

Chapter 5

Principles of thermodynamics

PRINCIPLES OF THERMODYNAMICS

- Thermodynamics: The science of energy.
- Energy: The ability to cause changes.
- The name thermodynamics stems from the Greek words therme (heat) and dynamis (power).
- *Thermo chemistry*: is the study of heat change in chemical reactions
- Thermodynamics is a branch of science concerned with heat and temperature and their relation to energy and work.
- **Biological thermodynamics** is the quantitative study of the energy transductions that occur in and between living organisms, structures, and cells and of the nature and function of the chemical processes underlying these transductions.
- The field of biological thermodynamics is focused on principles of chemical thermodynamics in biology and biochemistry.
- A simple use of thermodynamics would be to predict what compounds could possibly be used as energy sources for organism.
- Thermodynamics is usually concerned with the difference in energy between reactants and product
- Physical properties of materials and systems can often be categorized as being either:
- **intensive** or **extensive** quantities, according to how the property changes when the size (or extent) of the system changes

- According to IUPAC (International Union of Pure and Applied Chemistry), an **intensive** property is one whose magnitude is independent of the size of the system (i.e, density, pressure, temperature, and concentration). An **extensive** property is one whose magnitude is additive for subsystems (i.e, volume, weight, energy).

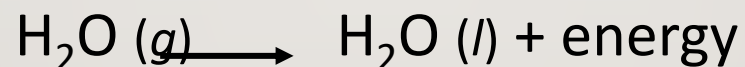


Thermodynamic process are either:

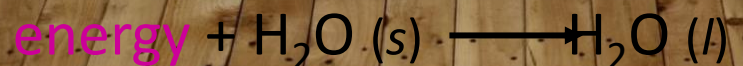
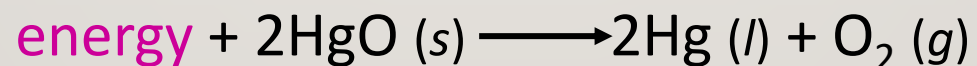
- Reversible: happens slow enough to be reversed
- irreversible: can not be reserved

2 types of process:

**Exothermic process* is any process that gives off heat – transfers thermal energy from the system to the surroundings.



***Endothermic process* is any process in which heat has to be supplied to the system from the surroundings.



WORK

- A system can do work on the surroundings, or the surroundings can do work on the system.
- Work: is defined as the product of force times a distance.

$$W = F \cdot dX ,$$

F is the force in newtons (N)

X is the distance in meter (m)

- W is the work done in [[joules (J), 1 erg = 10^{-7} J , 1 cal = 4.184 J]]
- Work is **positive** if the surroundings are doing work on the system.
- Work is **negative** if the system is doing work on the surroundings.



HEAT

- When two bodies are in contact with each other, their temperatures tend to become equal.
 - Energy is being exchanged. The hot body will lose energy and cool down; the cold body will gain energy and warm up. {heat transfer}
-
- Heat is +ve if it flows into the system(gain)
 - Heat is -ve if it flows out of the system(lose)
 - Heat is the transfer of thermal energy between two bodies that are at different temperatures.
 - Temperature is the measurement of the avg. KE(kinetic energy) of the molecules in a material

FIRST LAW OF THERMODYNAMICS

SYSTEMS

- System
- Surroundings
- Boundaries

✓ Two types of exchange can occur between the system and surroundings.

1- **Energy exchange** (heat, radiation....etc).

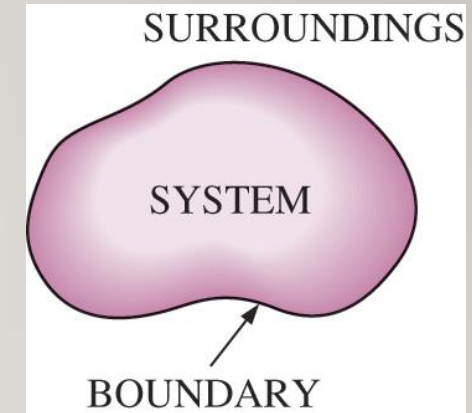
2- **Matter exchange** (movement of molecules across the boundary between the system and the surroundings).

- Based on the types of exchange which take place, three types of systems are identified.

1- **Isolated systems**: no exchange of matter or energy.

2- **Open systems**: Exchange of both matter and energy.

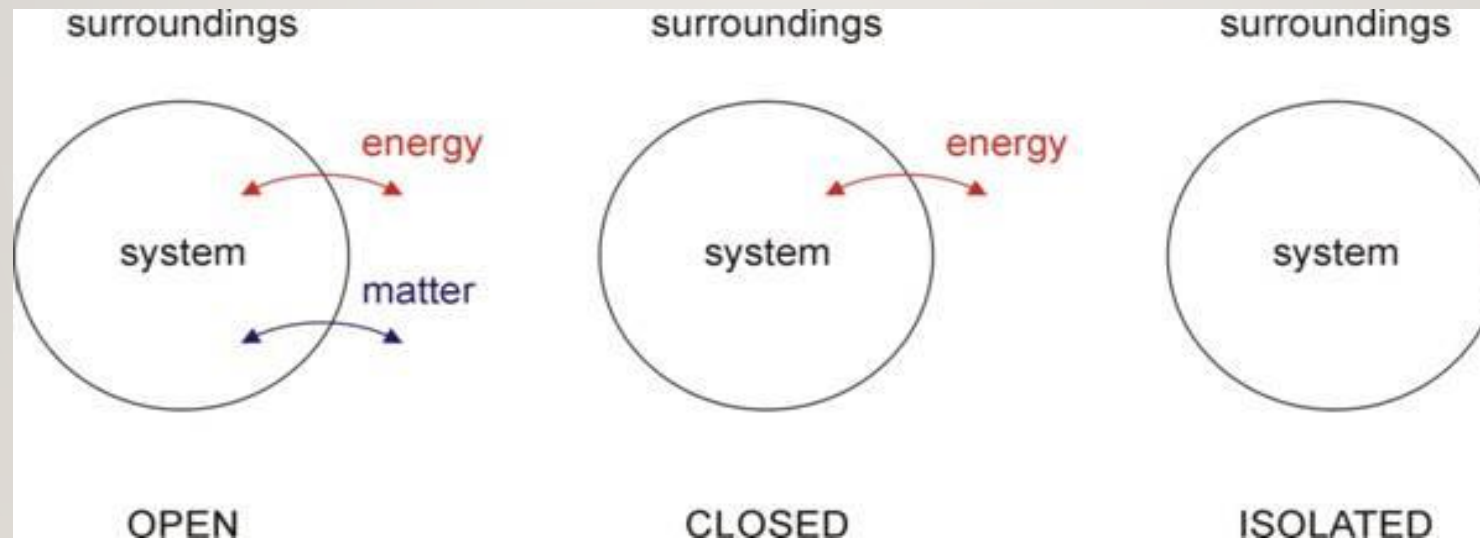
3- **Closed system**: no exchange of matter but exchange of energy.



