

Thermodynamics

Thermodynamics

- Thermodynamics is the study of the effects of work, heat, and energy on a system
- Thermodynamics is only concerned with macroscopic (large-scale) changes and observations

What is Energy?

“...the term **energy** is difficult to define precisely, but one possible definition might be the capacity to produce an effect”

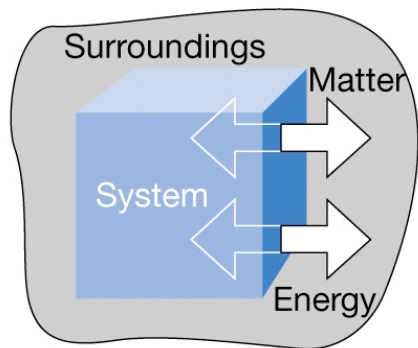
Basic Thermodynamic Definitions

- System - quantity of matter or region of space chosen for study
- Surroundings - mass or region outside of system
- Boundary - real or imaginary surface that separates system from surroundings
- Property - a characteristic of a system that can be defined without knowledge of the system's history
- Extensive Property - property that is dependent on system size
- Intensive Property - property that is independent of system size
- State - a condition of a system that is fully described by properties

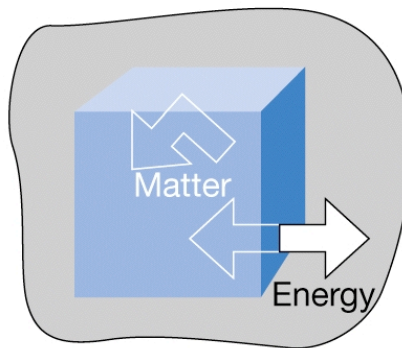
System and Surroundings

A **system** is defined as the matter within a defined region of space (i.e., reactants, products, solvent)

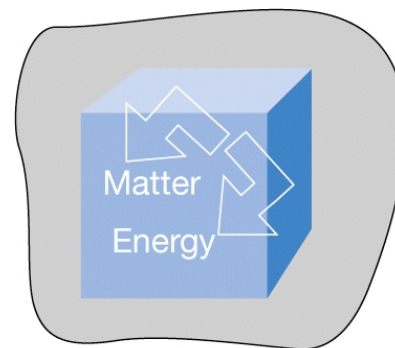
The matter in the rest of the universe is called the **surroundings**



(a) Open



(b) Closed



(c) Isolated

Internal Energy (U)

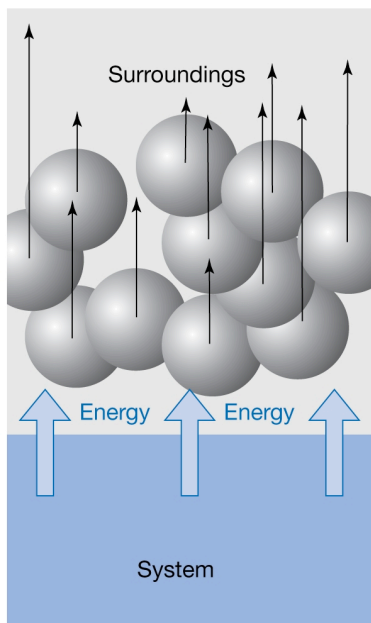
- Is the energy within the system in the absence of *external* effects
- The internal energy of a system is the total **kinetic energy** due to the motion of molecules (translational, rotational, vibrational) and the total **potential energy** associated with the vibrational and electric energy of atoms within molecules or crystals.
- U is a state function, that is, its value depends only on the current state of the system
- Only ΔU can be measured directly

Work (w) and Heat (q)

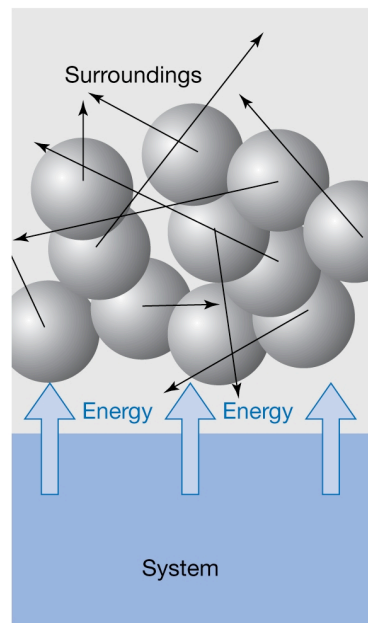
- **Heat and work are modes of transfer of energy and not 'energy' itself**
- Work (w) in mechanics is displacement (d) against a resisting force (F). $w = F \times d$
- Heat is defined as transfer of energy as a result of a temperature difference.
- Heat is NOT an entity or even a form of energy; heat is a mode of transfer of energy.

