

ABE 201

Biological Thermodynamics 1

Module 16

Mass and Energy Balances with
Chemical Reactions

Outline

- Review mass balances with chemical reactions
- Using enthalpies of reaction in 1st law energy balances with chemical reactions
- Applying the 1st and 2nd law to chemical reactions: Gibbs Free Energy
- Application to biochemical pathways in living cells

Energy Balances with Chemical Reactions

- In this class we are not going to worry about the rate of reaction, we will only solve problems for given reactions as completed.
- Kinetics (you will study next year) will give you the tools to work with transient effects (rate of reaction)

Review: Mass Balances with Chemical Reactions

Accumulation = In – Out + Generation - Consumption

- **Steady-state: Accumulation = 0**
- **Chemical Reactions - Extent of Reaction**

$$dX_i = \sum_{in} \dot{m}_{in} \cdot x_{i,in} dt - \sum_{out} \dot{m}_{out} \cdot x_{i,out} dt + \sum \nu_i \cdot \xi \cdot MW_i \cdot dt$$

$$\frac{dX_i}{dt} = \sum_{in} \dot{m}_{in} \cdot x_{i,in} - \sum_{out} \dot{m}_{out} \cdot x_{i,out} + \sum \nu_i \cdot \xi \cdot MW_i$$

Energy Balances for Chemical Reactions

- Same governing equations

$$\Delta U + \Delta E_k + \Delta E_p \rightarrow Q - W$$

$$\Delta H + \Delta E_k + \Delta E_p \rightarrow Q - W_s$$

- Enthalpy must contain thermodynamic state changes (T,P) due to both chemical reactions and traditional changes (heat, work, elevation changes, velocity changes)

Finding Enthalpy Changes

$$\Delta\dot{H} = \Delta\hat{H}_{sensible}\dot{m} + \Delta\hat{H}_{latent}\dot{m}$$

$$\Delta\dot{H} = \int_{T_1}^{T_2} C_p dT \cdot \dot{m} + \Delta\hat{H}_{latent}\dot{m}$$

$$\Delta\dot{H} = \left[\Sigma \left(\hat{H}_{i,out} \dot{m}_{i,out} \right) - \Sigma \left(\hat{H}_{i,in} \dot{m}_{i,in} \right) \right]$$

Steam Table
Combines
Sensible and
Latent Enthalpy

$$\Delta\dot{H} = \Delta H_{rxn} \cdot \xi$$

Finding Total Enthalpy Change

$$\Delta \dot{H} = [\sum_{out} \dot{H} - \sum_{in} \dot{H}] + \Delta H_{rxn} \cdot \xi$$

Where

$$\dot{H} = \Delta \dot{H}_{sensible} + \Delta \dot{H}_{latent}$$

or

$$\dot{H} = \dot{m} \cdot \hat{H} \quad (value \text{ from table})$$

Second Law and Chemical Reactions

Gibbs Free Energy

- More commonly used in biochemistry than heats of formation is the concept of “free” energy
- “Free” energy determines whether or not a chemical reaction will occur spontaneously
- Developed by Josiah Willard Gibbs in 1878
- Combines 1st and 2nd Laws of Thermodynamics

Gibbs Free Energy

$$\Delta G = \Delta H - T\Delta S = \Delta H - Q$$

Implications:

1. If heat loss (entropy) is greater than the change in enthalpy due to the chemical reaction ($\Delta G < 0$), the reaction can occur spontaneously (i.e. without energy input)
2. A system is at equilibrium when $\Delta G = 0$
3. If $\Delta G > 0$, the reaction requires the input of free energy

Gibbs Free Energy in Biochemical Systems

- In physical chemistry, Gibbs Free Energy (ΔG°) is standardized at pH = 0
- For convenience in biochemical systems, Gibbs Free Energy ($\Delta G^{\circ'}$) is standardized at pH = 7
- Note the apostrophe! The two Gibbs Free Energies are not equivalent!

Gibbs Free Energy in Biochemical Systems

- is path independent
- gives no information regarding rates of reaction
- depends upon reactant and product concentrations

Standard Gibbs Free Energy and Standard Equilibrium (K')

(how to measure ΔG°)

$$\Delta G^\circ = -RT \ln(K')$$

Where

$$K' = \frac{[C][D]}{[A][B]}, \text{ if } A + B \rightarrow C + D$$

and all concentrations = 1M

Using Gibbs Free Energy to Calculate Equilibrium Constants (K')

$$\Delta G^{o'} = -RT \ln(K')$$

$$K' = e^{-\Delta G^{o'}/RT}$$

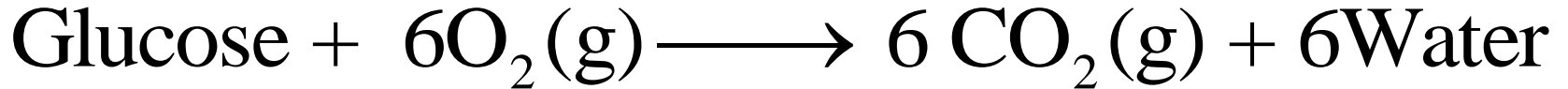
Standard Gibbs Free Energy versus Actual Gibbs Free Energy

$$\Delta G^{\circ'} = -RT \ln(K')$$

$$\Delta G = -RT \ln(K),$$

equilibrium at actual conditions!