- The **first law of thermodynamics** is a version of the law of conservation of energy.
- The law of conservation of energy states that the total energy of an isolated system is constant; energy can be transformed from one form to another, but cannot be created or destroyed.
- The first law of thermodynamics is often formulated by stating that the change in the internal energy of a closed system is equal to the amount of heat supplied to the system, minus the amount of work done by the system on its surroundings.
- $U=Q-W$



In thermodynamics, a **closed system** can exchange energy (as heat or work) but not matter, with its surroundings. An **isolated system** cannot exchange any heat, work, or matter with the surroundings, while an **open system** can exchange energy and matter.



- The total internal energy of the universe can be considered as divided into two functional areas: the system and the environment.
- The energy remains constant even though energy may flow *from the system* to the environment or *from the environment* to the system.
- For a change in state the first law of thermodynamics can be expressed by the equation:
- **$\Delta U = Q - W$**

Where, ΔU is the change in the internal energy of the system, Q is the heat flow, and W is the work done.

DEFINITION OF ENTHALPY

Thermodynamic Definition of Enthalpy (H): is a new variable of state

Enthalpy is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure

The energy change associated with a chemical reaction is called the **enthalpy of reaction** and abbreviated ΔH .

It is the thermodynamic quantity equivalent to the total heat content of a system. It is equal to the internal energy of the system plus the product of pressure and volume.

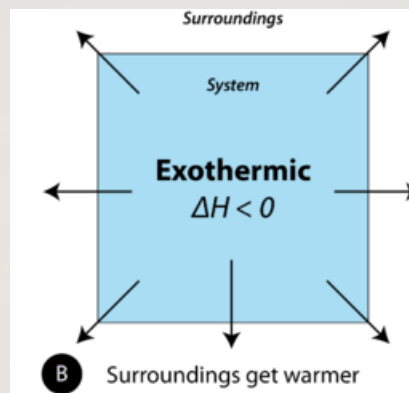
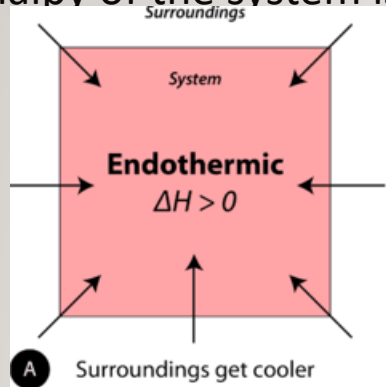
$$\Delta H = \Delta U + \Delta PV \dots\dots\dots$$

where,

H is the enthalpy of the system, U is the internal energy of the system, p is the pressure of the system, V is the volume of the system.



For a system absorbs heat it causes the surroundings to cool, and the change in heat content or enthalpy of the system is positive ($\Delta H > 0$)



The enthalpy change has a negative value in an **exothermic** reaction ($\Delta H < 0$).

The enthalpy change has a positive value in an **endothermic** reaction ($\Delta H > 0$).

Enthalpy depends only on the differences in heat content of the reactants and products and does not depend on the pathway or mechanism of the reaction.

ΔH = energy used in forming product bonds – energy released in breaking reactant bonds

Endothermic vs. exothermic reactions

- **Endothermic reactions: Heat is absorbed.**

Ex. Photosynthesis: Plants absorb heat energy from sunlight to convert carbon dioxide and water into glucose and oxygen.



Exothermic reactions: Heat is released.

Ex. Combustion: The burning of carbon-containing compounds uses oxygen, from air, and produces carbon dioxide, water, and lots of heat. For example, combustion of methane.



Hess's Law: When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

HEAT OF FORMATION ΔH_F

١٦

- The energy or enthalpy change when the teaspoon of sugar is converted to CO_2 and H_2O is the same whether sugar is burned in a reaction vessel or metabolized in human body, as long as the final states for the reaction are the same in the two cases.
- It does not matter whether the conversion involves a direct reaction with O_2 (combustion) or multiple enzyme-catalyzed steps inside a human being
- The bond dissociation energy is the **enthalpy** at 25°C and 1 atm, for the reaction.
- $\text{A-B}_{(g)} \rightarrow \text{A}_{(g)} + \text{B}_{(g)}$
- table 2.3

The First Law: Energy Is Conserved

TABLE 2.3		Average Bond Dissociation Energies at 25°C
Bond	D (kJ mol ⁻¹)	
C — C	344	
C = C	615	
C ≡ C	812	
C — H	415	
C — N	292	
C — O	350	
C = O	725	
C — S	259	
N — H	391	
O — O	143	
O — H	463	
S — H	339	
H ₂	436.0	
N ₂	945.4	
O ₂	498.3	
C (graphite)	716.7	

Source: After L. Pauling and P. Pauling,
Chemistry (San Francisco: Freeman, 1975).