Work (w) and Heat (q)

$$\Delta U = q + w = U_f - U_i$$



Work involves the non-random movement of particles



Heat involves the random movement of particles

First Law of Thermodynamics: Energy is Conserved

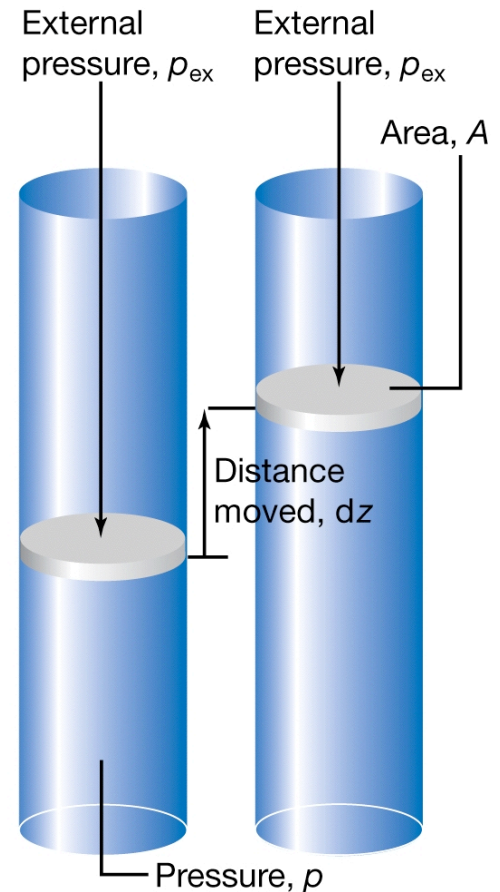
- Energy can be changed from one form to another, but it cannot be created or destroyed. The total amount of energy and matter in the Universe remains constant, merely changing from one form to another.
- In a chemical reaction, all the energy must be accounted for.
- The total energy of the universe is a constant

Enthalpy (H)

$$H = U + pV$$

$$\Delta H = q_p$$

The **enthalpy** is the heat absorbed or emitted by a system at constant pressure



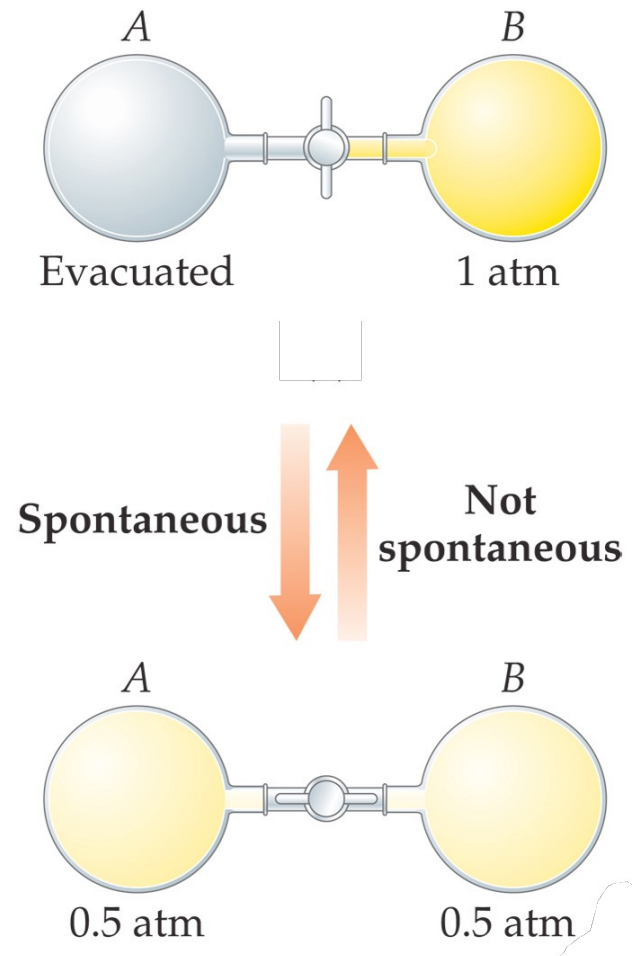
$$w = - p_{\text{ex}} V$$

Need for the second law

- The First Law of Thermodynamics tells us that during any process, energy must be conserved.
- First Law fails to answer these questions:
 - In which direction will a process proceed spontaneously?
 - Is there a limit to how much work can be obtained from a reaction?

