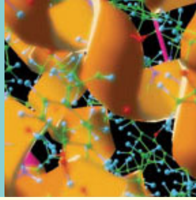
Bioenergetics

Bioenergetics

- Study of the energy changes accompanying biochemical reactions
  - **Adenosine Tris Phosphate, ATP**
  - **Free energy change, ΔG**
  - **Equilibrium constant, Keq**

- Study of generation, storage and utilization of energy in living system
  - **Caloric value of Carbohydrates, fats and proteins**
  - **Basal metabolic rate**
  - **Respiratory Quotient**

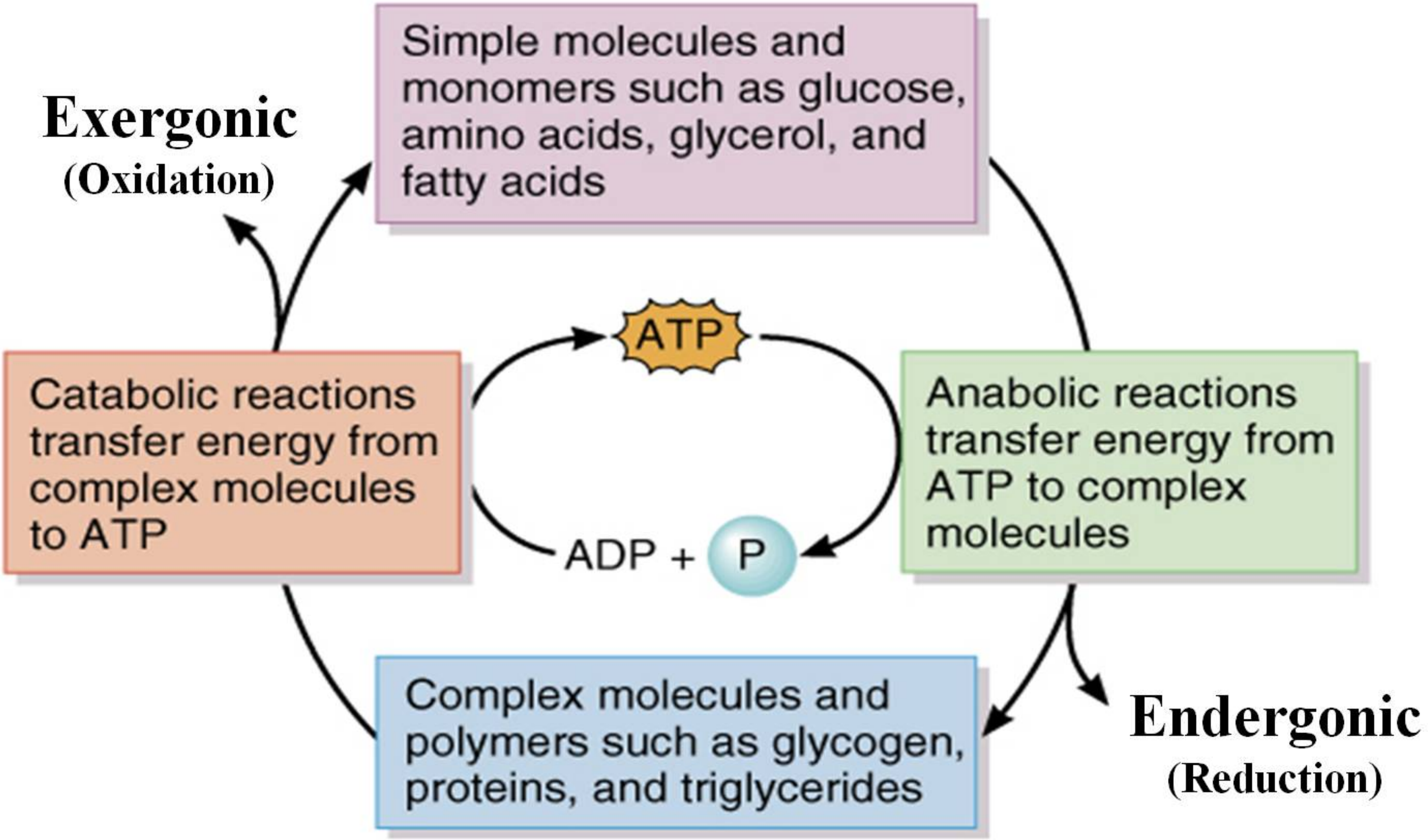
ATP as energy currency



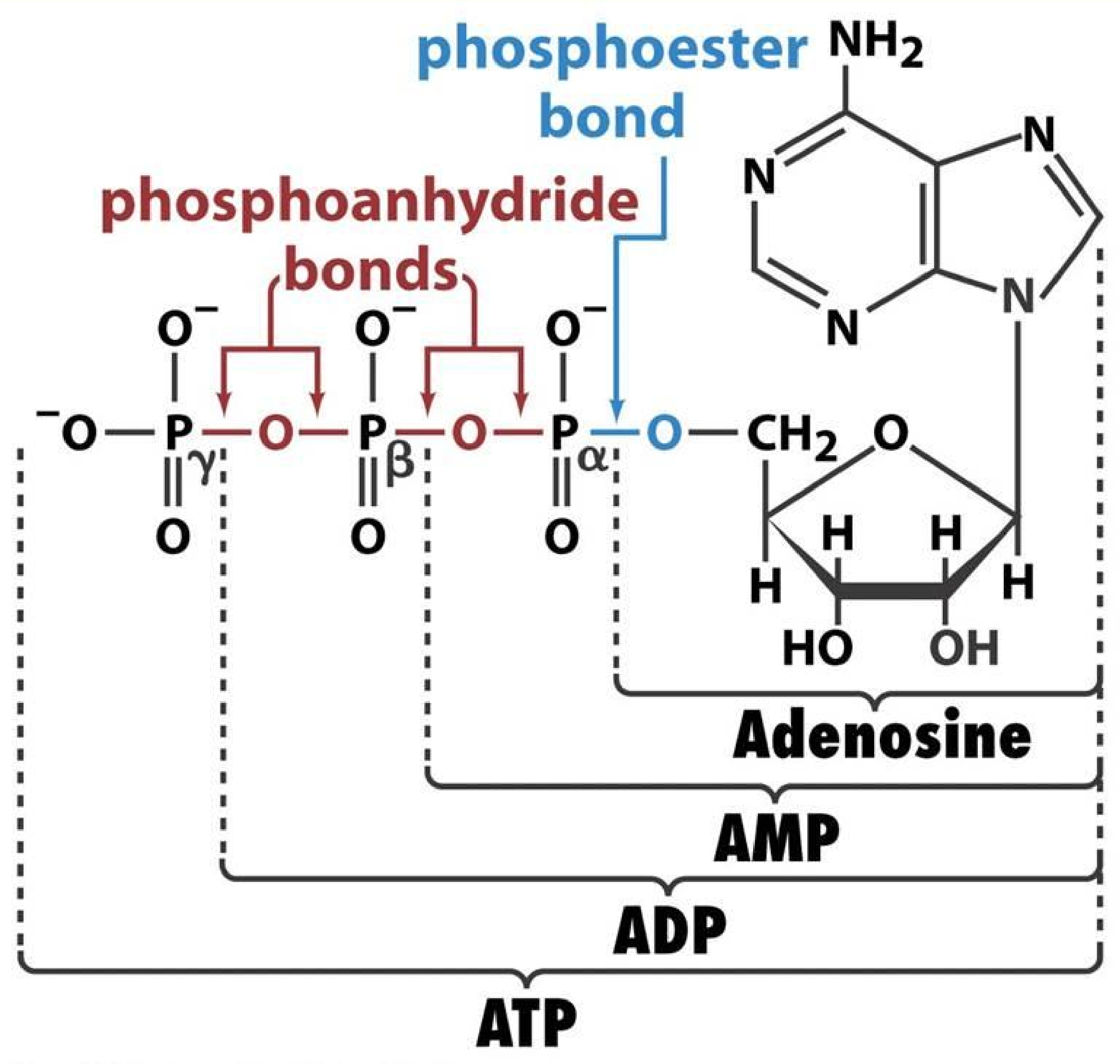
ATP acts as currency of energy

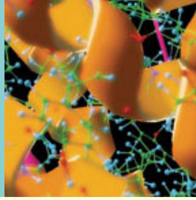
- **Energy is released from catabolic reactions**
- **Energy is stored in the form of ATP**
- **Energy in ATP is utilized for anabolic reactions**
- **ATP links catabolic and anabolic reactions**

