

Basic Thermodynamics

Concepts

Elements of Biophysics

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<http://biofold.org/>



Biomolecules
Folding and
Disease

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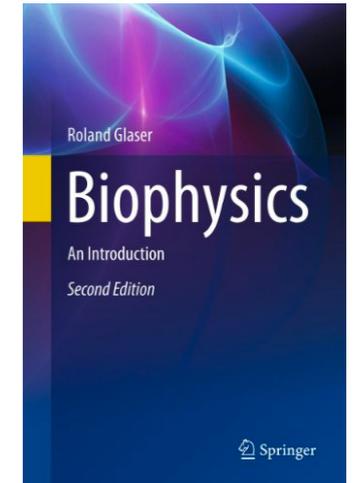


Main Topics

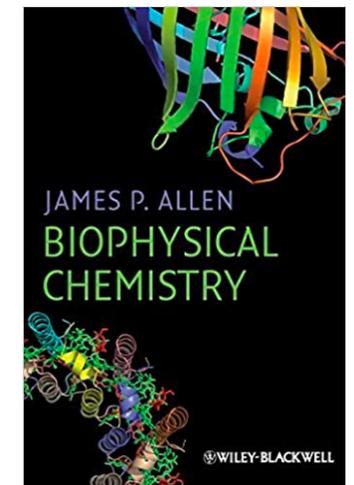
- Basic notions of **thermodynamics and kinetics**
- Basic elements of **structural and functional biology**.
- Basic elements of **cell biology**.

Suggested books

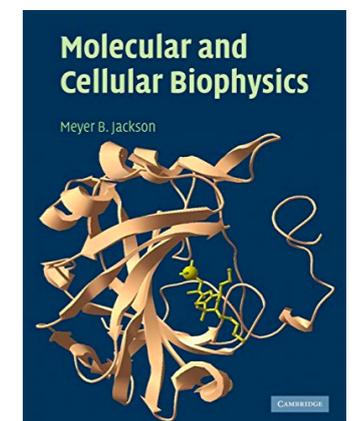
- **Biophysics: An Introduction** by Roland Glaser



- **Biophysical Chemistry** by James P. Allen



- **Molecular and Cellular Biophysics** by Meyer B. Jackson



What is Biophysics?

- The subjects of Biophysics are the **physical principles underlying** all processes of living systems.
- Biophysics is an **interdisciplinary science** which includes notions of biology and physics connected to other disciplines such as mathematics, physical chemistry, and biochemistry.
- Although not all biological reactions can be explained, there is **no evidence that physical laws are no longer valid in biological systems.**

Thermodynamics Concepts

- Definition: **Thermodynamics** is the characterization of the states of matter, namely gases, liquids, and solids, in terms of energetic quantities.
- Thermodynamic **rules are very general** and apply to all types of objects, ranging from gas molecules to cell membranes to the world.
- Fundamental thermodynamics **state variables** are: pressure, temperature and volume

State variables

- A state variable is a property of a system that **depends only on the current, equilibrium state of the system** and thus do not depend on the path by which the system arrived at its present state.
- The state of an ideal gas can be characterized by:
 - Pressure (P)**: is the force applied perpendicular to the surface of an object per unit area over which that force is distributed.
 - Temperature (T)**: physical quantity that expresses the hotness of matter or radiation. It is related to the average kinetic energy of microscopic particle, such as atom, molecule, or electron.
 - Volume (V)**: is a measure of the three-dimensional space occupied by an object.
- **Relationships among the different properties of the system.** For an ideal gas the relationship between state variable are described by the equation:

$$PV=nRT \quad (\text{van der Waals equation})$$

$$R = 0.082 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

I Law of Thermodynamics

- The law of conservation of energy states that **the total energy of any isolated system is constant**; energy can be transformed from one form to another, but can be neither created nor destroyed.

$$\Delta U = q + w$$

ΔU is the change in internal energy, w is the work done on (or done by the system) and q is the transferred heat.