Heats of Formation

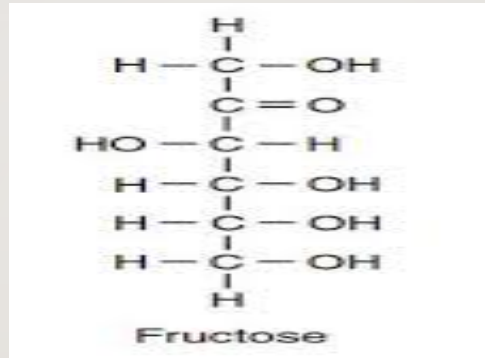
TABLE 8.2 Standard Heats of Formation for Some Common Substances at 25°C

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$\text{C}_2\text{H}_2(\text{g})$	226.7	Hydrogen chloride	$\text{HCl}(\text{g})$	-92.3
Ammonia	$\text{NH}_3(\text{g})$	-46.1	Iron(III) oxide	$\text{Fe}_2\text{O}_3(\text{s})$	-824.2
Carbon dioxide	$\text{CO}_2(\text{g})$	-393.5	Magnesium carbonate	$\text{MgCO}_3(\text{s})$	-1095.8
Carbon monoxide	$\text{CO}(\text{g})$	-110.5	Methane	$\text{CH}_4(\text{g})$	-74.8
Ethanol	$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.7	Nitric oxide	$\text{NO}(\text{g})$	90.2
Ethylene	$\text{C}_2\text{H}_4(\text{g})$	52.3	Water(g)	$\text{H}_2\text{O}(\text{g})$	-241.8
Glucose	$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-1260	Water(l)	$\text{H}_2\text{O}(\text{l})$	-285.8

➤ Calculate the heat of formation of fructose:

$$\underline{dH = H_{\text{reactant}} - H_{\text{product}}}$$

- Reactants of fructose: $C_6H_{12}O_6$
 $= (6C \times 716.7) + (6H_2 \times 436) + (3O_2 \times 498.3)$
 $= 8411.1 \text{ kJ/mol}$
- Products of fructose:

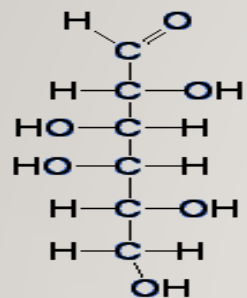


$$\begin{aligned} & 5 \text{ C-C}, 1 \text{ C=O}, 7 \text{ C-H}, 5 \text{ C-O}, 5 \text{ O-H} \\ & = (5 \times 344) + (1 \times 725) + (7 \times 415) + (5 \times 350) + (5 \times 463) \\ & = 9415 \text{ kJ/mol} \end{aligned}$$

- $dH = H_{\text{reactants}} - H_{\text{products}}$
 $= 8411.1 - 9415$
 $= -1003.9 \text{ kJ/mol}$

which is less than the heat of formation of fructose found in some tables (-1265.60 kJ/mol) and that is because our calculation does not include the heat of resonance.

Heat formation of glucose



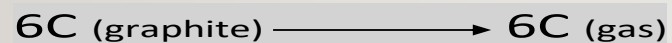
(C-C)=5

(C-H)=7

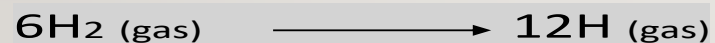
(C-O)=5

(C=O)=1

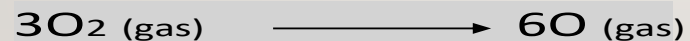
(O-H)=5



$$\Delta H_1 = 716.7 \times 6 = 4300.2$$



$$\Delta H_2 = 436 \times 6 = 2616$$



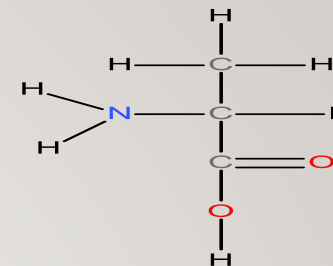
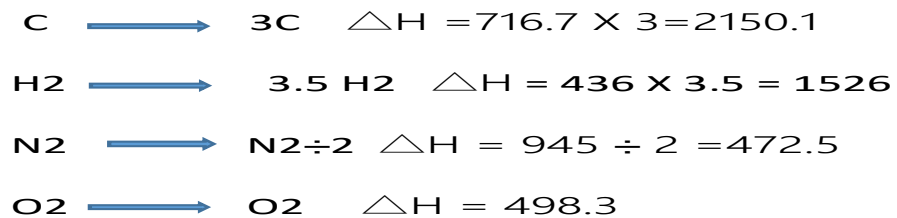
$$\Delta H_3 = 498.3 \times 3 = 1494.9$$

$$\begin{aligned} \Delta H_{\text{products}} &= 5(\text{C-C}) - 7(\text{C-H}) - 5(\text{C-O}) - 1(\text{C=O}) - 5(\text{O-H}) \\ &= 5(344) - 7(415) - 5(350) - 1(725) - 5(463) \\ &= -9415 \text{Kj} \end{aligned}$$

$$\begin{aligned} \Delta H_f &= \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 \\ &= 4300.2 + 2616 + 1494.9 - 9415 \\ &= -1003.9 \text{Kj} \end{aligned}$$

Calculate the heat information of one molecule of alanine ?

C₃H₇NO₂



$$\Delta H = 2150.1 + 1526 + 472.5 + 498.3 = 4646.9$$

$$2(\text{C} - \text{C}) \Delta H = 2 \times 344 = 688$$

$$4(\text{C} - \text{H}) \Delta H = 4 \times 415 = 1660$$

$$(\text{C} - \text{N}) \Delta H = 292$$

$$2(\text{N} - \text{H}) \Delta H = 2 \times 391 = 782$$

$$(\text{C} - \text{O}) \Delta H = 350$$

$$(\text{O} - \text{H}) \Delta H = 463$$

$$(\text{C} = \text{O}) \Delta H = 725$$

$$\Delta H = 688 + 1660 + 292 + 782 + 350 + 463 + 725 = -4960$$

$$\underline{\Delta H_f = \Delta H_p - \Delta H_r = 4646.9 - 4960 = -313.2}$$

THE SECOND LAW :THE ENTROPY OF THE UNIVERSE INCREASES

Spontaneous Processes

- **Spontaneous**: process that **does** occur under a specific set of conditions
 - **Nonspontaneous**: process that **does not** occur under a specific set of conditions
-

Often spontaneous processes are exothermic, but not always....