Two Basic Kinds of Chemical Reactions found in Biological System



"High energy" bond





Phosphoanhydride bond (formed between two phosphoric acids) is **high energy bond.**

Phosphoester bond (between alcohol and phosphoric acid) is low energy bond.

The two terminal phosphate bonds (beta and gamma) in ATP can be hydrolyzed to release energy

$$ATP \rightarrow ADP + P_i$$

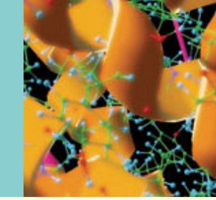
$$ADP \rightarrow AMP + P_i$$

Adenylate Kinase

$$2\ ADP \leftrightarrow ATP + AMP$$

ATP: complete with energy

AMP: deplete of energy



- **ATP** serves as an **energy source**

  Hydrolytic **cleavage** of one or both of the "high energy" bonds of ATP is **coupled** to an energy-requiring (non-spontaneous) reaction

- **AMP** functions as an **energy sensor** & **regulator** of metabolism

  When ATP production does not keep up with needs, a higher portion of a cell's adenine nucleotide pool is AMP. AMP stimulates metabolic pathways that produce ATP by activating the enzyme AMP-Activated Protein Kinase

Free Energy Change

$$S \rightleftharpoons P$$

(G_S) (G_P)

Free energy (G) -amount of energy present in a molecule

Free energy change, $\Delta G = G_P - G_S$

(depends on the concentration of S and P)

Spontaneous reaction: ΔG = negative

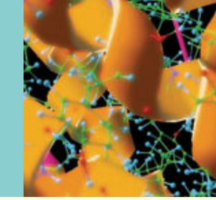
Standard free energy change

ΔG^0 =free energy change calculated at standard conditions

i.e., 1 M of substrates and products

Therefore, ΔG^o is a constant for a given reaction whereas ΔG is not because the latter varies depending on the concentrations of the substrates and products

Equilibrium constant



$$S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P$$

Law of mass action: V_F α [S] V_R α [P]

$V_F = k_1$ [S] $V_R = k_2$ [P]

k_1 = rate constant for the forward reaction

k_2 = rate constant for the reverse reaction

Therefore, at equilibrium, $V_F = V_R$

i.e., k_1 [S] = k_2 [P]

Equilibrium constant (K_{eq}) is expressed as = k1/k2 = [P]/[S]

K_{eq} is a constant for a given reaction

Relationship between ΔG and K_{eq}

For a reaction **A + B ←→ C + D**

$$\Delta G = \Delta G^{o} + RT \ln \left(\frac{[C]\,[D]}{[A]\,[B]} \right)$$

R = gas constant (1.987 cal/kelvin/mole)

T = temp. in kelvin (273+T^{o}C)

At **equilibrium,** $\Delta G = 0$

$$\Delta G = \Delta G^o + RT \ln \left(\frac{[C]\,[D]}{[A]\,[B]} \right)$$

$$0 = \Delta G^o + RT \ln \left(\frac{[C]\,[D]}{[A]\,[B]} \right)$$

$$\Delta G^o = - RT \ln \left(\frac{[C]\,[D]}{[A]\,[B]} \right)$$

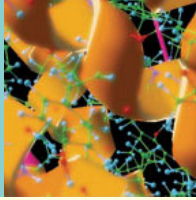
$$\text{Since } K_{eq} = \left(\frac{[C]\,[D]}{[A]\,[B]} \right)$$

