BCH 4053—Spring 2001—Chapter 3 Lecture Notes

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Chapter 3:

Thermodynamics of Biological Systems

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Energy and Work

- Work = force x distance
- Energy = ability to do work
- Mechanical Energy
  - Kinetic Energy = $mv^2/2$
    - (Energy from motion)
  - Potential Energy
    - (Energy from attraction or repulsion)

Both Work and Energy are products of intensive and extensive factors:
force x distance (mechanical work)
pressure x volume change (work of expansion)
voltage x current (electrical work)
etc.

One of the triumphs of the energy concept was the recognition that there is a relationship between heat and work.

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Energy and Work, con't.

- Heat is a form of energy
  - Experiments of Joule
- Calorimetry (see Figure 3.2)
- Units of energy
  - The **calorie**, was originally defined from heat measurements
  - The **joule** is the SI unit.
    - One calorie = 4.184 joules

Experiments of Joule showed mechanical work (turning a paddle wheel) could heat water just as an electrical heater could, showing the connection between heat and work. An earlier idea viewed heat as a **caloric**, some substance that flowed from one body to another.
The **Calorie** (with a capital C), a familiar term in measuring energy content of food substances, is actually one **kilocalorie**.

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Energy and Work, con't.

- Internal Energy (E or U)
  - An inherent property of matter
  - Independent of any microscopic interpretation of matter, but
  - Interpreted in terms of *kinetic* and *potential* energy of atoms and electrons .

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Thermodynamics Studies Energy Change ΔE (or ΔU)

- System and Surroundings
- Isolated Systems (See Figure 3.1)
  - No exchange between system and surroundings
- Closed Systems (See Figure 3.1)
  - Heat exchange and work exchange between system and surroundings (note book error)
- Open Systems (See Figure 3.1)
  - Matter, as well as heat and work, can exchange between system and surroundings.

The system is any portion of the universe you choose to study. It can be the earth, an individual organism, an individual cell, a test tube of reagents, or simply that part of a solution undergoing a chemical reaction.
The surroundings is everything else in the universe.

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Equilibrium versus Non-equilibrium Thermodynamics

- Equilibrium Thermodynamics deal with **closed systems**.
- Biological problems deal with **open systems**.
- While the field of **non-equilibrium thermodynamics** should apply to open systems, data from equilibrium thermodynamics can be useful.

Equilibrium thermodynamics represent idealized conditions—where any change is carried on with the system and surroundings always in the state of equilibrium with one another. One can calculate **maximum** or **minimum** values for thermodynamic quantity changes.

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State Functions

- State of a system depends only on **pressure**, **volume**, **temperature** and **composition** of a system.
- State functions depend only on initial and final state: e.g. internal energy change
  - $\Delta E = E_{\text{final state}} - E_{\text{initial state}}$
- We can generally measure **changes** in state functions such as E even if we don't know the inherent value

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State Functions, con't.

- A state function is independent of the **path** of a change.
- Heat and work are **not** state functions. They depend on path.
  - Battery discharge, energy of battery converted all to heat
  - Battery used to run a motor, energy of battery converted to heat **and** work.

The **distance** between two locations, such as Tallahassee and Jacksonville, is equivalent to a state function. The **travel distance** in traveling from Tallahassee to Jacksonville would depend on the route taken, and would not be a state function.

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First Law of Thermodynamics

- Conservation of Energy
  - Energy is neither created nor destroyed.
- In terms of change of state of a **closed system**
  - $\Delta E = q + w$
    - (q = heat absorbed by system)
    - (w = work done on system)
- Says nothing about **spontaneity** of a process.

Sign conventions: q and w are **positive** when energy is added to the system, and **negative** if energy is transferred from the system to surroundings. You might find an alternative statement of the first law in older textbooks which says $\Delta E = q - w$. In this case, work is defined as positive for work done **by** the system **on** the surroundings. There the analogy is to a steam engine, in which both q and w would be positive.

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Enthalpy

- In a **constant volume** change, no other work done, $\Delta E = q$, which is q_v.
- In a **constant pressure** change, some work of expansion or contraction will be done.
  - $\Delta E = q_p - P\Delta V$, or $q_p = \Delta E + P\,\Delta V$
  - ΔH, the **enthalpy change** is defined as q_p
- ΔH (q_p) and ΔE (q_v) can be measured in a calorimeter, and are both state functions

Actually, enthalpy, H is defined as $H=E+PV$, which reduces to this relationship when P is constant. One would measure q_v in a **constant volume** calorimeter, and q_p in a **constant pressure** calorimeter. Since the changes in biological systems we are interested in generally occur at constant pressure, the enthalpy change is a more appropriate measure of energy change. Think of it as the energy change not devoted to pressure-volume work when a gas is produced or consumed in a process.

