Stoichiometry of Biochemical Reactions I

Today's lecture

- Biochemical reaction stoichiometry
- Cell yield
- Half reactions

Oxidation-reduction (redox) reactions

- Involves changes in the oxidation state
- If there are oxidizing species, there should be reducing species as well
  - Total # of electrons are conserved
  - Oxidizing species – e^- donor / Reducing species – e^- acceptor
- Essential for life – many important biological processes involve redox reactions
  - Involves large free energy change (ΔG)

Biological benefit of redox reactions

Examples:

photosynthesis of glucose:

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

$\Delta G^0 = +2880$ kJ/mol $C_6H_{12}O_6$

Sunlight energy is converted to chemical energy (storable)

respiration using glucose:

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ $\Delta G^0 = -2880$ kJ/mol $C_6H_{12}O_6$

Chemical energy is released to be used to do something

Stoichiometry

- "An aspect of chemistry concerned with mole relationships among reactants and products"
- Simply put, balancing chemical reactions
- Based on mass conservation
  - Conservation of elements
  - Conservation of electrons (for redox reactions)

What can we do with stoichiometry?

A balanced biochemical reaction example

(ethanol fermentation of glucose at f_s=0.22)

$$0.0417C_6H_{12}O_6 + 0.011\ NH_4^+ + 0.011HCO_3^-$$

$$\rightarrow 0.011C_5H_7O_2N + 0.065C_2H_5OH + 0.076CO_2 + 0.044H_2O$$

[Bacterial cells]

Available information:

Using 1 g (or 1 mole) of glucose,

- How much ethanol can be produced?
- How much nutrients (NH_4-N) are required?
- How much biomass is produced?
- How much alkalinity is consumed?

Cell formula

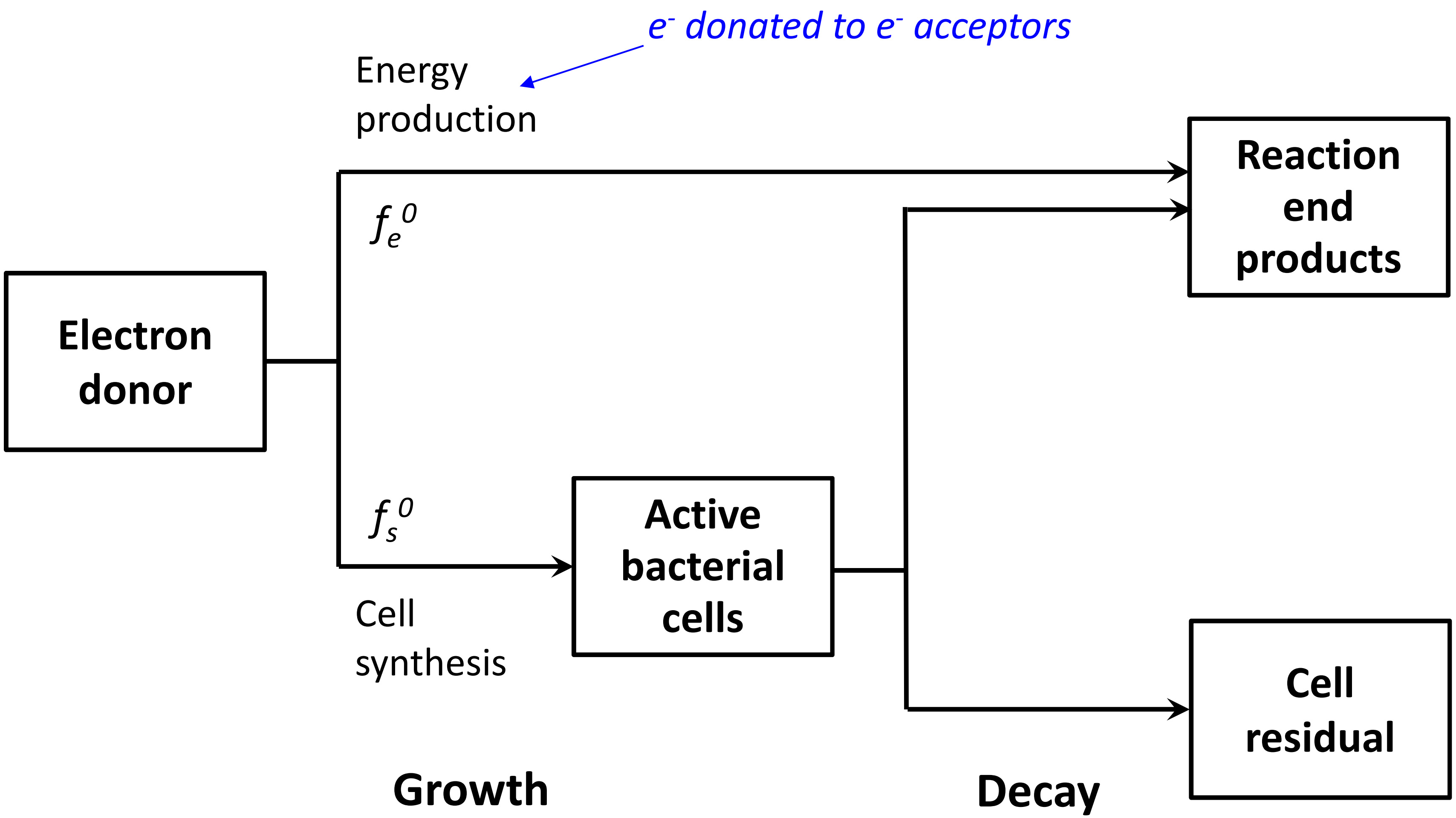
- Most common: $C_5H_7O_2N$
- What is the theoretical COD-per-weight value for a bacterial cell (i.e., g COD / g cells)?
  - Once you get trained with the stoichiometry, you will be able to write the balanced reaction as:

    $$C_5H_7O_2N + 5O_2 \rightarrow 5CO_2 + NH_3 + 2H_2O$$

  - Then you get: 1.42 g COD/g cells

You will find this value useful in the future!

Substrate partitioning



Textbook Fig. 2.1

Cell yield

- True yield, *Y*

  Y = (g cells produced) / (g substrate utilized)

- Conversion of f_s^0 to *Y*:

$$Y = f_s{}^0 \frac{(M_c \;\; g\ cells/mole\ cells)}{(n_e \;\; e^- \ eq\ cells/mole\ cells)(8\ g\ COD/e^- \ eq\ donor)}$$

For $C_5H_7O_2N$, M_c = 113 g/mole;

n_e = 20 e^- eq/mole (see Table 2.3)

then: $Y(in\ g\ cells/g\ COD) = 0.706 f_s{}^0$

Microbial growth rate

$$\frac{dX_a}{dt} = Y\left(\frac{-dS}{dt}\right) - bX_a$$

growth decay

X_a = active biomass concentration [M/L^3]

S = substrate concentration [M/L^3]

Y = true yield [M/M]

b = decay rate [1/T]

Decay

- Generally assumed to be proportional to the amount of cells
- A gross factor for anything that leads to decrease in cell biomass
- Decay = endogenous respiration (+ predation)
  - Endogenous respiration: use of cell matter for maintenance of cell functions (motility, repair, resynthesis, osmotic regulation, transport, compensate heat loss, …)

