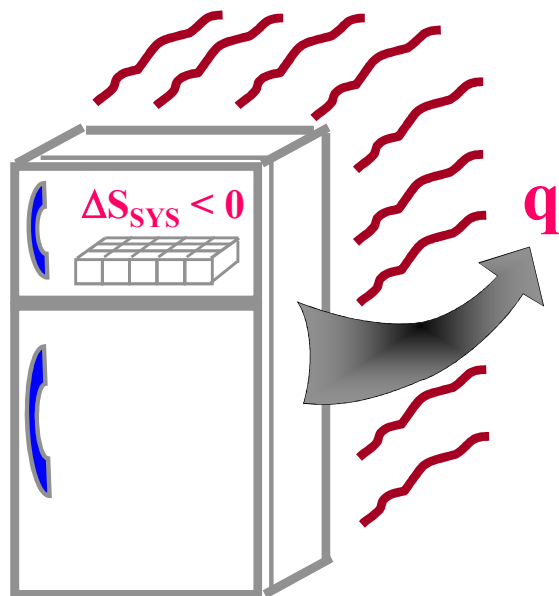


The Second Law of thermodynamics

$$\Delta S_{\text{Universe}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}} \geq 0$$

The net entropy will increase or stay the same. It will never decrease.



$$\Delta S_{\text{Surr}} > 0$$

$$\Delta S_{\text{Surr}} \geq \frac{q}{T}$$

$$\Delta S_{\text{Univ}} = 0 \quad \text{only for a reversible process}$$

$$\Delta S_{\text{Univ}} > 0 \quad \text{for all other processes}$$

Atkins: The entropy of the universe tends to increase

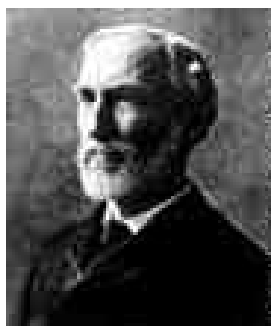


The Gibbs free enthalpy (“Gibbs energy”)

To judge whether a **chemical reaction is spontaneous**, we need to consider entropy changes in **both system and surroundings**


$$\Delta S_{Univ} = \Delta S_{Sys} + \Delta S_{Surr} = \Delta S_{Sys} - \frac{\Delta H}{T} \quad (@ \text{ constant } p, T)$$

⇒ Josiah Willard Gibbs (1839-1903; theoretician @ Yale):



Definition: $G = H - TS$

H, S are extensive
⇒ G is extensive
(increases with n)

 all state functions
⇒ G is a state function
(no memory of path)

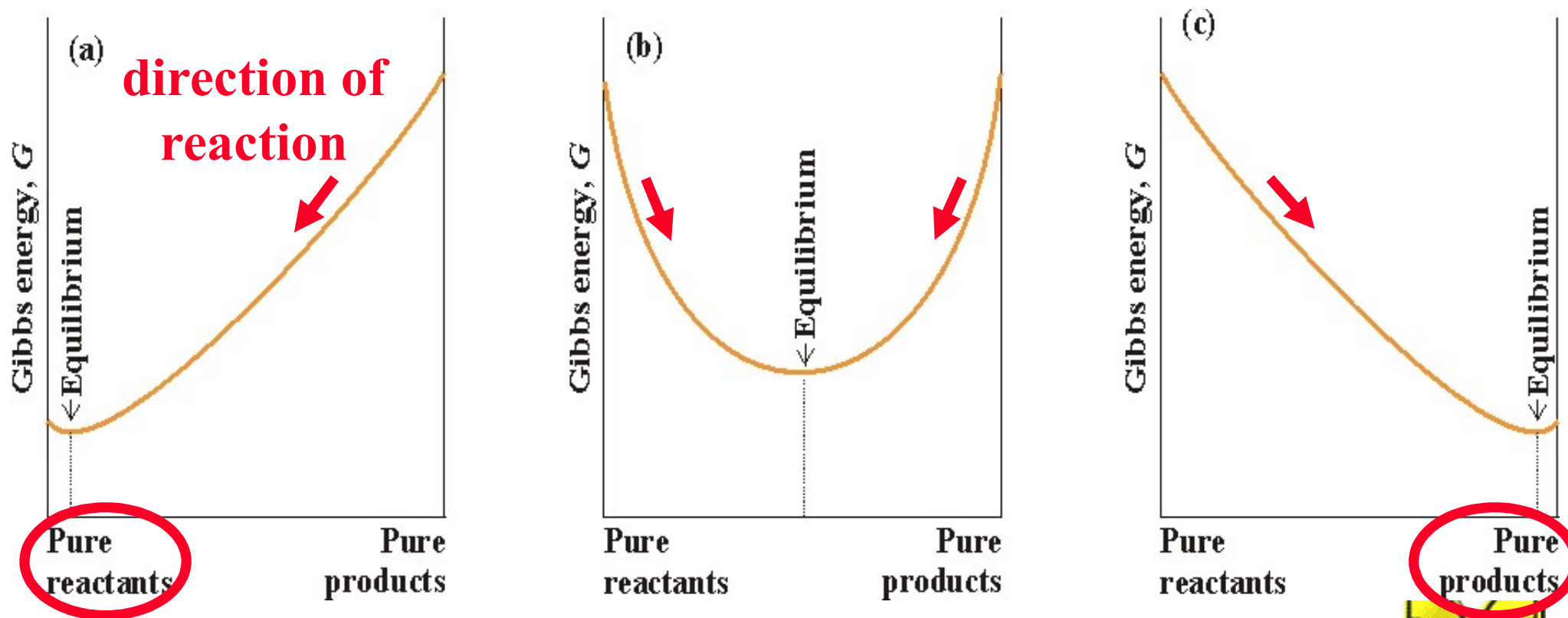
⇒ change in G: $\Delta G = \Delta H - T \Delta S = -T \Delta S_{Univ}$ (@ constant p, T)