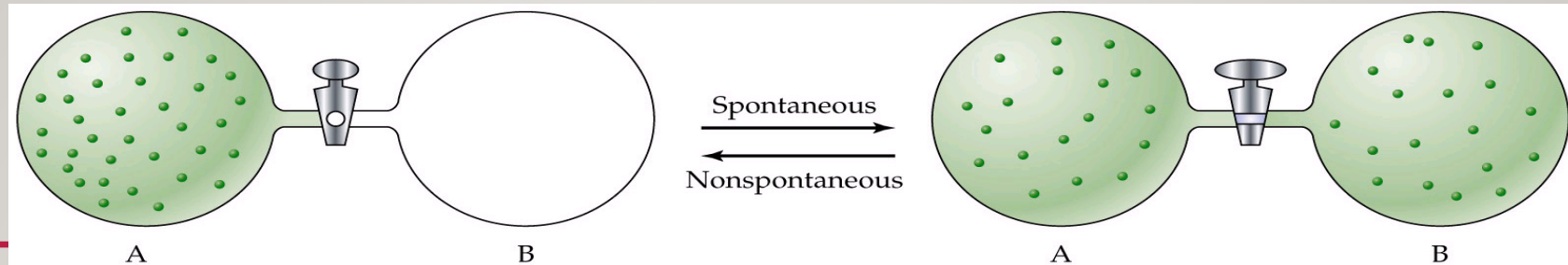
Methane gas burns spontaneously and is exothermic

Ice melts spontaneously but this is an endothermic process...

- **Example**: every time we freeze an ice tray full of water in the freezer, we are increasing the order in ice tray. However, **the disorder caused by the heat released outside the freezer compartment more than balances the order created in the ice.**
- The total disorder in the universe has increased; the total entropy of the universe has increased



One of the consequences of the 2nd law of thermodynamics is that spontaneous processes result in the system moving toward a state of equilibrium.



**Gas flows towards a vacuum
spontaneously.**

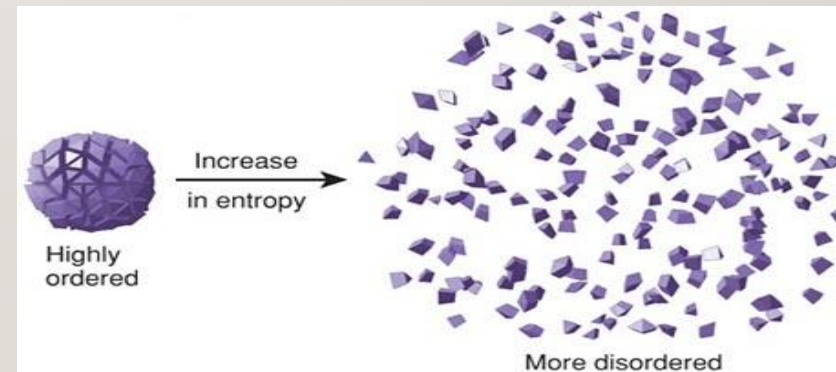
**vacuum does not naturally form.
nonspontaneous**

Familiar Spontaneous and Nonspontaneous Processes	
Spontaneous	Nonspontaneous
Ice melting at room temperature	Water freezing at room temperature
Sodium metal reacting violently with water to produce sodium hydroxide and hydrogen gas [Section 7.7]	Sodium hydroxide reacting with hydrogen gas to produce sodium metal and water
A ball rolling downhill	A ball rolling uphill
The rusting of iron at room temperature	The conversion of rust back to iron metal at room temperature
Water freezing at -10°C	Ice melting at -10°C

ENTROPY

Copyright McGraw-Hill 2009

- **Entropy (S):** Can be thought of as a measure of the *disorder* of a system
- **entropy [S] tends to increase in all processes.**
- **entropy is closely related to the randomness or disorder of the constituents**
- This means a disorder takes place to the arrangement of water molecules in its liquid (**high enthalpy**) form than in its solid form (**low enthalpy**)
- We see evidence that the universe tends toward **highest entropy** (disorder) many places in our lives.



TRENDS IN ENTROPY

Copyright McGraw-Hill 2009

- Entropy for gas phase is greater than that of liquid or solid of same substance
- $I_2(g)$ has greater entropy than $I_2(s)$
- More complex structures have greater entropy
 - $C_2H_6(g)$ has greater entropy than $CH_4(g)$
- Allotropes - more ordered forms have lower entropy

Standard Entropy Values (S°) for Some Substances at 25°C			
Substance	S° (J/K · mol)	Substance	S° (J/K · mol)
$H_2O(l)$	69.9	C(diamond)	2.4
$H_2O(g)$	188.7	C(graphite)	5.69
$Br_2(l)$	152.3	$CH_4(g)$ (methane)	186.2
$Br_2(g)$	245.3	$C_2H_4(g)$ (ethane)	229.5
$I_2(s)$	116.7	He(g)	126.1
$I_2(g)$	260.6	Ne(g)	146.2

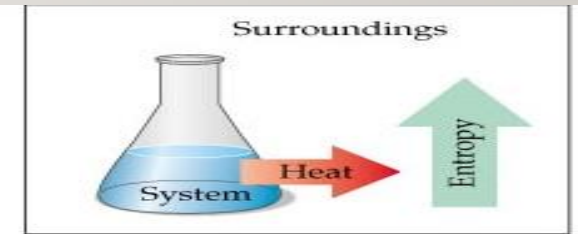
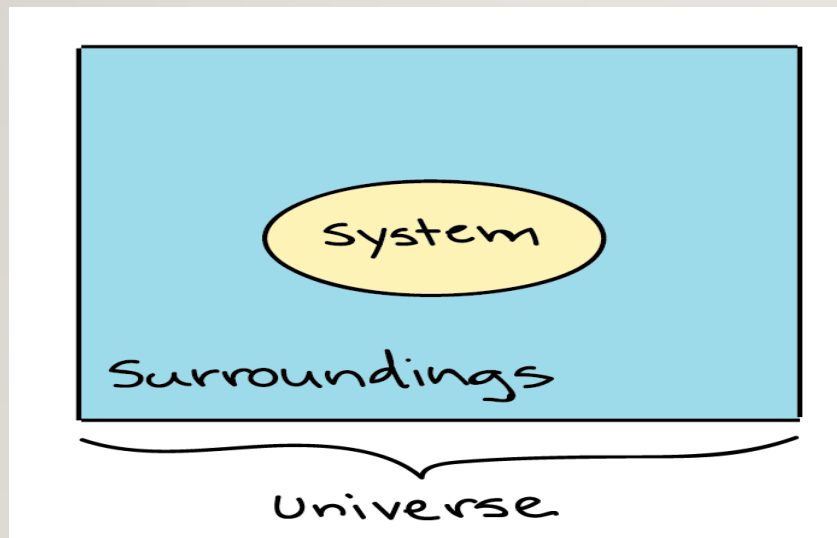
ΔS_{sys} positive implies that the system becomes *more disordered* during the reaction.