Spontaneous Processes

- Spontaneous processes are those that can proceed without any outside intervention.
- Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.
- Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures

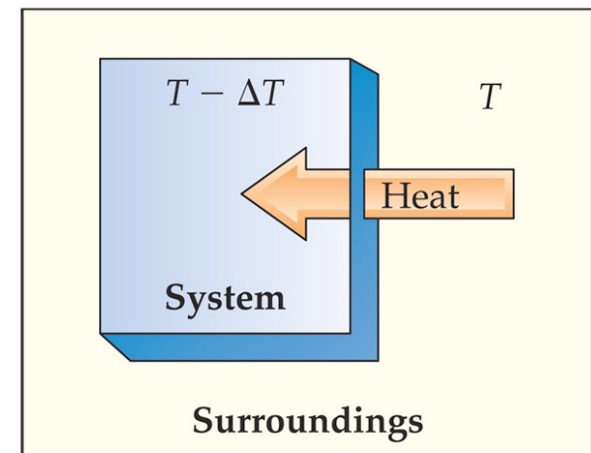
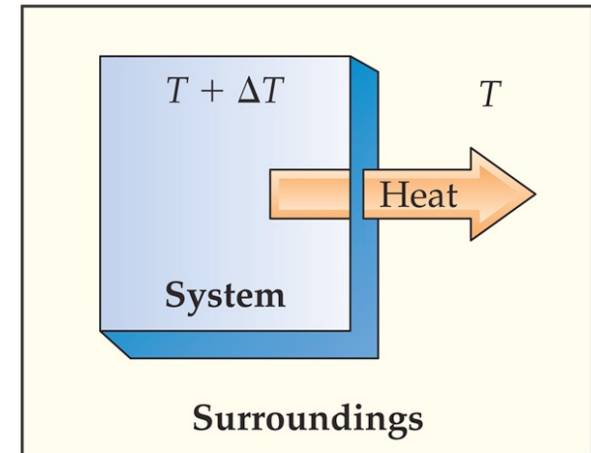


Spontaneous Processes

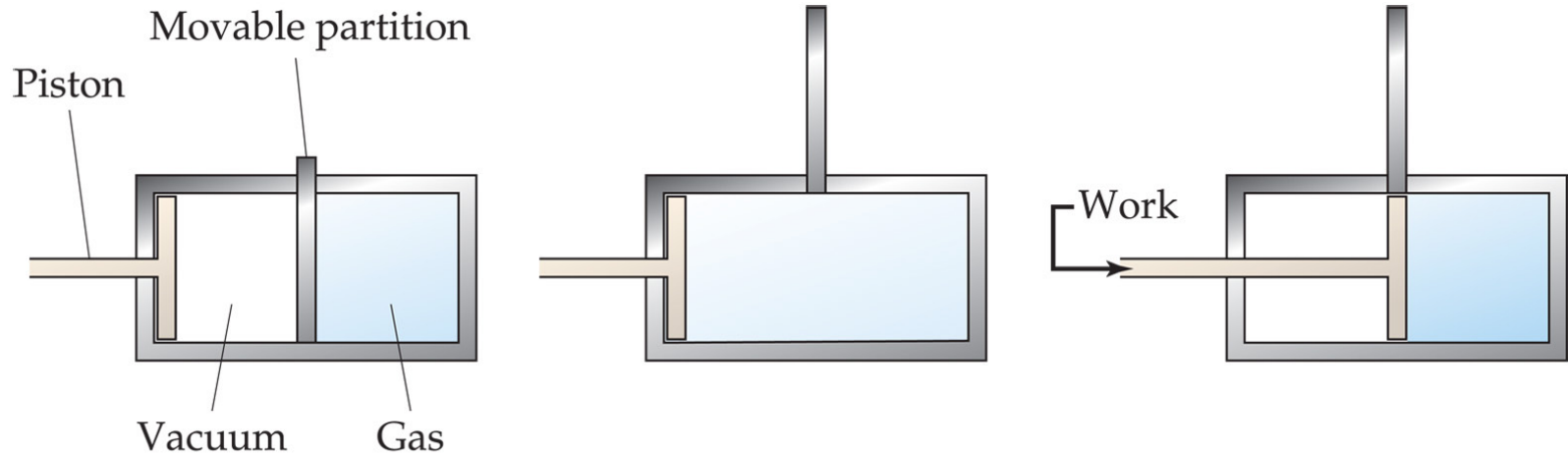
The apparent driving force of spontaneous change is the tendency of energy and matter to disperse

Reversible vs Irreversible Processes

- In a reversible process the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.
- Changes are infinitesimally **small** in a reversible process.



