. Thus, Rn should be the most reactive noble gas and He is the least. There is evidence that Rn reacts with F_2; however, the radioactive disintegration of Rn-isotopes makes the chemistry of Rn difficult to assess.

Uses of noble gases:

Helium is used in lighter than air crafts, and in low temperature work. Being noninflammable and less diffusible over hydrogen, it is used for filling airships and balloons. A mixture of (O_2 + He) is used for respiration in deep sea diving in preference to air. The reason is that

Nitrogen of air is highly soluble in blood under high pressure below, and on release of pressure, as the diver comes to the top, it evaporates suddenly causing great pain. The above mixture being less soluble does not cause this trouble.

Neon signs (sign advertising are made from discharge tubes containing. Neon gas at low pressure.

Argon is used to fill electric light bulbs, the gas does not react with the hot filament but rather conducts heat away from its, thus prolonging its life.

Argon is also used as an inert atmosphere in welding and high temperature metallurgical processes; the gas protects the hot metals from air oxidation. Radon has been used as a source of α-particles in cancer therapy.