(*entropy and enthalpy of product are higher than the reactant*)

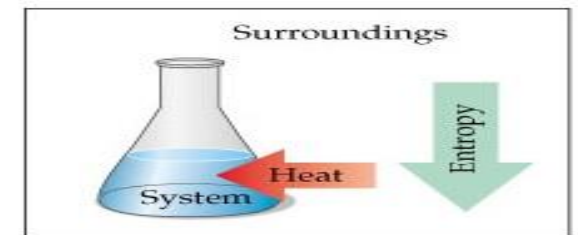
ΔS_{sys} negative implies that the system becomes *less disordered* during the reaction (*entropy and enthalpy of product are less than the reactant*)

For any constant process ($\Delta U=0$), a spontaneous process is characterized by $\Delta S > 0$. Since the energy of the universe is constant (conservation law of energy), any spontaneous process must cause the entropy of universe to increase:

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = \Delta S_{\text{universe}} > 0 \dots (9)$$



(a)



(b)

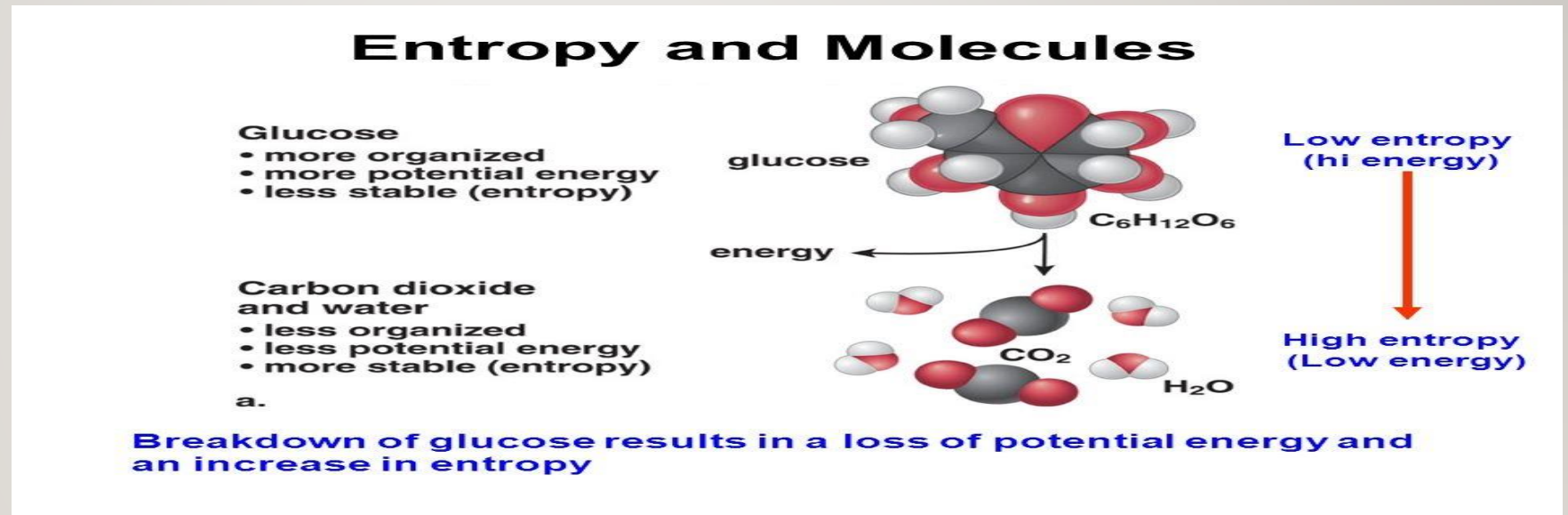
The last equation is the usual expression for the second law of thermodynamics. It is a statement of the general tendency of all spontaneous processes to disorder the universe; that is, the entropy of the universe tends towards a maximum.

A system can be ordered at the expense of disordering its surrounding by the application of energy to the system.

For example, living organisms, which are organized from the molecular level upwards and are therefore particularly well ordered, achieve this order at the expense of disordering the nutrients they consume.



Thus eating is as much a way of acquiring order as it of gaining energy.



Measuring Entropy

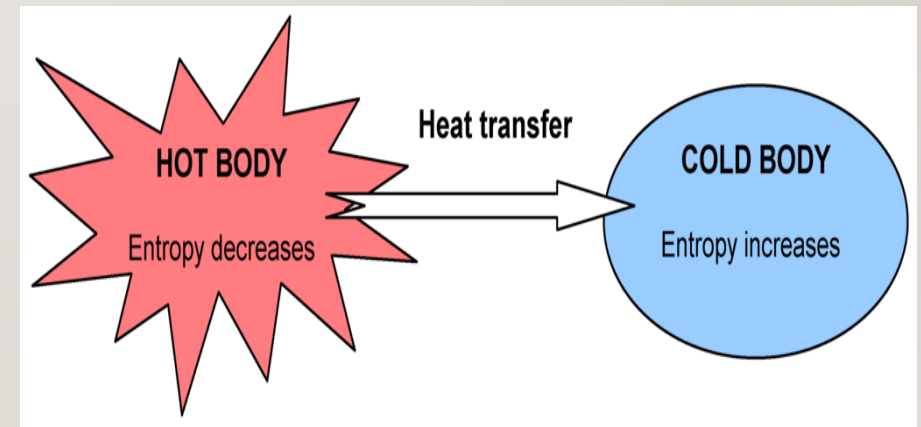
- One useful way of measuring entropy is by the following equation: $\Delta S = Q/T$ (10)
- For spontaneous processes

$$\Delta S \geq Q/T \text{(11)}$$

where S represents entropy, ΔS represents the change in entropy, Q represents heat transfer (change in heat), and T is the absolute temperature (Kelvin temperature).

Using this equation it is possible to measure entropy changes using a calorimeter. The units

of entropy are J/K.

