

Thermodynamics and chemical equilibria

- Lecture 2 8/27/09
- Chapter 1 Voet, Voet and Pratt

Classical Thermodynamics

- Key goals for today's lecture:
 - Define:
 - Gibbs Free Energy (G)

$$G = H - TS$$
 - Thermodynamics as a prediction as to the spontaneous nature of a chemical reaction

$$A + B \longrightarrow C$$
- State Functions
- First and Second Laws
- Heat, work, internal energy, enthalpy, entropy, free energy, chemical potential, System, property, state, adiabatic, diathermal, reversible
- Equilibrium constants

Gibb's Free Energy

- Is a state function (a property of a system that depends only on the current state of the system *and not its history*)
- Gibb's Free Energy is determined at constant T and P :

$$G = H - TS$$

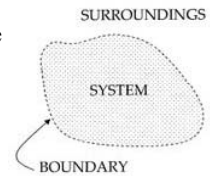
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

- The **Gibbs free energy (G)** of a **system** is defined by an **enthalpy term (H)** (change of the total energy with the system), and the **entropy term (S)** (change in the disorder) at **temperature (T)**

Thermodynamic Definitions: *(What is Enthalpy and Entropy and their relationship to the First and Second Laws?)*

First, Let's Define a System...

- a defined part of the universe
- a chemical reaction
- a bacteria
- a reaction vessel
- a metabolic pathway



Surroundings: the rest of the universe

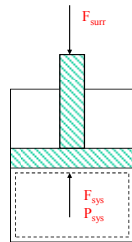
Open system: allows exchange of energy and matter

Isolated system: no exchange of matter or energy.

i.e. A perfect insulated box.

Reversible and Irreversible Processes

- Reversible processes
 - Proceed infinitesimally out of balance.
 - Requires zero friction, epsilon heat gradients
 - Are hypothetical only
- Irreversible process
 - "Real world" process
 - Have finite changes and losses.

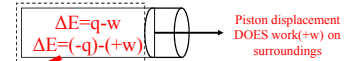


$$F_{\text{sys}} = F_{\text{surr}} + dF$$

First Law of Thermodynamics: Energy is Conserved

- Energy is neither created or destroyed.
 - In a chemical reaction, all the energy must be accounted for.
- Equivalence of work w and energy (heat) q
 - Work (w) is defined as $w = F \times D$ (organized motion)
 - Heat (q) is a reflection of random molecular motions (heat)
- Heat q :
 - If q is positive reaction is endothermic system absorbs heat from surroundings
 - If q is negative exothermic system gives off heat.
- Work w :
 - If w is **positive**, the system does work **ON** the surroundings.

Remember sign conventions of thermodynamics from a steam engine



Cylinder "Feels" hot as it loses heat (- q) to surroundings

Control Volume: Defines the system boundary

Piston displacement DOES work(+ w) on surroundings

Direction of heat flow by definition is most important.

q = heat absorbed by the system from surroundings

If q is positive reaction is endothermic
system absorbs heat from surroundings

If q is negative exothermic
system gives off heat.

$$\Delta U = U_{\text{final}} - U_{\text{initial}} = q - w$$

Exothermic system releases heat = $-q$

Endothermic system gains heat = $+q$

ΔU = a state function dependent on the current properties only.

State Function → Any quantity whose value is independent of its history.

ΔU is **path independent** while q and w are not state functions because they can be converted from one form of energy to the other. (excluding other forms of energy, e.g. electrical, light and nuclear energy, from this discussion.)

Enthalpy (H)

At constant pressure $w = P\Delta V + w^1$

w^1 = work from all means other than pressure-volume work.

$P\Delta V$ is also a state function.

By removing* this type of energy from U , we get enthalpy or 'to warm in'

***remember the signs and direction**

$$H = U + PV$$

$$\Delta H = \Delta U + P\Delta V = q_p - w + P\Delta V = q_p - w^1$$

Enthalpy (H)

When considering only pressure/volume work

$$\Delta H = q_p - P\Delta V + P\Delta V = q_p$$

$$\underline{\Delta H = q_p \text{ when other work is 0}}$$

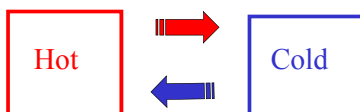
q_p is heat transferred at constant pressure.

In biological systems the differences between

ΔU and ΔH are negligible (e.g. volume changes)

The change in enthalpy in any hypothetical reaction pathway can be determined from the enthalpy change in any other reaction pathway between the same products and reactants.

This is a calorie (joule) "bean counting"



Which way does heat travel? This directionality, is not mentioned in First Law

Second Law and Entropy:

Entropy is the arrow of time and in any cyclic process the entropy will either increase or remain the same.