Glucose Metabolism



- How much heat is generated by the metabolism of glucose?

$$\begin{aligned}\Delta H_r &= -1 * \Delta H_f(\text{glu}) + -6 * \Delta H_f(\text{O}_2) + 6 * \Delta H_f(\text{CO}_2) + 6 * \Delta H_f(\text{water}) \\ &= -1(-1267.12) - 6(0) + 6(-393.50) + 6(-286.65) = \mathbf{-2813.9 \text{ kJ/mol}}\end{aligned}$$

- What is the standard Gibb's free energy change?

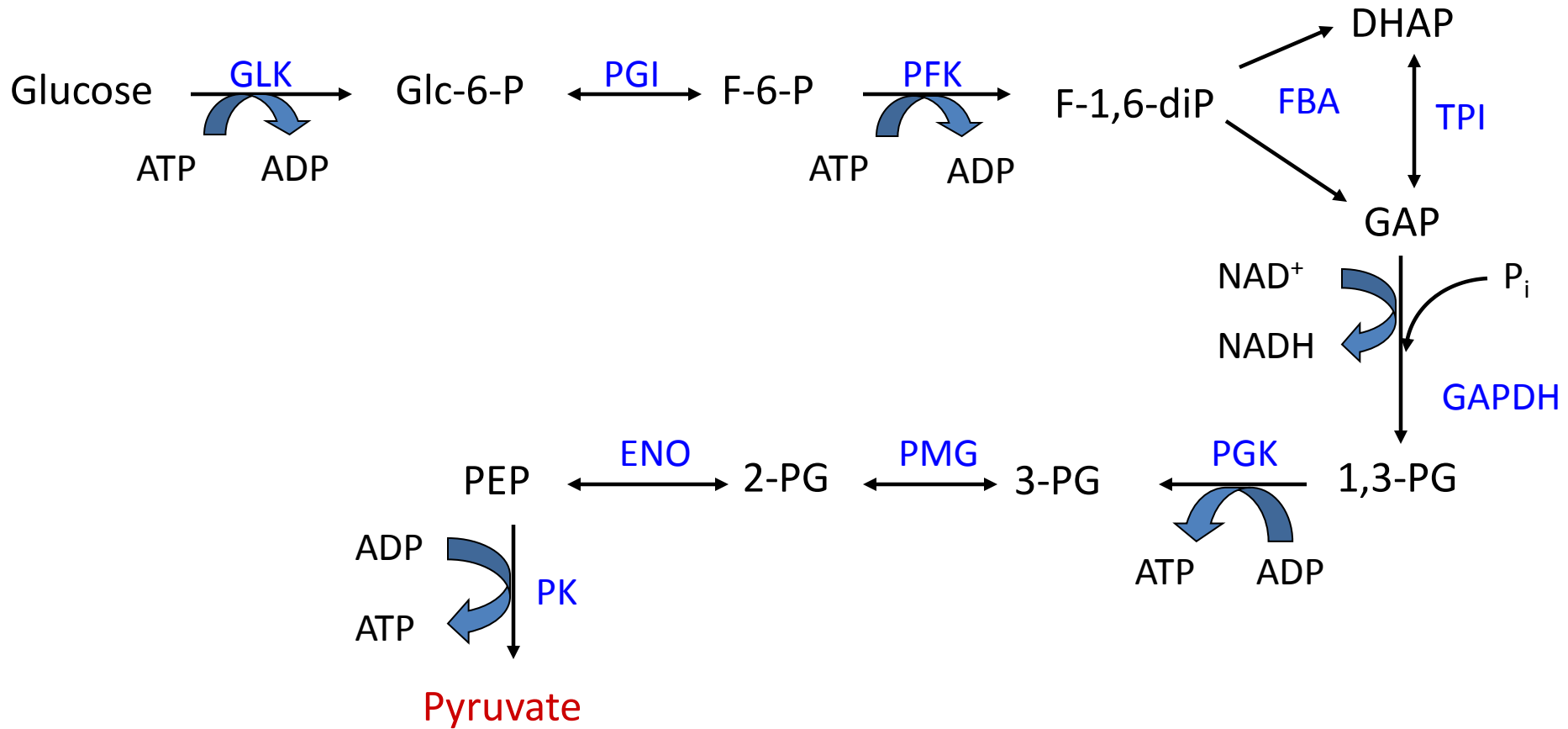
$$\begin{aligned}\Delta G &= -1 * \Delta G_f(\text{glu}) + -6 * \Delta G_f(\text{O}_2) + 6 * \Delta G_f(\text{CO}_2) + 6 * \Delta G_f(\text{water}) \\ &= -1(-426.71) - 6(0) + 6(-394.36) + 6(-155.66) = \mathbf{-2873.4 \text{ kJ/mol}}\end{aligned}$$