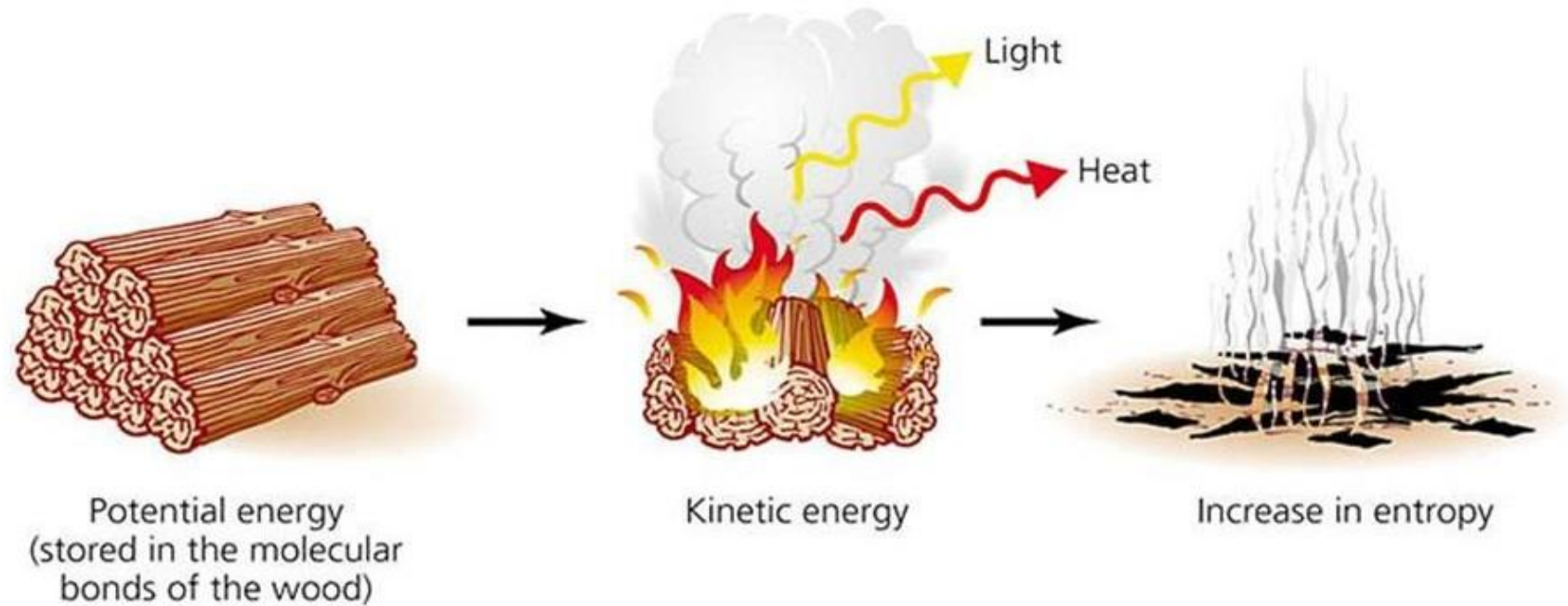


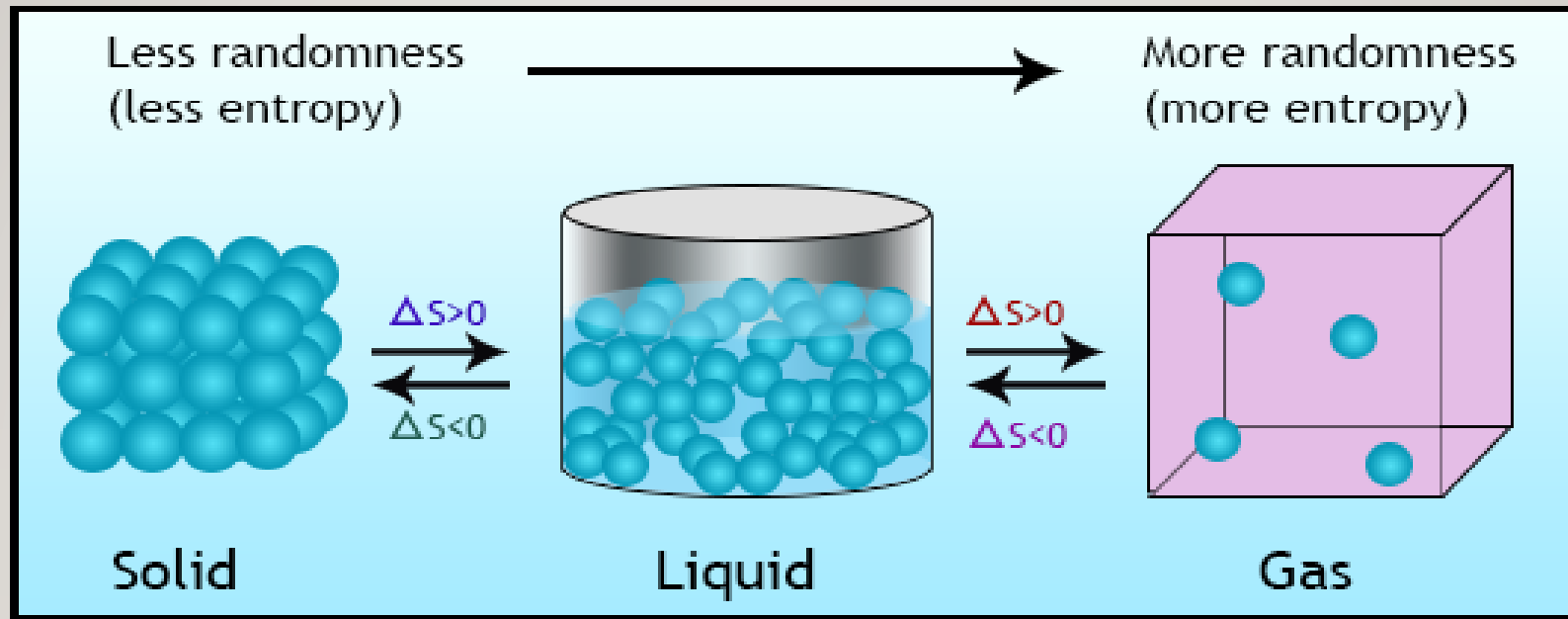
The temperature in this equation must be measured on the absolute, or Kelvin temperature scale. On this scale, zero is the theoretically lowest possible temperature that any substance can reach. At absolute 0 (0 K), all atomic motion ceases and the disorder in a substance is zero.