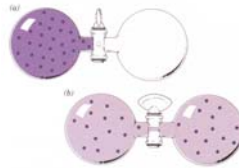
$$G = H - TS$$

- Entropy
 - measure the degree of randomness
 - drives it to the most probable state or maximum disorder
- Lord Kelvin stated that it is impossible take heat from a hot reservoir and convert it to work without transferring heat to a cooler reservoir.
- Entropy defines directionality of a ΔE

Entropy

- Two ways of formulating entropy.
 - **Probable distribution of energies:** Number of way of arranging N particles in n_i groups
 - **Carnot cycle:** Examining the efficiency of a idealized reversible cycle and realize that even “perfect” process cannot convert 100% heat into work.
 - Implies $q_{low} > 0$
 - ie. Efficiency < 1

Gas on its own will expand to the available volume.



- Disorder increases
- N identical molecules in a bulb, open the stop cock you get 2^N equally probable ways that N molecules can be distributed in the bulb.

Entropy (S)

measure the degree of randomness

$$S = k_b \ln W$$

Each molecule has an inherent amount of energy which drives it to the most probable state or maximum disorder.

k_B or Boltzman’s constant equates the arrangement probability to calories (joules) per mole.

Entropy is a state function and as such its value depends only on parameters that describe a state of matter.

The process of diffusion of a gas from the left bulb initially $W_2 = 1$ and $S = 0$ to Right $(N/2) +$ Left $(N/2)$ at equilibrium gives a :

ΔS that is (+) with a constant energy process such that $\Delta U = 0$ while $\Delta S > 0$

This means if no energy flows into the bulbs from the outside expansion will cool the gas! Conservation of Energy says that the increase in Entropy is the same as the decrease in thermal (kinetic) energy of the molecules!!

It is difficult or (impossible) to count the number of arrangements or the most probable state!

So how do we measure entropy?

$$\Delta S \geq \int_{\text{initial}}^{\text{final}} \frac{dq}{T}$$

It takes 80 kcal/mol of heat to change ice at zero °C to water at zero °C

$$\frac{80,000}{273} = 293 \text{ ev's or entropy units}$$

A Reversible process means at equilibrium during the change. This is impossible but makes the calculations easier but for irreversible process

$$\Delta S \geq \frac{q}{T}$$

At constant pressure we have changes in q_p (Enthalpy) and changes in order - disorder (Entropy)

A spontaneous process gives up energy and becomes more disordered.

$$G = H - TS$$

Describes the total usable energy of a system, thus a change from one state to another produces:

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

If ΔG is negative, the process is spontaneous

ΔS	ΔH	
+	-	All favorable at all temperature spontaneous
-	-	Enthalpy favored. Spontaneous at temperature below $T = \frac{\Delta H}{\Delta S}$
+	+	Entropy driven, enthalpy opposed. Spontaneous at Temperatures above $T = \frac{\Delta H}{\Delta S}$
-	+	Non-spontaneous

Equilibrium Constants and ΔG

Now if we are at equilibrium or $\Delta G = 0$ and ΔG° is the free energy of the reaction in the standard state. Then:

$$\Delta G = 0 = \Delta G^\circ + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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

OR

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

i.e. $\Delta G^\circ = \sum \Delta G_f^\circ(\text{products}) - \sum \Delta G_f^\circ(\text{reactants})$

STP

Standard Temperature and Pressure and at 1M concentration.

We calculate ΔG 's under these conditions.

$$aA + bB \rightleftharpoons cC + dD$$

We can calculate a G for each component

(1) $\Delta G = c\bar{G}_c + d\bar{G}_d - a\bar{G}_a - b\bar{G}_b$

(2) $\bar{G}_a - \bar{G}_a^\circ = RT \ln[A]$

combining (1) and (2)

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

So what does ΔG° really mean?

If $K_{eq} = 1$ then $\Delta G = 0$

ΔG° equates to how far K_{eq} varies from 1!!

The Variation of K_{eq} with ΔG° at 25 °C

K_{eq} can vary from 10^6 to 10^{-6} or more!!!

K_{eq}	ΔG° (kJ·mole ⁻¹)
10^6	-34.3
10^4	-22.8
10^2	-11.4
10^1	-5.7
10^0	0.0
10^{-1}	5.7
10^{-2}	11.4
10^{-4}	22.8
10^{-6}	34.3

ΔG° is a method to calculate two reactions whose K_{eq} 's are different; however the initial products and reactants may be far from their equilibrium concentrations

so $\frac{[C]^c [D]^d}{[A]^a [B]^b}$ Must be used

The van't Hoff Relationship

- Methodology of finding ΔH and ΔS from experimental data.

$$\ln K_{eq} = -\frac{\Delta G^\circ}{RT} = -\left(\frac{\Delta H^\circ - T\Delta S^\circ}{RT}\right)$$

$$\ln K_{eq} = \frac{1}{R} \left(\Delta S^\circ - \frac{\Delta H^\circ}{T}\right)$$

Van't Hoff plot

$$\ln K_{eq} = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$$

Most times $\Delta G'^{\circ} = \Delta G^{\circ}$

However, species with either H₂O or H⁺ requires consideration.