Gibb's Free Energy

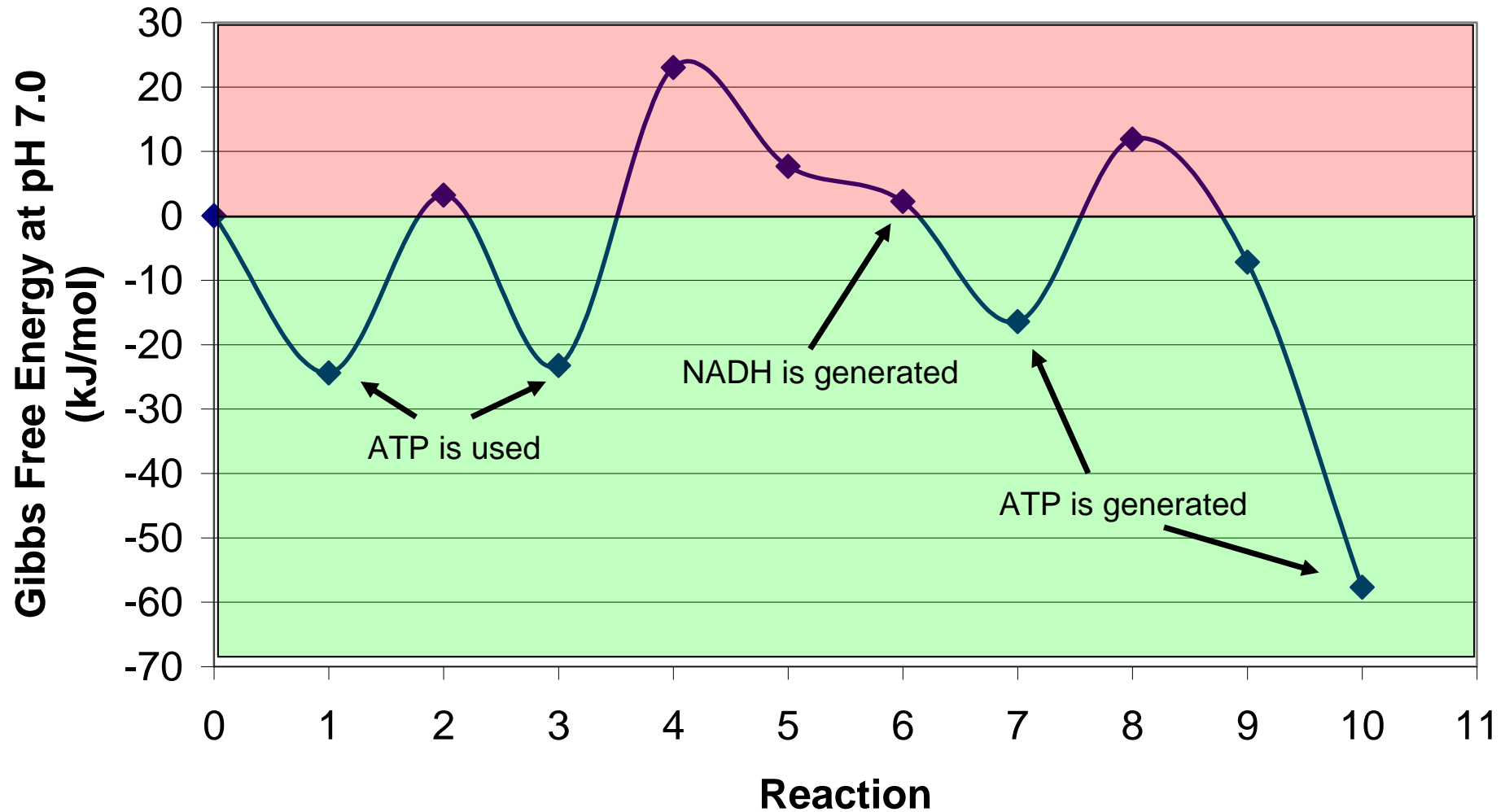
- Standard – assumes all reactants and products have 1 M concentration
- Actual – corrects for actual concentrations
- *Most cellular metabolites have concentration $\ll 1\text{ M}$*