Reversible vs Irreversible Processes



- Irreversible processes cannot be undone by exactly reversing the change to the system.
- All **Spontaneous** processes are **irreversible**.
- All **Real** processes are **irreversible**.

Spontaneous Processes

The apparent driving force of spontaneous change is the tendency of energy and matter to disperse

Entropy

- Entropy can be thought of as a measure of the randomness of a system.
- It is related to the various modes of motion in molecules.
- Like total energy, E , and enthalpy, H , entropy is a state function.
- Therefore,

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

2nd Law of Thermodynamics

- The entropy of the universe does not change for reversible processes and increases for spontaneous processes.

Reversible (ideal):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

Irreversible (real, spontaneous):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

2nd Law of Thermodynamics

$$\Delta S = \frac{q_{rev}}{T}$$

(reversible)

$$\Delta S > \frac{q_{irrev}}{T}$$

(irreversible)

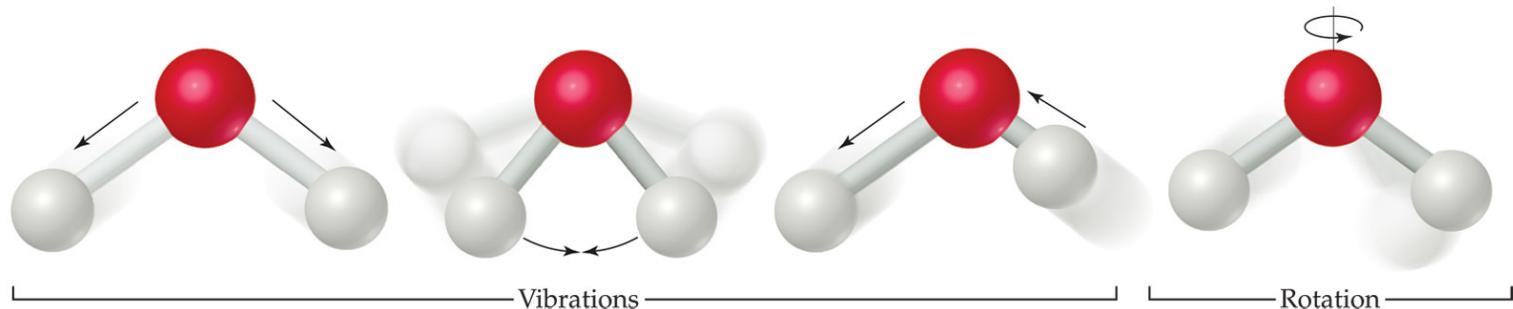
- Some of the enthalpy in a system is not convertible into work (PdV work for instance) because it is consumed by an increase in entropy
- Which could be restated that it requires some amount of work to increase entropy

Meaning of entropy and the second law

- Second Law provides a way of describing the conversion of heat into work
- The Second Law is about the tendency of particles to go from being concentrated to being spread out in space – spontaneously. It is also about the tendency of energy to go from being “concentrated” to being “spread out” – spontaneously
- If we put some quantity of heat q into the system, whatever work w is done by the system will be such that $w < q$.

Entropy on the Molecular Scale

- Temperature is a measure of the average kinetic energy of the molecules in a sample.
- Molecules exhibit several types of motion
- Boltzmann envisioned the motions of a sample of molecules at a particular instant in time.
 - This like to taking a snapshot of all the molecules.
- He referred to this sampling as a **microstate** of the thermodynamic system.



Entropy on the Molecular Scale

- Each thermodynamic state has a specific number of microstates, W , associated with it.
- Entropy is

$$\Delta S = \Delta S_f - \Delta S_i = k \ln W$$

where k is the Boltzmann constant, 1.38×10^{-23} J/K.

Gibbs Free Energy (G)

- The amount of energy capable of doing work during a reaction at constant temperature and pressure.
- 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

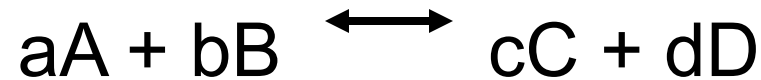
Gibbs Free Energy (G)

TABLE 1-4 Variation of Reaction Spontaneity (Sign of ΔG) with the Signs of ΔH and ΔS

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$
—	+	The reaction is both enthalpically favored (exothermic) and entropically favored. It is spontaneous (exergonic) at all temperatures.
—	—	The reaction is enthalpically favored but entropically opposed. It is spontaneous only at temperatures <i>below</i> $T = \Delta H/\Delta S$.
+	+	The reaction is enthalpically opposed (endothermic) but entropically favored. It is spontaneous only at temperatures <i>above</i> $T = \Delta H/\Delta S$.
+	—	The reaction is both enthalpically and entropically opposed. It is nonspontaneous (endergonic) at all temperatures.