Work

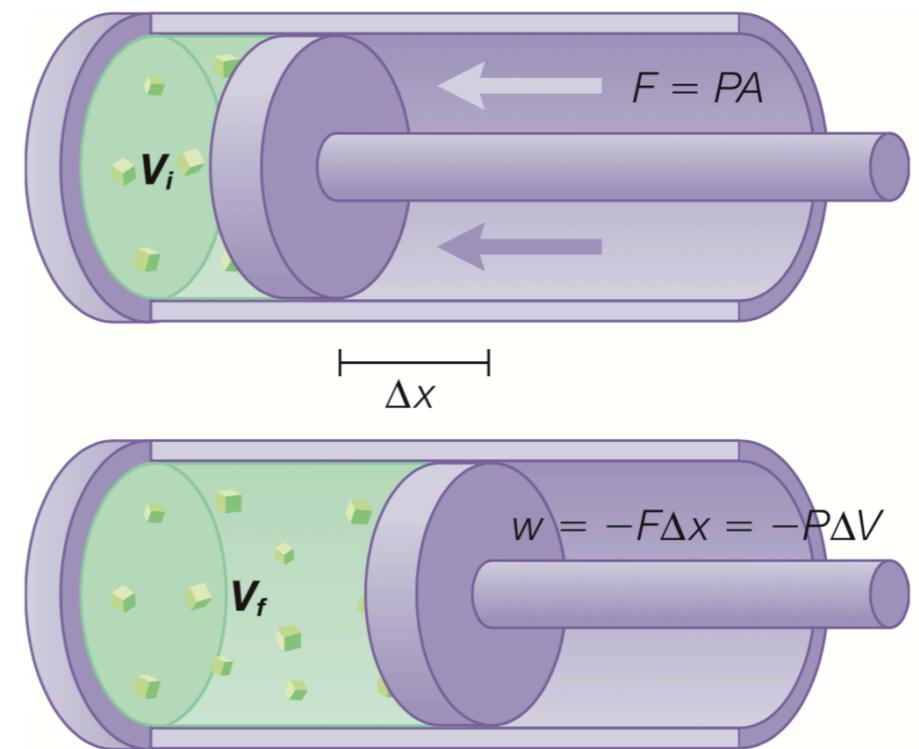
The **work** is performed when a **force** (F) is used to move an object through a **distance** (Δx),

$$w = -F\Delta x$$

$$w = -F\Delta x = -(PA)\Delta x = -P\Delta V$$

$$w = -\int_{V_1}^{V_2} P dV$$

$$w = -\int_{V_i}^{V_f} P dV = -\int_{V_i}^{V_f} \left(\frac{nRT}{V} \right) dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$



Enthalpy

Formally, enthalpy (H), is defined in terms of internal energy (U), and the product of pressure (P) and volume (V) according to:

$$H = U + PV$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + P\Delta V \quad P = \text{constant}$$

$$\Delta H = \Delta U + P\Delta V = (q - P\Delta V) + P\Delta V = q$$

At constant pressure, the change in enthalpy is equal to the heat transferred.

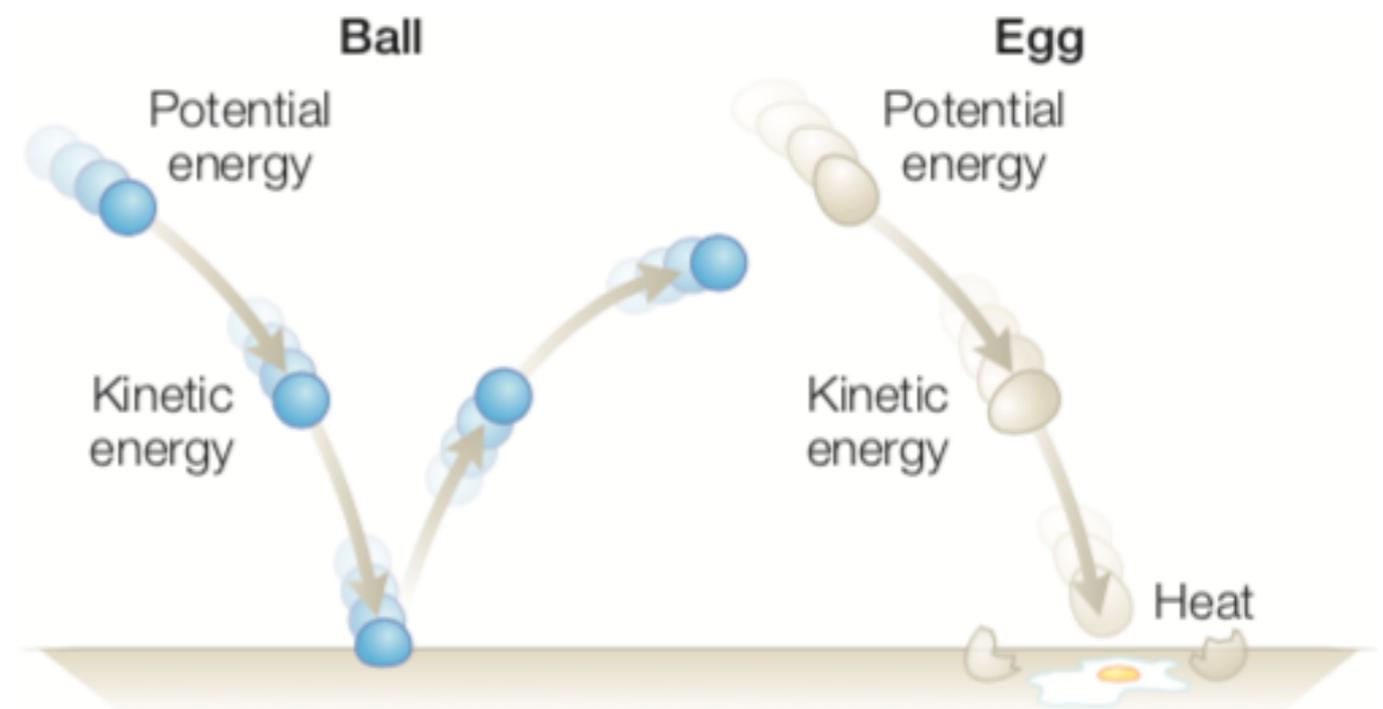
II Law of Thermodynamics

- The second law states that if the physical **process is irreversible**, the combined **entropy of the system and the environment must increase**.