Glycolysis

Embden-Meyerhof-Parnas (EMP) pathway

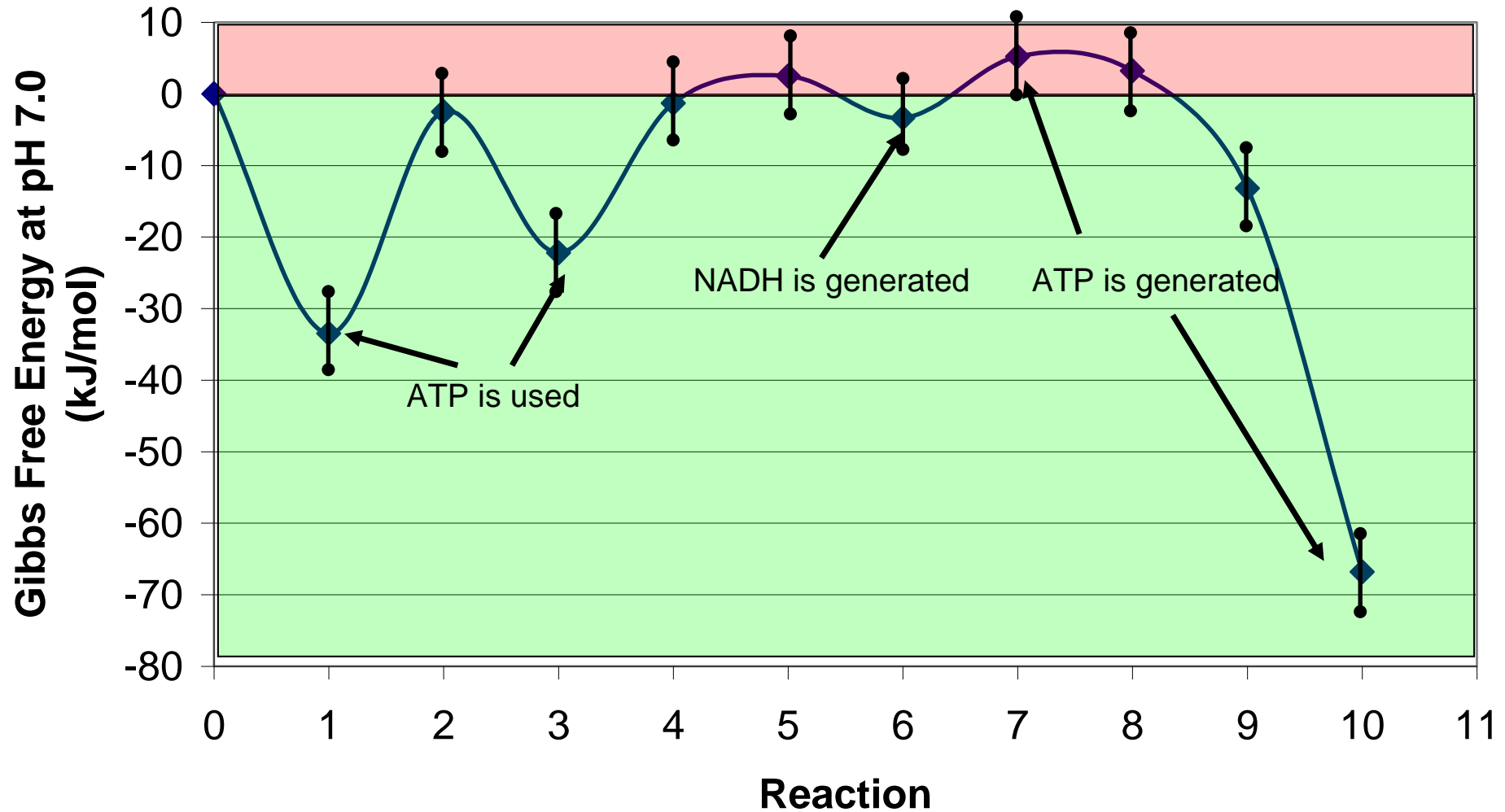


Standard Gibbs Free Energies for Glycolysis (per mole Glucose)



Actual Gibbs Free Energies for Glycolysis (per mole Glucose)

Based on Measured Concentrations of Metabolites



Summary

- Extent of reaction (ξ) can be used in both mass and 1st law energy balances where chemical reactions occur.
- 1st and 2nd Laws of Thermodynamics combine as Gibbs Free Energy: describes the thermodynamic feasibility of a chemical reaction
- Living systems operate near the edge of thermodynamic equilibrium where Gibbs Free Energy favors the “harvest” of energy as ATP or as electrons (NAD(P)H).