- Any system becomes progressively disordered (**its entropy increases**) as its temperature rises.
- According to the second law of thermodynamics, every energy transfer or transformation increases the entropy (disorder) of the universe.

Increase in entropy

Burning firewood demonstrates the second law of thermodynamics.





$$S_{\text{solid}} < S_{\text{liquid}} \ll S_{\text{gas}}$$

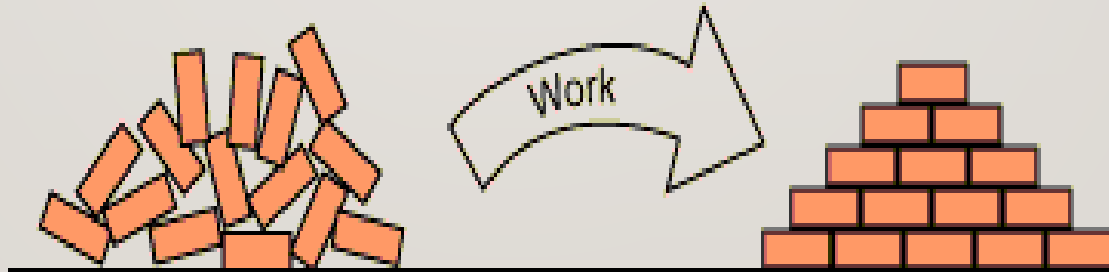
The universe's entropy change in any real process is always greater than its ideal. This means that when a system departs from and then returns to its initial state via a real process, the entropy of the universe must increase even though the entropy of the system does not change.



Entropy in biological system

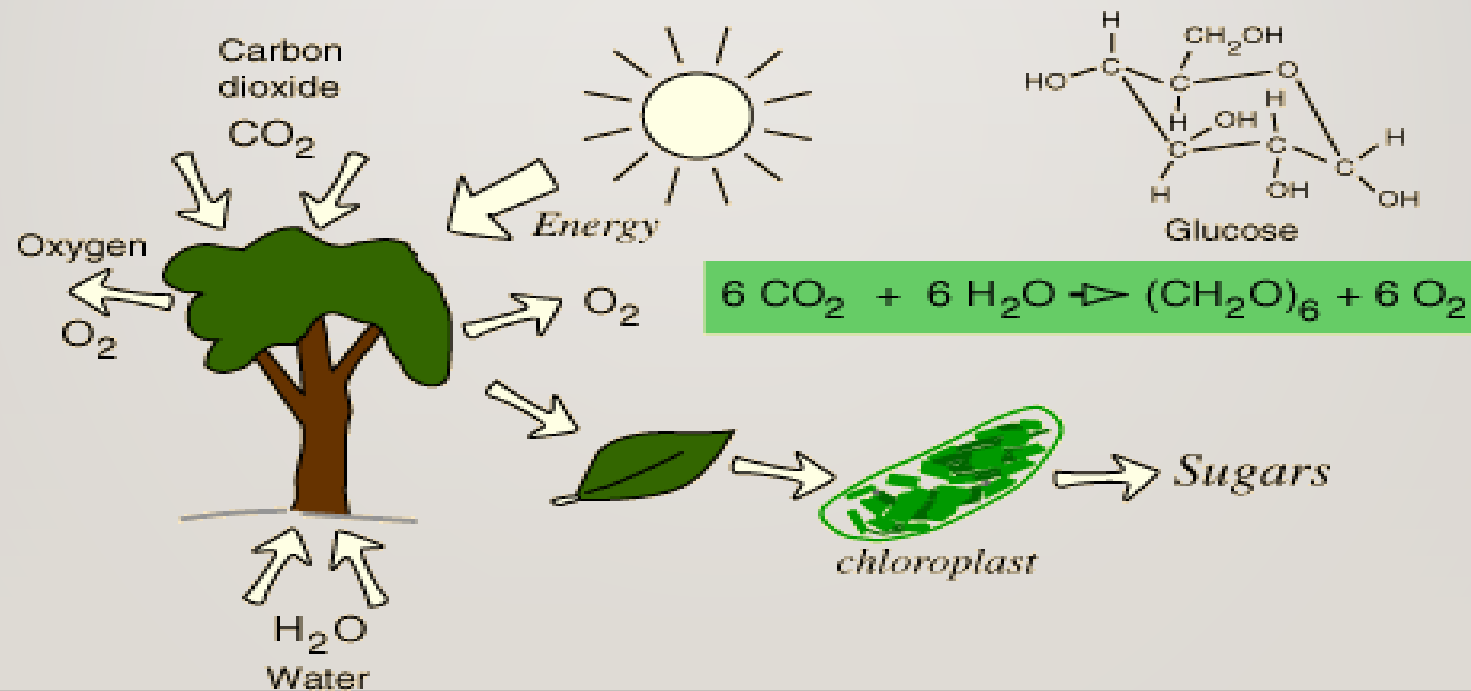
- The concept of entropy and the second law of thermodynamics state that systems naturally progress from order to disorder.
- Living organism can convert the system from the disorder to be a high degree of order
- The conversion from disorder to order state consume energy

Work is generally required to produce order out of disorder, so energy must be used to produce a highly ordered state.



Example

- The plants in the process of photosynthesis use the sun visible light (400-700) energy to make the highly ordered sugar molecules from the highly disordered building materials, carbon dioxide (gas) from the air and water (liquid) from the earth



GIBBS FREE ENERGY

۳۷

A system tends toward the lowest enthalpy and the highest entropy”. Neither of these terms alone makes it possible to predict whether a reaction will proceed or not.

Gibbs was the first to consider that “ in reactions occurring at equilibrium and constant temperature and pressure (the case of most biochemical processes) , such as the phase change of ice going to water at 0°C, that

$$\Delta S = \Delta H/T$$

or $\Delta H - T \Delta S = 0$ (at equilibrium

- **Gibbs free energy G**, defined as the enthalpy H minus the product of the absolute temperature [T] and the entropy [S]

$$G = H - TS$$

- ΔG is -ve → the process occurs spontaneously
- ΔG is +ve → the process can not occurs spontaneously.
- $\Delta G = 0$ → the system is at equilibrium
- Thermodynamics allows us to decide which reactions are impossible under given conditions and how the conditions can be changed to make impossible reactions probable
- Enzymes facilitate many nonspontaneous reactions

EX:

Calculate the Gibbs free energy change (ΔG) for the following chemical reaction:



The reaction occurs at 68 °F, the change in heat (ΔH) = 19,070 cal, and the change in entropy (ΔS) = 90 cal/K.