Standard Temperature and Pressure and at 1M concentration

We calculate ΔG 's under these conditions.



We can calculate a G for each component

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

$$(2) \quad \bar{G}_a - \bar{G}_a^0 = RT \ln[A]$$

combining (1) and (2)

$$(3) \quad \Delta G = \Delta G^0 + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

At equilibrium or $\Delta G = 0$

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

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

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

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

Le Chatelier's principle

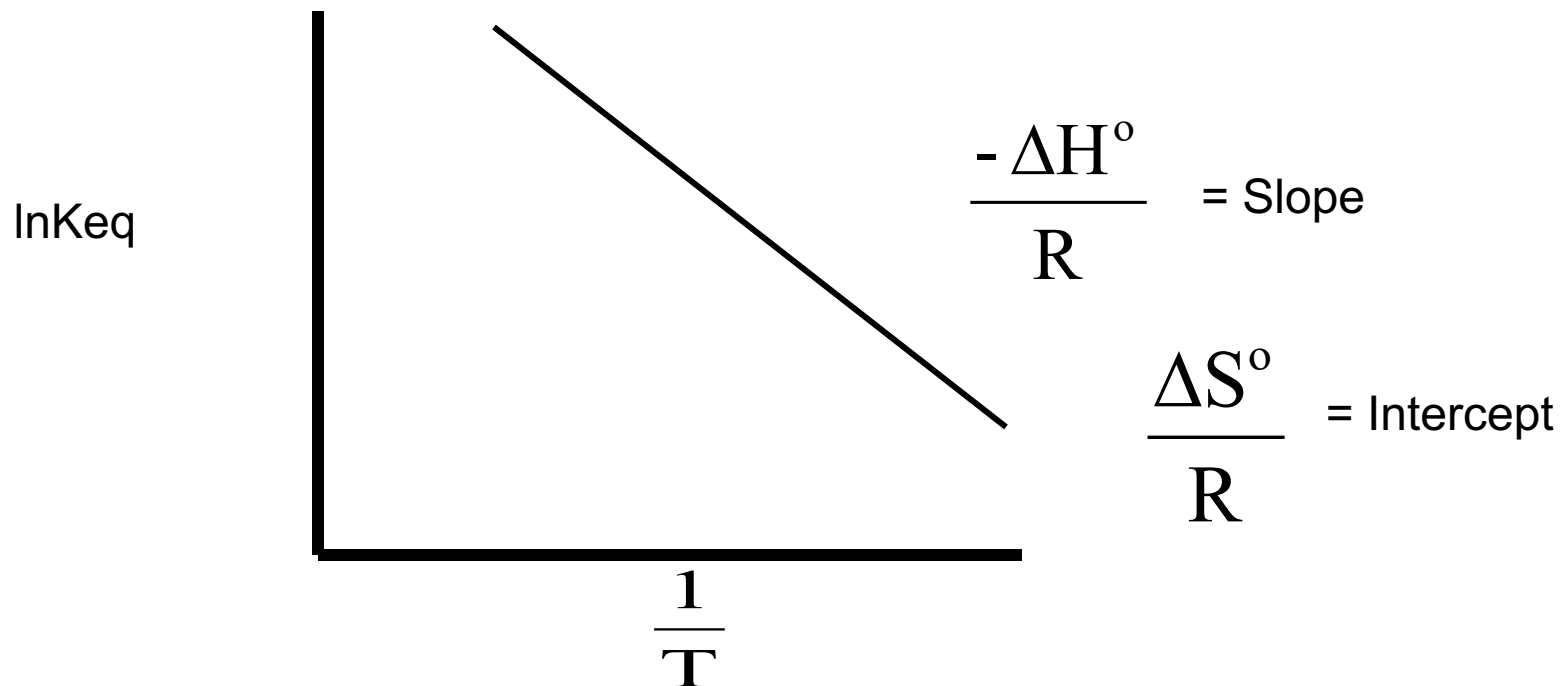
Any deviation from equilibrium stimulates a process which restores equilibrium. All closed systems must therefore reach equilibrium

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

R = gas constant for a 1M solution

Plot $\ln K_{\text{eq}}$ vs. $1/T$ (remember T is in absolute degrees Kelvin)

Van't Hoff plot



Standard State for Biochemistry

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}

$\Delta G'^0$

$\Delta G'$