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Some Thermodynamic Terms

- Equilibrium
  - Macroscopic properties of system do not change with time
- Spontaneous Process
  - A change that occurs naturally.
  - System moves **toward** equilibrium.
  - Process capable of **doing work.**

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Some Thermodynamic Terms, con't.

- Non-spontaneous process
  - Does not occur naturally without intervention.
  - Requires work from surroundings to proceed.
- Reversible process
  - A change carried out so that system and surroundings are always in a state of equilibrium.

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Spontaneity—Example in Gas Expansion (P_1V_1 to P_2V_2)

- Let gas expand against surroundings pressure.
  - Work done = $P_2(V_2-V_1)$, spontaneous
- Let gas expand at initial pressure
  - Work done = $P_1(V_2-V_1)$, not-spontaneous
- Let gas expand "reversibly" (at equilibrium)

$$-\text{work done} = \int_{P_1}^{P_2} PdV = RT\ln\frac{V_2}{V_1}$$

Illustrated by drawing graphs on board. Sorry that I haven't yet been able to develop these graphs in a computer format.

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Spontaneity, con't.

- Reversible process will
  - produce **maximum work** on surroundings

  or
  - require **minimum work** needed to occur

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Entropy

- Heat change in a reversible process (q_{rev}) defines another state function, **entropy.**
  - Entropy change, $\Delta S = q_{rev}/T$
- Another definition of entropy is based upon the extent of potential disorder of a system (W, which is the number of microscopic states of a system).
  - S = klnW (k = the Boltzmann constant, which is R/N)
- Both definitions lead to notion of entropy as a measure of **disorder.**

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Second Law of Thermodynamics

- The second law speaks to the spontaneity of a process.
- Total entropy increases in a spontaneous process.
- Must include entropy change of surroundings as well as system.

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Third Law of Thermodynamics

- Entropy of a crystalline, perfectly ordered substance is 0 at T = O K.
- One can calculate the entropy of a substance by calculating the heat energy necessary to heat the substance to the appropriate temperature.
- Therefore one can define an **absolute** entropy value, even though absolute energy and enthalpy values cannot be defined.

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Free Energy

- Gibbs Free Energy, G is defined as
  $G = E + PV – TS$
- For Constant T and P changes:
  $\Delta G = \Delta E + P \Delta V - T \Delta S$
- Part of the internal energy change is required for expansion work ($P \Delta V$), part is required for the thermal disorder of increasing entropy. The rest is available to do **useful work.**

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Interpretations of Free Energy

- The **maximum useful work** that can be obtained from a process
  - Spontaneous processes will always yield less than the maximum work
- The **minimum work necessary** to cause a non-spontaneous process to occur.

One would only get the maximum work from a spontaneous process, or require the minimum work of a non-spontaneous process, if the change were carried out **reversibly**, that is slowly with all intermediate steps at equilibrium. By “useful work” is meant work other than the pressure volume work inherent in a volume change, such as the production of a gas in a chemical reaction.

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Interpretations of Free Energy, con’t.

- As a criterion of equilibrium related only to measurements of the system.
- $\Delta G < 0$, spontaneous process
  - (capable of doing work, where ΔG is **maximum** work available)
- $\Delta G > 0$, not a spontaneous process
  - (work required to make change occur; ΔG is the **minimum** work necessary)
- ΔG = O, system at equilibrium

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Free Energy and Entropy

- At constant Temperature and Pressure
  - $\Delta G = \Delta H - T\,\Delta S$
- The enthalpy change is related to making and breaking chemical bonds
- The entropy change is related to order-disorder transitions
- Free energy is that part of enthalpy not related to the order-disorder transitions

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Temperature Effect on ΔG

- The effect of Temperature on ΔG depends on the sign of ΔH and ΔS
- Sign of ΔH indicates whether process is *exothermic* or *endothermic*
- Sign of ΔS indicates whether process proceeds to *more* or *less* **order**

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Spontaneity of Process As a Function of Temperature

ΔH	ΔS	Spontaneity
-	+	Spontaneous at all T
+	-	Non-spontaneous at all T
+	+	Spontaneous at high T
–	-	Spontaneous at low T

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Free Energy and Entropy (ice to water as an example)

- For the transition ice→water
  - At $T = 0^{o}C$, equilibrium, $\Delta G = O$, $\Delta H = T\,\Delta S$
  - At $T > 0^{o}C$, $\Delta H < T\,\Delta S$, so $\Delta G < 0$,
    - melting is spontaneous
  - At $T < 0^{o}C$, $\Delta H > T\,\Delta S$, so $\Delta G > 0$,
    - melting is not spontaneous

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Chemical Potential

- The **chemical potential** (μ) of a substance is the **partial molar** free energy change associated with formation or disappearance of the substance.

$$\mu_i = \left(\frac{\delta G_i}{\delta n_i}\right)_{T,P,n_1,n_2....}$$

The chemical potential μ , or the **partial molar free energy change,** represents the change in free energy of the system as component i is added or removed from the system while all other conditions are held constant.