⇒ The Gibbs free enthalpy calculates changes in entropy of both system and surroundings from system parameters alone

Principles of chemical equilibrium

Atkins, Chapter 7

At constant T and p a reaction mixture tends to adjust its composition until its Gibbs energy is at a minimum



Coupled reactions can overcome an unfavorable $\Delta_r G$

@ equilibrium: $\Delta_r G^\ominus = -RT \ln K$ $K = \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$



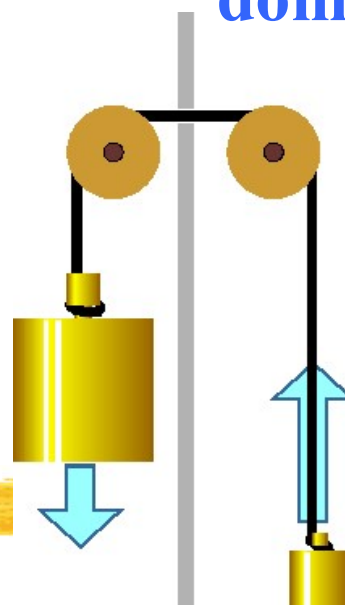
exergonic:

$\Delta_r G^\ominus < 0 \Rightarrow K > 1 \Rightarrow a_C^c \times a_D^d > a_A^a \times a_B^b \Rightarrow$ **products will dominate in equilibrium**

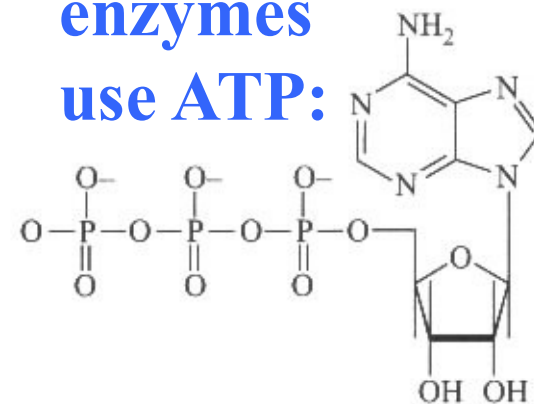
endergonic:

$\Delta_r G^\ominus > 0 \Rightarrow K < 1 \Rightarrow a_C^c \times a_D^d < a_A^a \times a_B^b \Rightarrow$ **reactants will dominate in equilibrium**

BUT: If an endergonic reaction ($\Delta_r G^\ominus > 0$) is coupled with a strongly exergonic one ($\Delta_r G^\ominus < 0$):
 $\Delta_r G^\ominus + \Delta_r G^\ominus' < 0$