For $A + B \leftrightarrow C + D + nH_2O$

$$\Delta G^{\circ} = -RT \ln \frac{[C][D][H_2O]^n}{[A][B]} \quad \Delta G'^{\circ} = -RT \ln K'_{eq} = -RT \ln \frac{[C][D]}{[A][B]}$$

This is because water is at unity. Water is 55.5 M and for 1 mol of H₂O formed:

$$\Delta G'^{\circ} = \Delta G^{\circ} + nRT \ln [H_2O]$$

$$\Delta G'^{\circ} = \Delta G^{\circ} + 9.96 \text{ kJ} \cdot \text{mol}^{-1} \star$$

Standard State for Biochemistry

or

ΔG° versus $\Delta G'^{\circ}$

Unit Activity
25 °C
pH = 7.0 (not 0, as used in chemistry)

[H₂O] is taken as 1, however, if water is in the K_{eq} equation then [H₂O] = 55.5

The prime indicates Biochemical standard state

K'_{eq} $\Delta G'^{\circ}$

Coupled Reactions

$$A + B \rightarrow C + D \quad \Delta G_1 \quad (1)$$

$$D + E \rightarrow F + G \quad \Delta G_2 \quad (2)$$

If $\Delta G_1 \geq 0$ reaction 1 will not occur as written.

However, if ΔG_2 is sufficiently exergonic so $\Delta G_1 + \Delta G_2 \leq 0$

Then the combined reactions will be favorable through the common intermediate D

$$A + B + E \rightarrow C + F + G \quad \Delta G_3 \quad \Delta G_3 = \Delta G_1 + \Delta G_2 \leq 0$$

As long as the overall pathway is exergonic, it will operate in a forward manner.

\star Thus, the free energy of ATP hydrolysis, a highly exergonic reaction, is harnessed to drive many otherwise endergonic biological processes to completion!! \star

\star \star

Units

Biochemical Conventions

Modern biochemistry generally uses Systeme International (SI) units, including meters (m), kilograms (kg), and seconds (s) and their derived units, for various thermodynamic and other measurements. The following table lists the commonly used biochemical units, some useful biochemical constants, and a few conversion factors.

* Units	Energy: heat	joule (J)	kg · m ² · s ⁻² or C · V	
	Electric potential	volt (V)	J · C ⁻¹	
* Prefixes for units	mega (M)	10 ⁶	nano (n)	10 ⁻⁹
	kilo (k)	10 ³	pico (p)	10 ⁻¹²
	milli (m)	10 ⁻³	femto (f)	10 ⁻¹⁵
	micro (μ)	10 ⁻⁶	atto (a)	10 ⁻¹⁸
Constants	Avogadro's number (N)			
		6.0221 × 10 ²³	molecules · mol ⁻¹	

Coulomb (C)	6.241 × 10 ¹⁶ electron charges
Faraday (F)	96,485 C · mol ⁻¹ or 96,485 J · V ⁻¹ · mol ⁻¹
* Gas constant (R)	8.3145 J · K ⁻¹ · mol ⁻¹
Boltzmann constant (k _B)	1.3807 × 10 ⁻²³ J · K ⁻¹ (R/N)
Planck's constant (h)	6.6261 × 10 ⁻³⁴ J · s
Conversions	
angstrom (Å)	10 ⁻¹⁰ m
calorie (cal)	4.184 J
Kelvin (K)	degrees Celsius (°C) + 273.15

Throughout this text, molecular masses of particles are expressed in units of daltons (D), which are defined as 1/12th the mass of a ¹²C atom (1000 D = 1 kilodalton, kD). Biochemists also use molecular weight, a dimensionless quantity defined as the ratio of the particle mass to 1/12th the mass of a ¹²C atom, which is symbolized M_r (for relative molecular mass).

Questions:

A. True or False?

- Free energy change is a measure of the rate of reaction.
- Free energy change is a measure of the maximum amount of work available from a reaction.
- Free energy change is a constant for a reaction under any conditions.
- Free energy change is related to the equilibrium constant for a specific reaction.
- Free energy change is equal to zero at equilibrium.
- A spontaneous process always happens very quickly.
- A spontaneous process can occur with a large decrease in entropy.

B. Consider the following reaction:

Glucose-1-phosphate \rightleftharpoons glucose-6-phosphate
 $\Delta G^\circ = -1.7$ kcal/mole.

What is the equilibrium constant for this reaction at pH 7 and 25°C?

C. Consider the reaction with $\Delta H = 10$ kJ and $\Delta S = 45$ J•K⁻¹.
Is the reaction spontaneous (1) 10°C, (2) at 90°C ?

Lecture 3
Tuesday 9/01/09
Molecules and Water