$$\Delta G^o = - RT \ln K_{eq}$$

$$\Delta G^o = - RT \ln K_{eq} = -1.987 \times 298 \times 2.3 \log_{10} K_{eq}$$

(@ Room temperature 25 ^oC)

$$= - 1.36 \log_{10} K_{eq} \text{ (kcal/mol)}$$

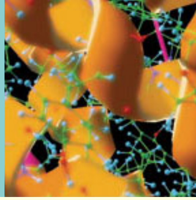


$$\Delta G^o = -1.36 \log_{10} K_{eq} \text{ (kcal/mol)}$$

Relationship between K_{eq} and ΔG^o

K_{eq}	ΔG^0 kcal/mol	Starting with 1 M reactants & products, the reaction:
100	**- 2.72**	proceeds forward (spontaneous)
10	**- 1.36**	proceeds forward (spontaneous)
1	**0**	is at **equilibrium**
0.1	**+ 1.36**	reverses to form “reactants”
0.01	**+ 2.72**	reverses to form “reactants”

Energy coupling



- ***ΔG^o of forward reaction (e.g. $A \rightarrow B$) is equal in magnitude but opposite in sign to that of the backward reaction (i.e. $B \rightarrow A$)***

- ***Free energy changes of coupled reactions are additive.***

For example, in the reaction catalyzed by the glycolysis enzyme **Hexokinase**, the half-reactions are:

ATP + H_2O → ADP + P_i $\Delta G^o = -7.3$ kcal/mol

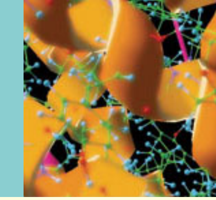
P_i + Glucose → Glucose-6-P + H_2O $\Delta G^o = +4$ kcal/mol

Coupled reaction:

ATP + Glucose → ADP + Glucose-6-P

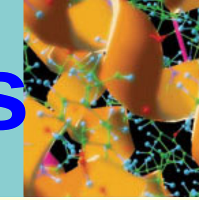
$\Delta G^o = -3.3$ kcal/mol

High Energy Compounds



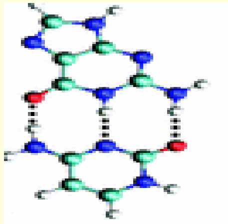
Phosphoenolpyruvate	– 14.8 kcal/mole
Carbamoyl phosphate	– 12.3 kcal/mol
1,3-Diphosphoglycerate	– 11.8 kcal/mole
bond between -COOH and phosphate	
Acetyl phosphate	– 10.3 kcal/mole
Creatine phosphate	– 10.3 kcal/mole
Acetyl CoA	– 7.7 kcal/mole
ATP γ-phosphodiester bond	– 7.3 kcal/mole

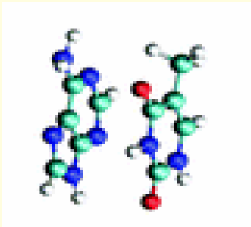
Sources of Energy In Human cells



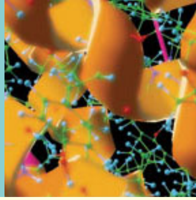
Free energy is released during oxidation of organic compounds in catabolic reactions

- Carbohydrates (Glucose)
- Proteins (Amino acids)
- Fats (Fatty acids)





Caloric Value



calorie: basic unit of measurement of energy in biological system. Indicated by a “c”

Calorie is kilocalorie or 1,000 calories. Indicated by a “C”

Caloric value of dietary components:

Carbohydrate = 4 Calories/g

(polysaccharide, disaccharide or monosaccharide)

Proteins = 4 Calories/g

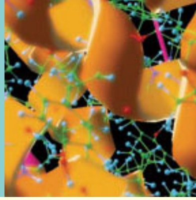
(proteins, peptides, amino acids)

Fat = 9 Calories/g

(triglycerides and fatty acids)

Alcohol = 7 Calories/g

Why is caloric value of fat more than carbohydrate and protein?