Net yield

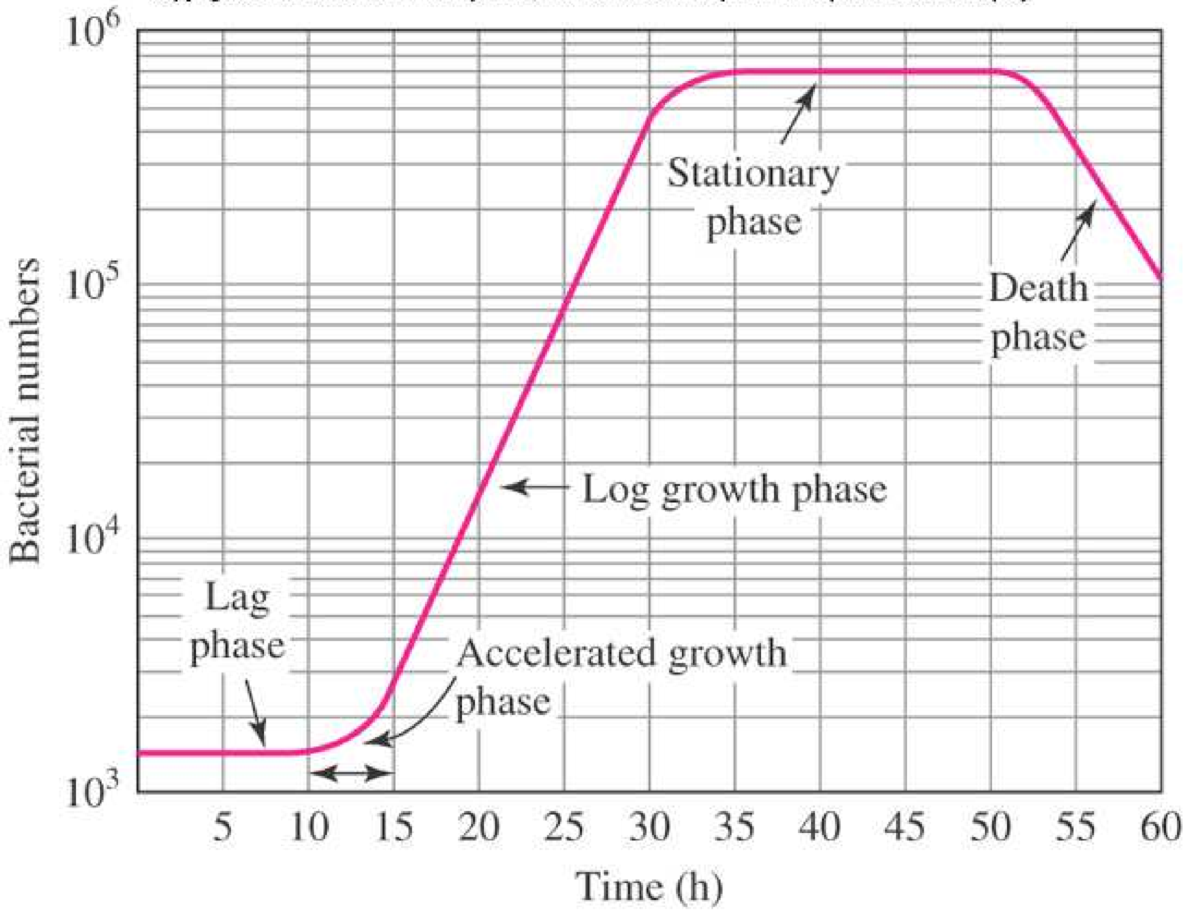
- Net yield, Y_n

  Y_n = (g net cell growth) / (g substrate utilized)

$$= \frac{dX_a / dt}{-dS / dt}$$

$$= Y - b \frac{X_a}{-dS / dt}$$

Net yield



Bacterial growth curve for pure culture

Log (exponential) growth:

Stationary phase:

Death phase:

Net yield

- Electron partitioning considering net yield, Y_n:

$f_s^0 \rightarrow f_s \qquad (f_s < f_s^0)$

$f_e^0 \rightarrow f_e \qquad (f_e > f_e^0)$

still, $f_s + f_e = 1$

Energy reactions

- Microorganisms need energy for growth and maintenance

	ΔG^0 (in kJ/mole glucose)
Aerobic oxidation:	
$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$	-2,880
Denitrification:	
$5C_6H_{12}O_6 + 24NO_3^- + 24H^+ \rightarrow 30CO_2 + 42H_2O + 12N_2$	-2,720
Sulfate reduction:	
$2C_6H_{12}O_6 + 6SO_4^{2-} \rightarrow 12CO_2 + 12H_2O + 3H_2S + 3\ HS^-$	-492
Methanogenesis:	
$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$	-428
$(C_6H_{12}O_6 + 3CO_2 \rightarrow 6CO_2 + 3CH_4)$	
Ethanol fermentation:	
$C_6H_{12}O_6 \rightarrow 2CO_2 + 2C_2H_5OH$	-244

Half reactions

- For complex biochemical redox reactions, it is easier to use half reaction approach
- The oxidation reaction for an electron donor and the reduction reaction for an electron acceptor can be splitted
- Usually written as a reduction reaction

  (see [Table 2.2] & [Table 2.3])

Half reactions

Step 1 Write oxidized form on the left and reduced form on the right

Step 2 Add other species involved in the reaction

Step 3 Balance the reaction for all elements except for oxygen and hydrogen

Step 4 Balance oxygen using water

Step 5 Balance hydrogen using H^+

Step 6 Balance charge using e^-

Step 7 Convert the equation to the e^--equivalent form