Ball vs Egg

For the ball the kinetic energy is transformed in potential energy.

For the egg the kinetic energy is converted in to heat but the egg is in a more disordered state.



Entropy

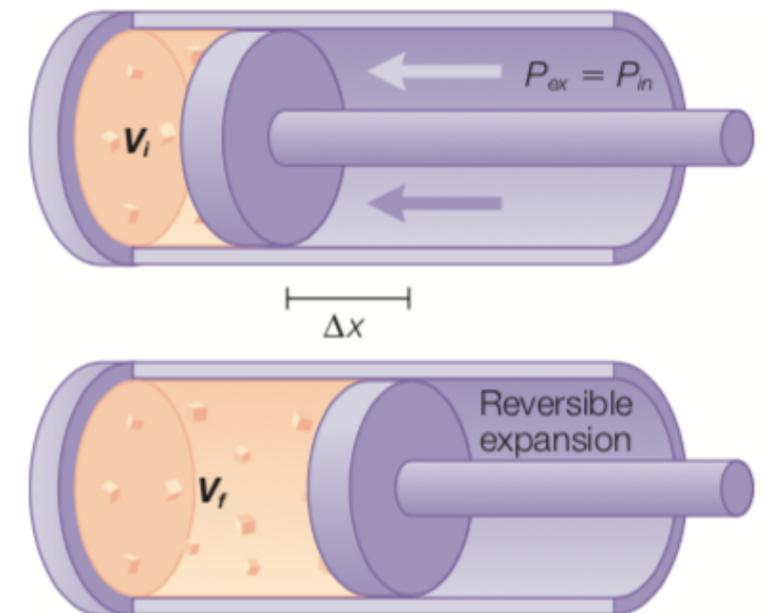
The **entropy represents the molecular disorder of a system**. The concept of entropy is explicitly defined in terms of the heat and temperature of a system. In an isothermal process, the change in entropy is

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

For an ideal gas, when temperature is fixed, internal energy does not change and the heat flow balances the work, yielding:

$$q = -w = nRT \ln \frac{V_f}{V_i} = T \left(nR \ln \frac{V_f}{V_i} \right)$$

$$\Delta S = \frac{q}{T} = \left(nR \ln \frac{V_f}{V_i} \right)$$



III Law of Thermodynamics

- The third law of thermodynamics states that the **entropy of all perfectly crystalline substances is zero at a temperature of zero Kelvin.**

In general, as **temperature is decreased**, random motion due to **thermal motion is quenched**. For a crystal, all of the atoms or molecules are located in well-defined, regular arrays and hence **spatial disorder is absent**.

From a molecular viewpoint, the entropy can also be viewed as being zero as the **arrangement of molecules is uniquely defined**.

Gibbs energy

- The **Gibbs energy** is a quantity that is used to measure the **maximum amount of work** done in a thermodynamic system when the **temperature and pressure are kept constant**.

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

$$\Delta G = 0$$

Equilibrium

$$\Delta G < 0$$

Spontaneous process

$$\Delta G > 0$$

Unfavourable process

Gibbs energy for ideal gas

For an ideal gas, the change in the Gibbs energy can be directly related to its thermodynamic parameters

$$dG = dH - d(TS)$$

$$dH = dU + PdV + VdP$$

$$dU = TdS - PdV \quad \text{with} \quad q = TdS \quad \text{and} \quad w = -PdV$$

$$dG = TdS - PdV + PdV + VdP - TdS - SdT$$

$$dG = VdP - SdT$$

$$dG = VdP \quad T = \text{constant}$$

$$\Delta G = \int_{P_i}^{P_f} \frac{nRTdP}{P} = nRT \ln \frac{P_f}{P_i}$$

Equilibrium Constant

For any given reaction $A \rightarrow B$ with an equilibrium constant K , the value of the equilibrium constant can be written in terms of the change in the Gibbs energy:

$$K = \frac{[B]}{[A]} = e^{-\Delta G/kT}$$

The **equilibrium constant** for a reaction is simply an **alternative representation of the Gibbs energy change**.

$$K=1 \rightarrow \Delta G = 0$$

Equilibrium

$$K>1 \rightarrow \Delta G < 0$$

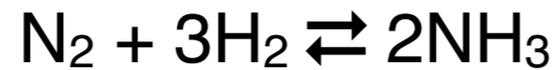
Proceeds forward

$$K<1 \rightarrow \Delta G > 0$$

Proceeds backward

Exercise

Given the following reaction with $\Delta G^\circ = -33.0 \text{ kJ} \times \text{mol}$ at 298 K calculate the equilibrium constant



- calculate the equilibrium constant
- what happen when at $T= 1000 \text{ K}$ and $\Delta G^\circ = 106.5 \text{ kJ} \times \text{mol}$?
- what happen when at $T= 464 \text{ K}$ and $\Delta G^\circ = 0 \text{ kJ} \times \text{mol}$?