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Effect of Concentration on Chemical Potential

- Chemical potential is related to the activity (or concentration) of the substance:

$$\mu_i = \mu_i^o + RT\ln a_i \text{ or } \mu_i = \mu_i + RT\ln[i]$$

- (The higher the concentration, the greater the *order*, and the lower the entropy, hence increasing the concentration is unfavorable)

In other words, the higher the concentration of i, the greater the free energy change in adding or subtracting i from the system.

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Free Energy Change in Chemical Reactions

- A chemical reaction represents the disappearance of reactants, the appearance of products:

$$aA + bB \rightleftarrows cC + dD$$

- Partial free energy change for each component is given by the chemical potential times the change in quantity:

$$\Delta G_i = \mu_i \Delta n_i$$

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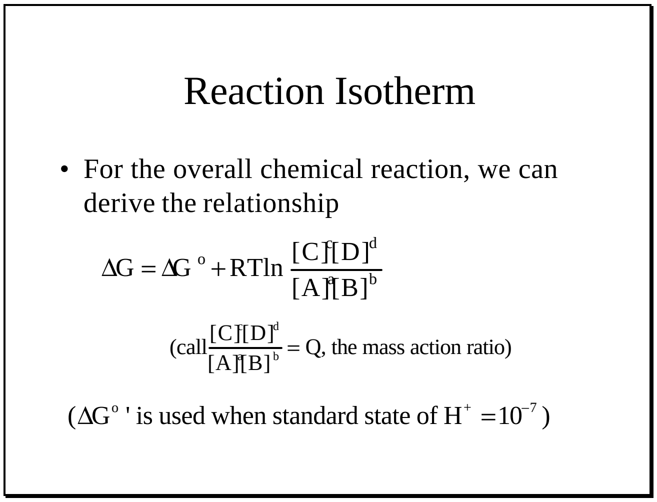

Reaction Isotherm

- For the overall chemical reaction, we can derive the relationship

$$\Delta G = \Delta G^{o} + RT\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$(\text{call}\frac{[C]^c[D]^d}{[A]^a[B]^b} = Q, \text{ the mass action ratio})$$

$$(\Delta G^{o}\text{' is used when standard state of } H^{+} = 10^{-7})$$

The reaction isotherm can be derived from the definition of the chemical potential. We will not go into that derivation here. This equation shows how changing concentrations of reactants and products will effect the free energy change of the reaction.

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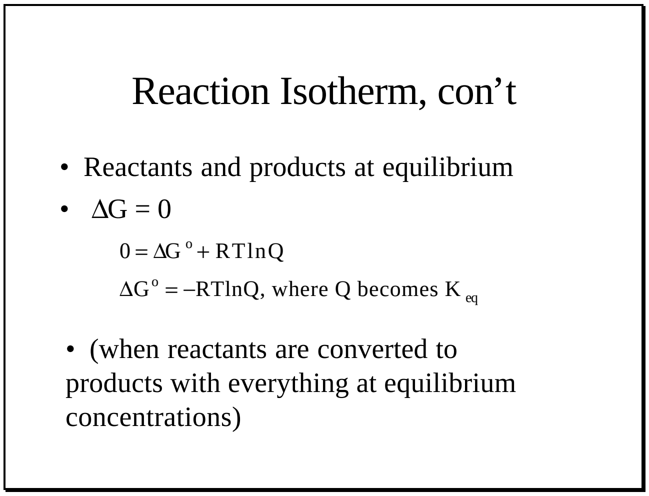

Reaction Isotherm, con't

- Reactants and products at equilibrium
- $\Delta G = 0$

$$0 = \Delta G^{o} + RT\ln Q$$

$$\Delta G^{o} = -RT\ln Q, \text{ where Q becomes } K_{eq}$$

- (when reactants are converted to products with everything at equilibrium concentrations)

