

Physical Principles in Biology
Biology 3550
Spring 2024

Lecture 27

Enthalpy, the Gibbs Free Energy and Equilibrium Constants

Friday, 22 March 2024

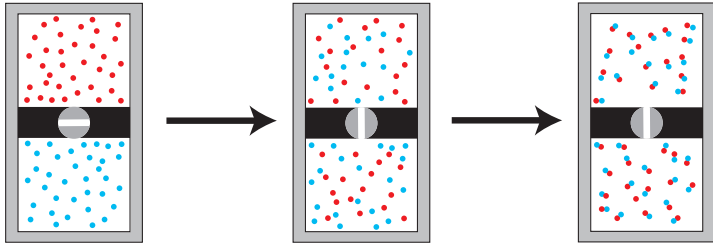
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Announcements

- Problem Set 4:
 - Due Monday, 1 April at 11:59 PM
 - Submit pdf file on Gradescope
- Quiz 4:
 - Friday, 29 March
 - 25 min, second half of class
 - Will cover thermodynamics
 - 50 min
- Review Session:
 - 5:15 PM, Thursday, 28 March
 - HEB 2002
 - Come with questions!
- No class on Monday, 8 April

A Hypothetical Example of a Chemical Reaction

- What happens if a chemical reaction takes place in a perfectly insulated chamber?

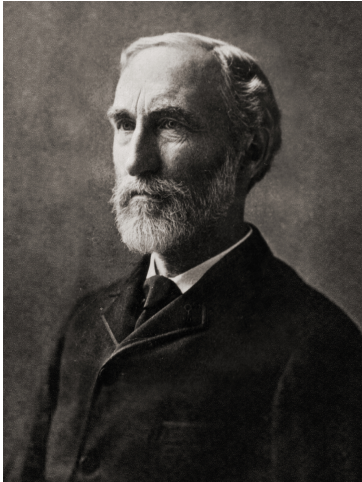


- $q = 0$ and $w = 0$, so ΔE must be zero.
- Can the temperature change?
- Potential energy of the molecules can be converted to kinetic energy (thermal energy), or vice versa.

Potential Energy of Molecules

- When atoms or molecules react chemically, their energies often change.
 - Forming a chemical bond *usually* reduces potential energy of molecules.
 - Breaking a chemical bond *usually* increases potential energy of molecules.
- If the potential energy decreases, where can that energy go?
 - Kinetic energy (temperature) increases.
 - Heat flows out of the system. ($q < 0$)
 - Work is done by the system. ($w < 0$)
 - Some combination of the above.
- Exactly what happens depends on pathways available for heat flow or work.
- Using the second law directly, with ΔS_{sys} and ΔS_{surr} , gets awkward.

J. Willard Gibbs



1839–1903

- Arguably the first great American theoretical scientist.
- Consolidated thermodynamics into a consistent theory.
- Applied thermodynamics to chemistry.
- Also made important contributions in math and optics.

A New State Function: Enthalpy (H)

- Enthalpy, H , is closely related to the internal energy, E .

$$H = E + PV$$

The product PV has the units of energy or work.

- For a process at constant pressure:

$$\Delta H = \Delta E + P\Delta V$$

$P\Delta V$ is work due to a change in volume at constant pressure.

- Two new quantities:

- $w_p = -P\Delta V$ = work done on system in constant pressure process
- q_p = heat absorbed by system in constant pressure process

- From the first law:

$$\Delta E = q_p + w_p = q_p - P\Delta V$$

$$P\Delta V = q_p - \Delta E$$

$$\Delta H = \Delta E + P\Delta V = \Delta E + (q_p - \Delta E) = q_p$$

A New State Function: Enthalpy (H)

Two consistent definitions for ΔH at constant pressure:

- ΔE plus work done on the system due to volume change

$$\Delta H = \Delta E + P\Delta V$$

If there is no volume change, then $P\Delta V = 0$, and $\Delta H = \Delta E$.

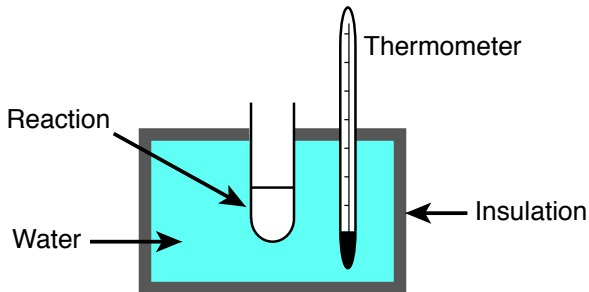
- The heat absorbed during the constant pressure process:

$$\Delta H = q_p$$

Chemical and biochemical reactions are usually studied under conditions of constant (or nearly constant) pressure, and ΔV is usually very small.