Caloric value is determined as the amount of energy released when carbon atoms present in 1g of the compound is completely oxidized to CO_2 in the body

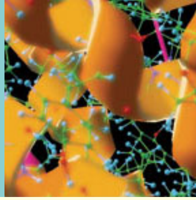
- Glucose $C_6H_{12}O_6$

  Carbohydrates are already oxidized to some extent

- Fatty Acid $C_{16}H_{32}O_2$

  Fats are less oxidized than carbohydrates or proteins

Basal Metabolic Rate



BMR is the minimum energy required by a person at rest 12 h after previous meal (determined in the early morning)

Energy needed per day = BMR + Energy for physical activity

BMR = 24 x Body weight in Kg (Cal/day)

BMR is influenced by age, gender, physical condition, body weight, and genes.

Energy balance

- Energy balance: energy intake = energy need

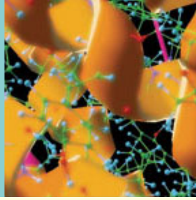
- Positive energy balance leads to weight gain

  when energy intake is greater than energy need
  e.g., growth in children or obesity in adults

- Negative energy balance leads to weight loss

  when energy need is greater than energy intake
  as in atrophy in old age, loss of weight during
  starvation & severe illness

Energy balance



Weigh gain/loss is about fat (not carbohydrate or protein)

1 g Fat gives 9 Calories

Excess 3,500 Calories = $\frac{3500}{9}$ gram of fat

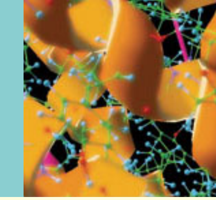
Adipocytes have 15% water content

Excess 3,500Calories = $\frac{3500}{9} \times \frac{100}{85}$ gram of fat

= 458 g (1 lb)

3,500 Calories = 1 lb   7,700 Calories = 1 kg

Fuel Composition



Fuel store in an average 70 Kg man:

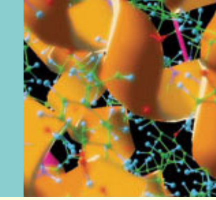
Fat	**15 Kg**	**135000 Kcal (85%)**
Protein	**6 Kg**	**24000 Kcal (15%)**
Liver glycogen	**0.08 Kg**	**320 Kcal (0.2%)**
Muscle glycogen	**0.16 Kg**	**640 Kcal (0.4%)**

Order of preference of fuels for use: glycogen > fat > protein

100-meter race: Most of the energy comes from ATP, creatine phosphate and glycolysis

Marathon: Most of the energy comes from fatty acids because ATP, creatine phosphate, and glycogen stores are all exhausted at the early stages of marathon running.

Respiratory Quotient (R.Q)



The Respiratory Quotient or R.Q value is a measure of the ratio of carbon dioxide produced to oxygen consumed by an organism. The respiratory quotient is a ratio and therefore has NO UNITS.

$$\text{R.Q} = \frac{\text{amount of carbon dioxide produced}}{\text{amount of oxygen consumed}}$$

The respiratory quotient is a valuable measurement as it provides information regarding the nature of the substrate being used for energy

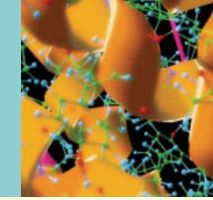
The equation for oxidation of glucose is:

$$C_6H_{12}0_6 \quad + \quad 6O_2 \quad = \quad 6CO_2 \quad + \quad 6H_2O$$

In this reaction, SIX CARBON DIOXIDE MOLECULES are produced and SIX OXYGEN MOLECULES are consumed

R.Q for this reaction is $6\ CO_2/6\ O_2 = 1$

Respiratory Quotient (R.Q)



The following equation represents the complete oxidation of palmitic acid when used as a substrate for energy

The equation for oxidation of palmitic acid is:

$$C_{16}H_{32}O_2 \quad + \quad 23\ O_2 \quad = \quad 16\ CO_2 \quad + \quad 16\ H_2O$$

R.Q for this reaction is $16\ CO_2 / 23\ O_2 = 0.7$

How do you determine the ratio of
carbohydrate and fat used as the energy
for a given physical activity if you know the value of RQ?