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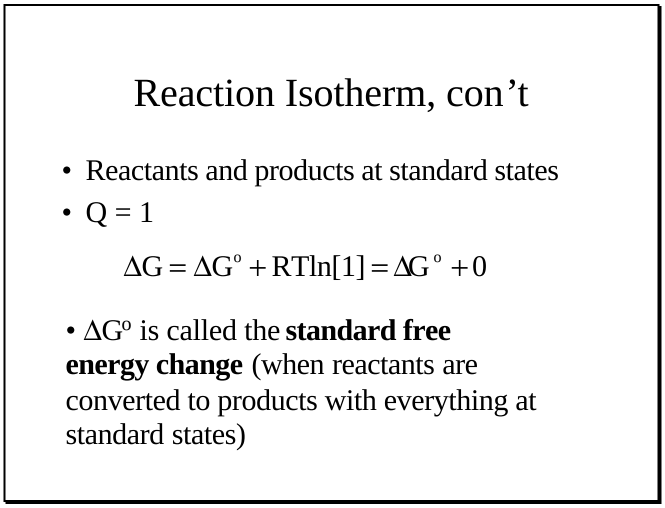

Reaction Isotherm, con't

- Reactants and products at standard states
- Q = 1

$$\Delta G = \Delta G^{o} + RT\ln[1] = \Delta G^{o} + 0$$

- ΔG^{o} is called the **standard free energy change** (when reactants are converted to products with everything at standard states)

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Reaction Isotherm, con't

- Reactants and products at other concentrations

$$\Delta G = \Delta G^o + RT\ln\frac{[C]^c[D]^d}{[A]^a[B]^b} = -RT\ln K_{eq} + RT\ln Q$$

$$\Delta G = RT\ln\frac{Q}{K_{eq}}$$

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ΔG Depends on Relationship of Q to K_{eq}

- $Q/K < 1$; $\Delta G < 0$; spontaneous
- $Q/K > 1$; $\Delta G > 0$; not-spontaneous
- $Q/K = 1$; $\Delta G = 0$; at equilibrium

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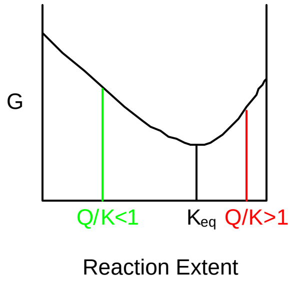
Relationship of Q, K_{eq}, and ΔG



ΔG is also a **partial molar** free energy change, representing the **slope** of the curve at any position **Q.**

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RTlnQ is a Correction Factor to ΔG^o

- Q = 0.01, RT lnQ = -11.4 kJ/mol
- Q = 0.1, RT lnQ = -5.74 kJ/mol
- Q = 1, RT lnQ = 0 kJ/mol
- Q = 10, RT lnQ = +5.74 kJ/mol
- Q = 100, RT lnQ = +11.4 kJ/mol

Remember, R is the gas constant given in appropriate units, i.e. 8.314 J/mol-K. Assume T = 25°C, or 298 K.

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Metabolic Reactions at Steady State

- Calculate ΔG from steady state concentrations
  - It must be negative if reaction is proceeding
    - ($Q/K < 1$)
  - If $Q/K > 0.05$, steady state is **near equilibrium**
  - If $Q/K < 0.05$, steady state is **displaced from equilibrium**
- Regulatory steps are usually displaced from equilibrium

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Coupling of Chemical Reactions

- For a reaction to proceed, ΔG must be negative.
- A reaction with a positive ΔG can be **coupled** to a reaction with a negative ΔG in order for the overall reaction to occur
- For example, consider

glucose + P_i ¾ glucose-6-phosphate + H_2O

ΔG^o = + 13.9 kJ/mol (see Table3.3)

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Coupling of Chemical Reactions, con't

- This reaction is coupled to hydrolysis of ATP

ATP + H_2O ¾ ADP + $P_{i,}$

$\Delta G^o = -30.5$ kJ/mol

- Therefore, for the coupled reaction

ATP+glucose ¾ glucose-6-phosphate + ADP

$\Delta G^o = -30.5 + 13.9 = -16.6$ kJ/mol

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ATP Hydrolysis is a Major Source of "Energy Coupling"

- ATP contains two phosphate anhydride bonds and 5 dissociable protons.
  - (See Fig. 3.15)
- $\Delta G^{o'}$ of ATP hydrolysis depends on pH
  - (See Fig. 3.16)
- $\Delta G^{o'}$ of contributions from H^+ dissociation and electrostatic repulsion
  - (See Fig. 3.11)

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Factors Affecting $\Delta G^{o'}$ of ATP

- Mg^{2+} concentration
  - (see Fig. 3.17)
- Mass action ratio (Q)
  - (see Fig. 3.18)

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Other “High Energy Phosphate” Compounds

- Phosphoenolpyruvate has a very high negative ΔG of hydrolysis (-62.2 kJ/mol), enough to drive ATP synthesis
  - (See Fig 3.14)
- ADP
  - (See Fig. 3.11)
- Pyrophosphate
  - (See Fig. 3.10)
- Creatine phosphate is a “storage form” of ATP in muscle
  - (See Table 3.3)