ΔH can be experimentally measured.

Measuring ΔH with a Calorimeter



- The water bath represents the “surroundings”.
- If $\Delta H < 0$, heat flows from the reaction vessel and warms the water.
- If $\Delta H > 0$, heat flows into the reaction vessel, and water temperature decreases.

$$\Delta H = -\frac{\Delta T_{\text{water}}}{\text{mass of water (g)}} \quad (\text{in calories})$$

The Gibbs Free Energy, a State Function

- $G = H - TS_{\text{sys}}$

- For a process at constant temperature:

$$\Delta G = \Delta H - T\Delta S_{\text{sys}}$$

- Since $\Delta S_{\text{surr}} = -q/T$, at constant temperature:

$$\Delta S_{\text{surr}} = -q_p/T$$

$$T\Delta S_{\text{surr}} = -q_p = -\Delta H$$

$$\Delta H = -T\Delta S_{\text{surr}}$$

$$\Delta G = -T\Delta S_{\text{surr}} - T\Delta S_{\text{sys}} = -T(\Delta S_{\text{surr}} + \Delta S_{\text{sys}})$$

$$\Delta G = -T\Delta S_{\text{univ}}$$

- Or, $\Delta S_{\text{univ}} = -\Delta G/T$

The Gibbs Free Energy is Used to Apply the Second Law

- From the previous slide:

$$\Delta S_{\text{univ}} = -\Delta G/T$$

- If $\Delta G < 0$
 - $\Delta S_{\text{univ}} > 0$, and the process will be spontaneous.
- If $\Delta G > 0$
 - $\Delta S_{\text{univ}} < 0$, and the reverse process will be spontaneous.
- If $\Delta G = 0$
 - $\Delta S_{\text{univ}} = 0$, and the process is reversible.
(Can be pushed in either direction.)
 - $\Delta G = 0$ defines a system at equilibrium.
- All based on state functions of the system! (at constant pressure)
Don't have to worry about the surroundings.

What About Free Energy as Energy Available to do Work?

- The change in Helmholtz free energy, as previously defined:

$$\Delta F = w_{\text{rev}}$$

– w_{rev} is the maximum work available from a spontaneous process.

- From the first law:

$$\Delta E = q_{\text{rev}} + w_{\text{rev}}$$

$$w_{\text{rev}} = \Delta E - q_{\text{rev}}$$

$$\Delta F = \Delta E - q_{\text{rev}}$$

- For a constant-temperature process:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}$$

$$q_{\text{rev}} = T \Delta S_{\text{sys}}$$

$$\Delta F = \Delta E - T \Delta S_{\text{sys}}$$

The Helmholtz and Gibbs Free Energy Functions

- For a constant temperature process:

$$\Delta F = \Delta E - T\Delta S_{\text{sys}}$$

- The standard definition of the Helmholtz free energy:

$$F = E - TS_{\text{sys}}$$

- Compare to:

$$\Delta G = \Delta H - T\Delta S_{\text{sys}}$$

- Since $\Delta H = \Delta E - w_p$:

$$\Delta G = \Delta F - w_p$$

$-\Delta G$ is the maximum work available from a process ($-\Delta F$) minus the work due to volume change at constant pressure.

The Helmholtz Free Energy

- From previous slide:

$$\Delta G = \Delta F - w_p$$

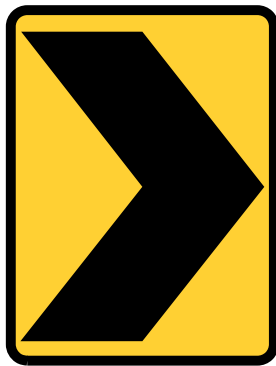
- If volume change is small, and w_p can be ignored:

- $\Delta G \approx \Delta F$
- If $\Delta G < 0$: Process is favorable, and the maximum work available from the process is: $-\Delta F = -\Delta G - w_p \approx -\Delta G$
- If $\Delta G > 0$: Process is unfavorable, and the minimum work required to drive the process is: $\Delta F = \Delta G + w_p \approx \Delta G$

- Commonly made assumptions for chemical reactions in dilute solutions:

- $P\Delta V = -w_p \approx 0$
- $\Delta H \approx \Delta E$: ΔH Represents change in internal energy.
- $\Delta G \approx \Delta F$: $-\Delta G$ Represents maximum work from a spontaneous process.

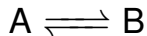
Warning!



Direction Change

Equilibrium Constants

The Equilibrium Constant for a Chemical Reaction



- The reaction can occur in either direction. (at least in principle)
- The probability that any molecule of A will be converted to a molecule of B is the same as for any other molecule of A.
 - The total rate of conversion of A to B is proportional to the concentration of A.
 - Similarly, the total rate of conversion of B to A is proportional to the concentration of B.
- A differential equation:

$$\frac{d[A]}{dt} = -k_f[A] + k_r[B]$$

The constants k_f and k_r are called rate constants.