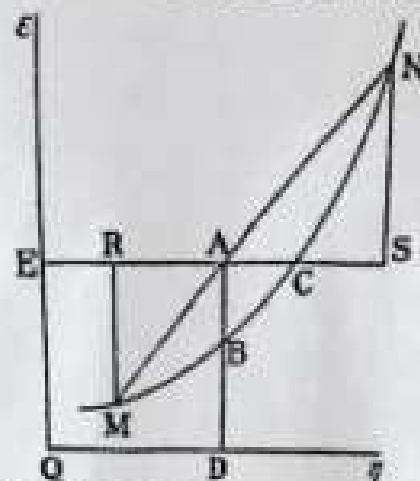


enzymes use ATP:



ref: Chem 451

**REMEMBER:
AVAILABLE FREE ENERGY**



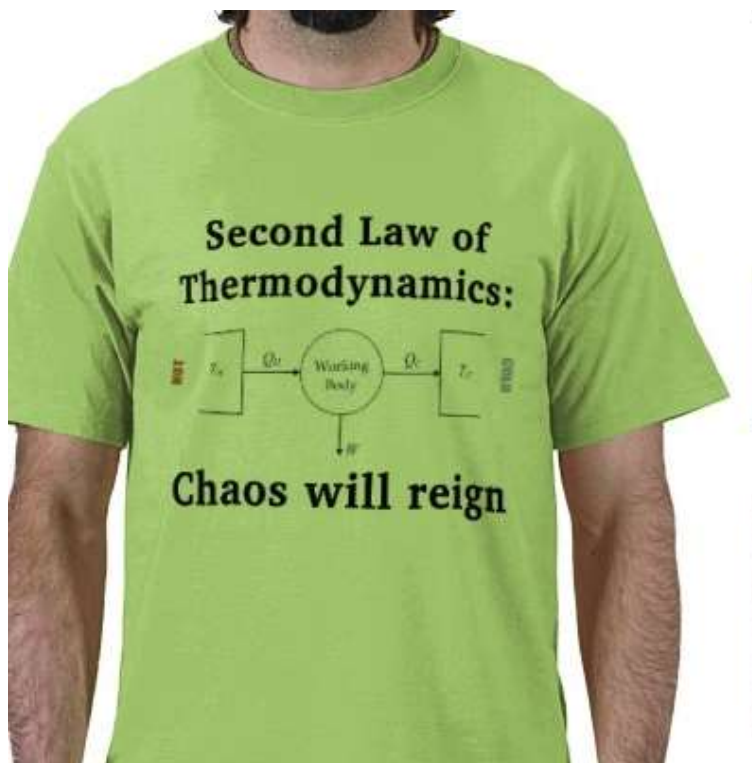
IS A THEORETICAL CONCEPT

(H. P. R. & B. G. 1991)



Chapter 3: What have we learned?

- ☺ Review of the first and second laws of thermodynamics
- ☺ Review of the state functions of internal energy, enthalpy, and free energy



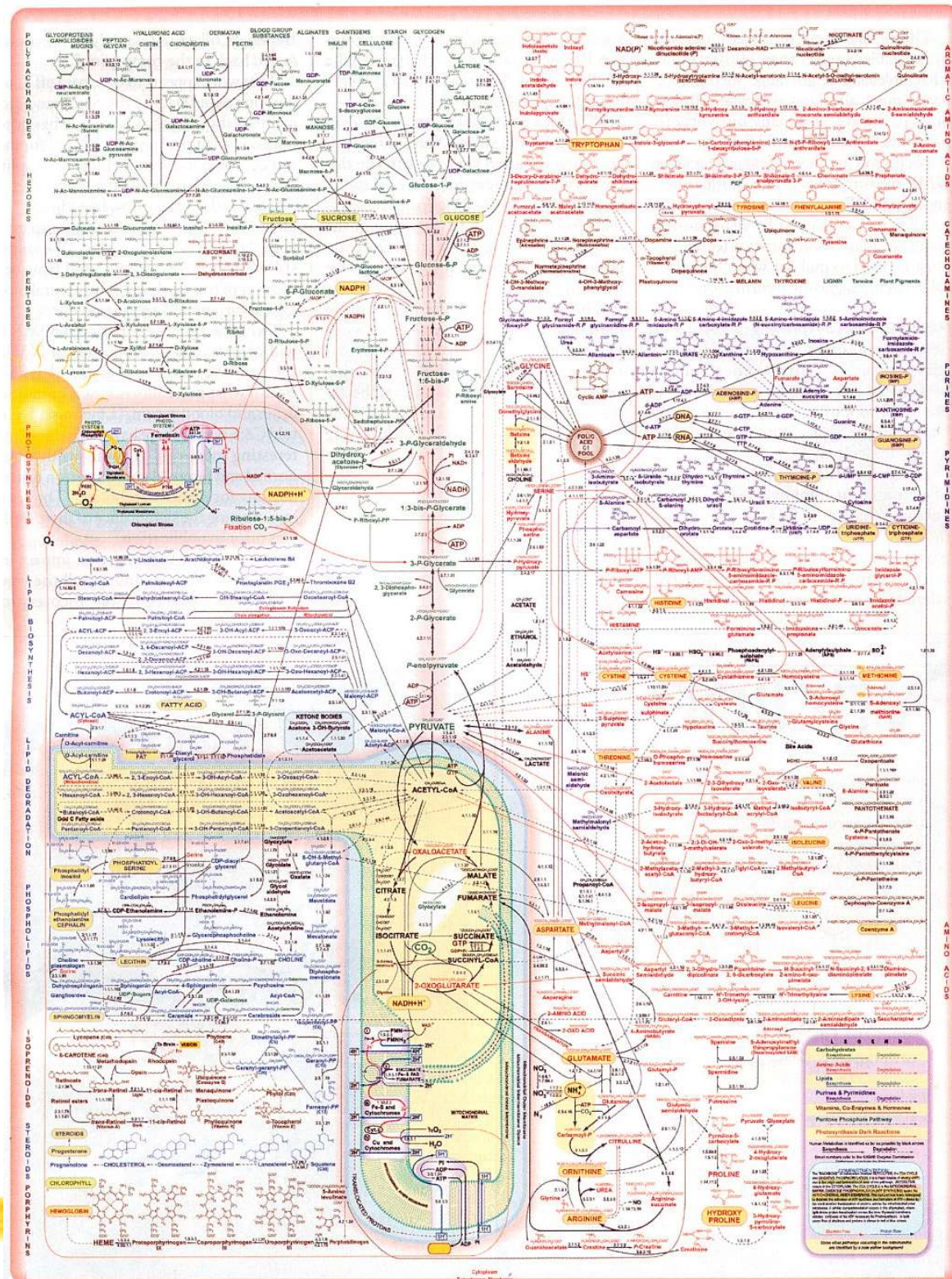
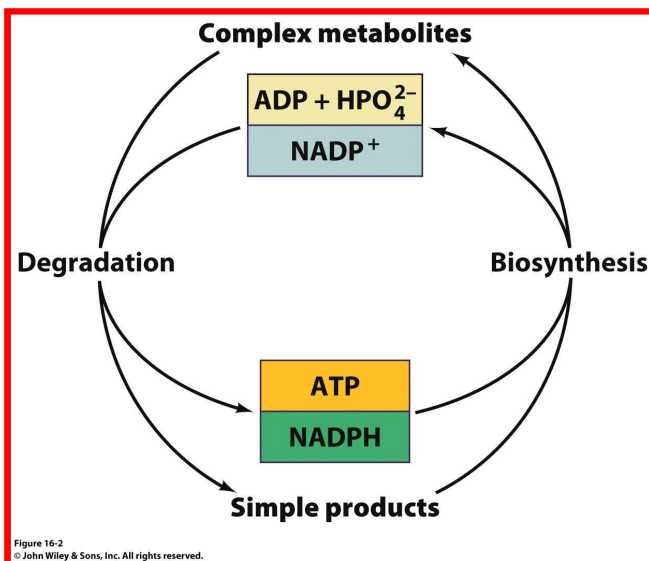
- ☺ Entropy

- ☺ ΔG as a driving force towards equilibrium that includes both enthalpic and entropic forces