The Equilibrium Constant for a Chemical Reaction



■ From the previous slide:

$$\frac{d[A]}{dt} = -k_f[A] + k_r[B]$$

■ Whatever the starting concentrations, $[A]$ and $[B]$ will eventually adjust so that they no longer change.

■ At equilibrium:

$$\frac{d[A]}{dt} = -\frac{d[B]}{dt} = 0$$

The Equilibrium Constant for a Chemical Reaction



- At equilibrium:

$$\frac{d[A]}{dt} = -\frac{d[B]}{dt} = -k_f[A]_{\text{eq}} + k_r[B]_{\text{eq}} = 0$$

$[A]_{\text{eq}}$ and $[B]_{\text{eq}}$ are the concentrations of A and B at equilibrium.

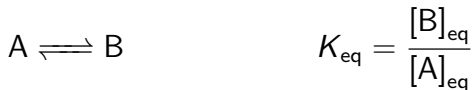
- Rearranging:

$$k_r[B]_{\text{eq}} = k_f[A]_{\text{eq}}$$

$$\frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = \frac{k_f}{k_r} = K_{\text{eq}}$$

K_{eq} is defined as the equilibrium constant.

The Equilibrium Constant and Free Energy Change for a Chemical Reaction



- At equilibrium, a little bit of work can push the reaction in either direction.

This defines the condition where $\Delta G = 0$

No work can be done!

- Definition of ΔG for a chemical reaction:

The free energy change for converting one mole of reactants to one mole of products, at specified concentrations, without significantly changing concentrations(!).

Implies a very, very large volume!

Or, a mechanism that restores concentrations continuously.

The Relationship Between Free Energy and the Equilibrium Constant



■ ΔG depends on concentrations of A and B.

- If $\frac{[B]}{[A]} < K_{\text{eq}}$, the reaction will try to shift towards B, $\Delta G < 0$
- If $\frac{[B]}{[A]} > K_{\text{eq}}$, the reaction will try to shift back to A, $\Delta G > 0$

■ Define standard concentrations to specify ΔG :

- Concentrations of all species are 1 M for solutions or 1 atm for gasses.
- Free energy change at these concentrations is called ΔG° .

The Relationship Between Free Energy and the Equilibrium Constant

- If reactants and products are at equilibrium concentrations:

$$\Delta G = 0$$

- If reactants and products are at standard state concentrations (1 M):

$$\Delta G \equiv \Delta G^\circ$$

$$\Delta G^\circ = -RT \ln \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = -RT \ln K_{\text{eq}}$$

ΔG° and K_{eq} convey essentially the same information.

- For other concentrations:

$$\Delta G = \Delta G^\circ + RT \ln \frac{[B]}{[A]}$$

The Relationship Between the Standard Free Energy Change and the Equilibrium Constant

$$\Delta G^\circ = -RT \ln K_{\text{eq}} \quad \text{A} \rightleftharpoons \text{B} \quad K_{\text{eq}} = \frac{[\text{B}]_{\text{eq}}}{[\text{A}]_{\text{eq}}}$$

- If $K_{\text{eq}} > 1$:
 - Reaction favors B over A.
 - $\Delta G^\circ < 0$

- If $K_{\text{eq}} < 1$:
 - Reaction favors A over B.
 - $\Delta G^\circ > 0$

- If $K_{\text{eq}} = 1$:
 - A and B have equal free energies.
 - $\Delta G^\circ = 0$

Clicker Question #1

For a hypothetical reaction, $A \rightleftharpoons B$, $K_{\text{eq}} = 1500$ at 25°C .

What is the standard free energy change at this temperature?

$$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$$

A) -8 kJ/mol

B) -18 kJ/mol

C) 0 kJ/mol

D) 8 kJ/mol

E) 18 kJ/mol

$$\begin{aligned}\Delta G^\circ &= -RT \ln K_{\text{eq}} = -8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 298 \text{ K} \times \ln 1500 \\ &= -18,000 \text{ J/mol} = -18 \text{ kJ/mol}\end{aligned}$$

Clicker Question #2

For a different hypothetical reaction, $C \rightleftharpoons D$, $\Delta G^\circ = 5 \text{ kJ/mol}$ at 25°C .

What is the equilibrium constant at this temperature?

- A) -1
- B) -0.13
- C) 0.13
- D) 1
- E) 7.5

$$K_{\text{eq}} = e^{-\Delta G^\circ / (RT)} = e^{-5,000 \text{ J/mol} / (8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 298 \text{ K})} = 0.13$$