Introduction to Metabolism

Voet & Voet, Chapter 16

**Metabolism =
Catabolism (degradation) +
Anabolism (biosynthesis)**



Metabolism: Food processing

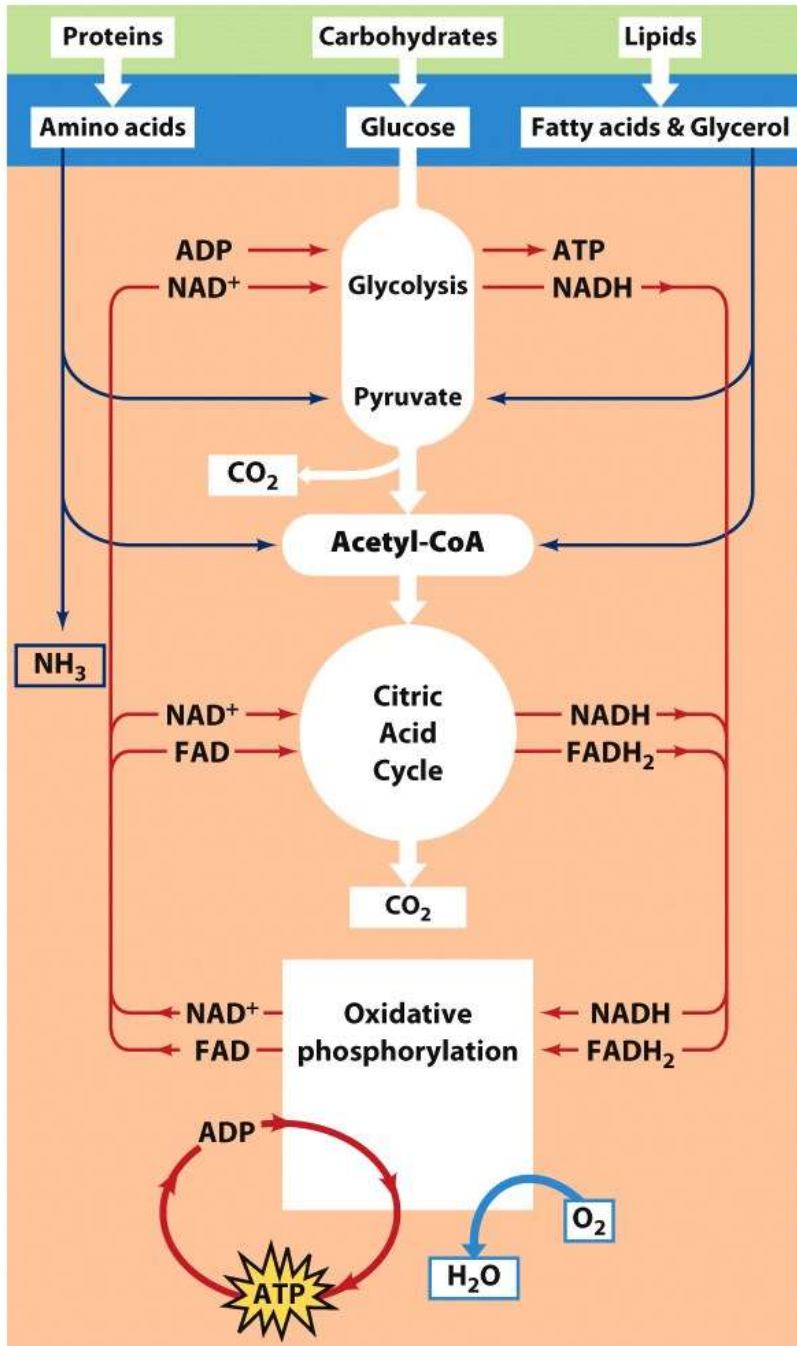
➤ Metabolic pathways are irreversible (and highly exergonic)

➤ Catabolic and anabolic pathways must differ

➤ Every metabolic pathway has a first committed (irreversible) step

➤ All metabolic pathways are regulated

➤ In eukaryotic cells, metabolic pathways occur in specific cellular locations

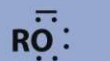


It's all chemistry, of course!

(a) Nucleophiles

(b) Electrophiles

Nucleophilic form



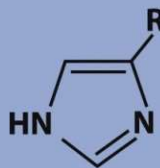
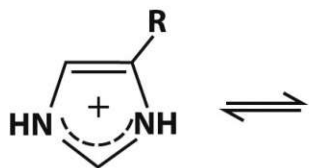
+ H^+ **Hydroxyl group**



+ H^+ **Sulfhydryl group**



+ H^+ **Amino group**



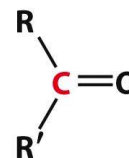
+ H^+ **Imidazole group**



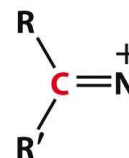
Protons



Metal ions

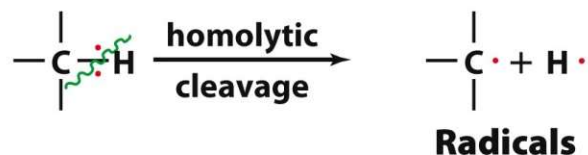


Carbonyl carbon atom

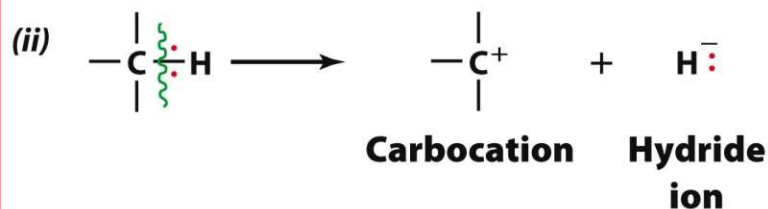
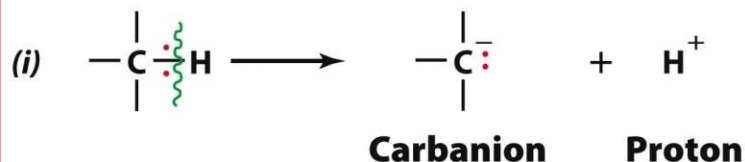


Cationic imine (Schiff base)

Homolytic:

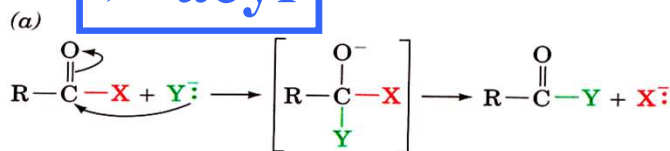


Heterolytic:



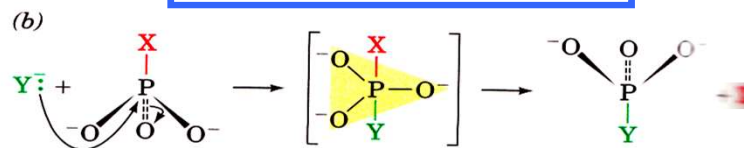
Metabolism: Group transfer reactions

➤ acyl

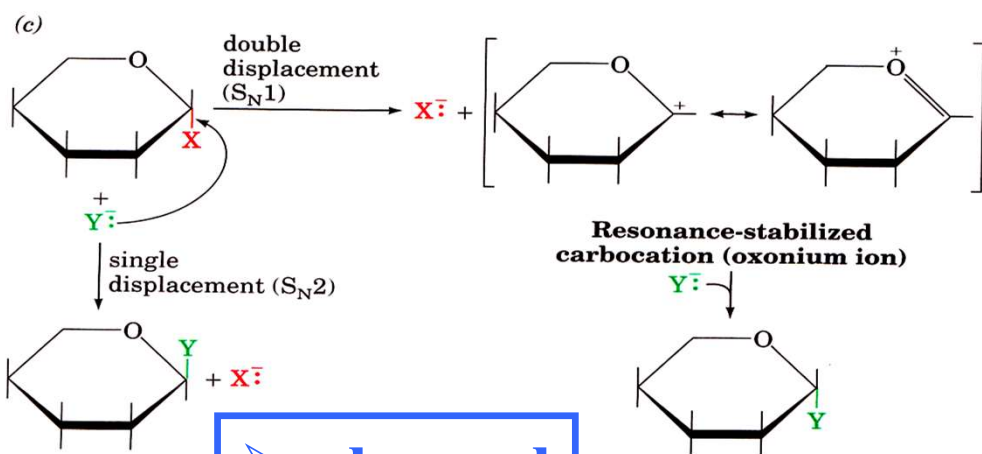
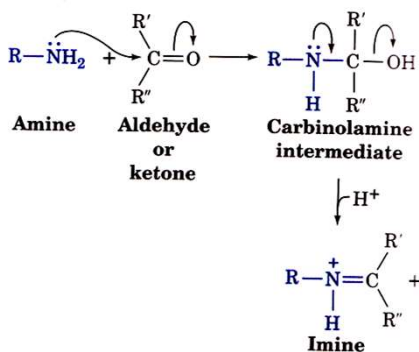


Tetrahedral intermediate

➤ phosphoryl



Trigonal bipyramid intermediate



➤ glycosyl