T= 293 K, therefore the equation is set up in the following way:

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

$$\Delta G = 19,070 \text{ cal} - (293 \text{ K}) (90 \text{ cal/K})$$

$$\Delta G = -7300 \text{ cal} = \mathbf{-7.3 \text{ kcal}}$$

The reaction with ATP in #1. The change in Gibbs free energy (ΔG) is **negative** for exothermic reactions and can only be negative for **spontaneous reactions**. However, the activation energy required would still cause this reaction to occur slowly

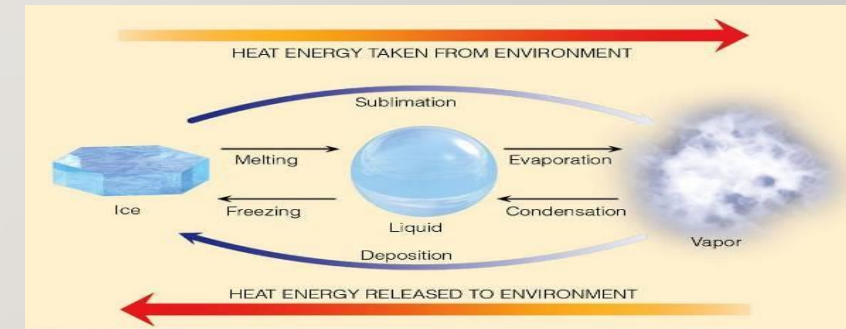
Free energy: the indicator of spontaneity

- “A system tends toward the lowest enthalpy H and the highest entropy S ”. Neither of these terms alone makes it possible to predict whether a reaction will proceed or not.
- Gibbs proposed a new energy (or function) called the **free energy** (ΔG) defined by the equation:

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

This function is a criterion for spontaneity.

- For a reaction occurring at equilibrium , such as the melting of ice at 0°C , $\Delta G = 0$



For the same reaction occurring in non-equilibrium condition, such as an ice and water mixture at 25°C, ,
 $\Delta G = -ve$; the melting would occur spontaneously.



Spontaneous processes, those with negative ΔG values, are said to be **exergonic**, they can be utilized to do work.

In the **reverse reaction**, the conversion of water to ice, there would be positive ΔG ($\Delta G = +ve$) and the reaction would not occur.

Processes that are not spontaneous, those with positive ΔG values are termed **endergonic**

Ice at 25 °C will spontaneously melt:

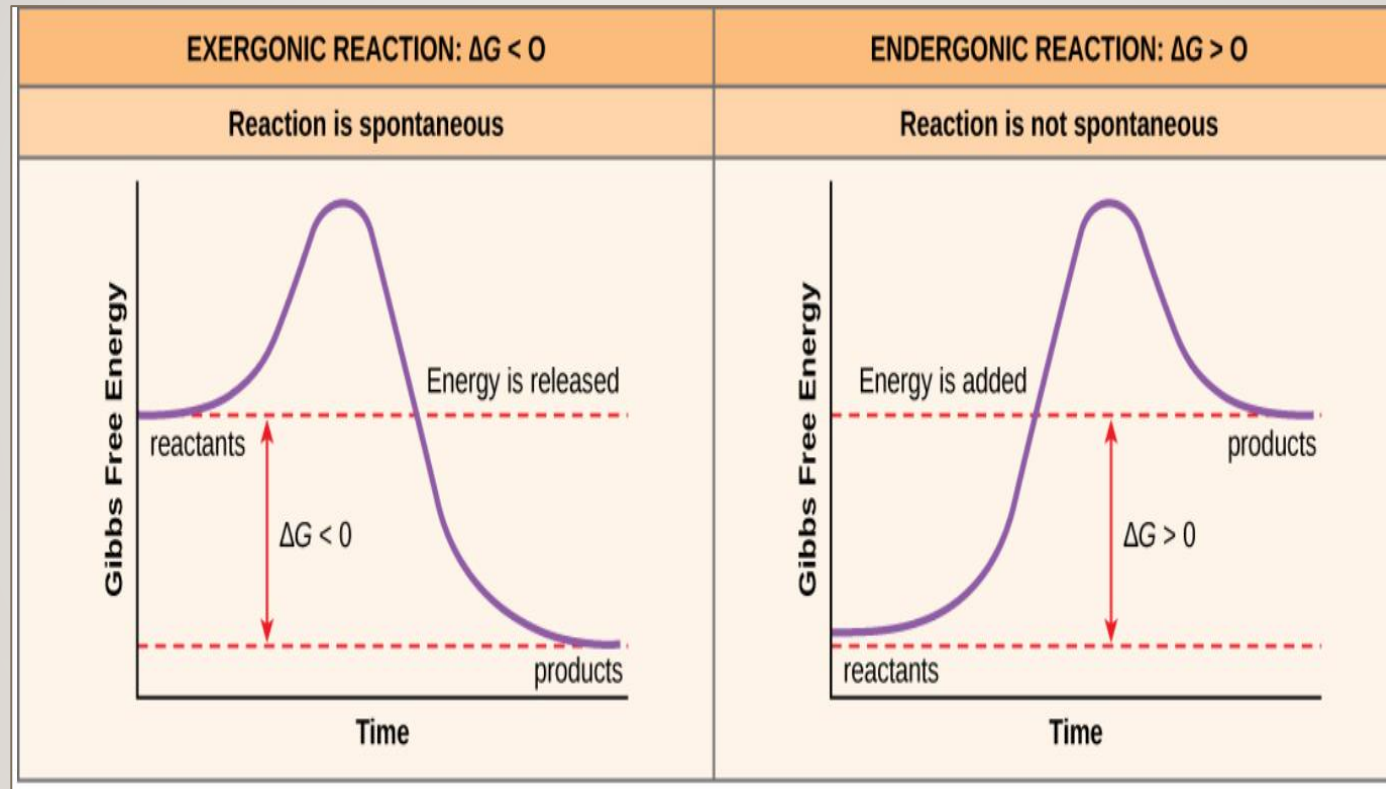
ice  **spontaneous**  **water**

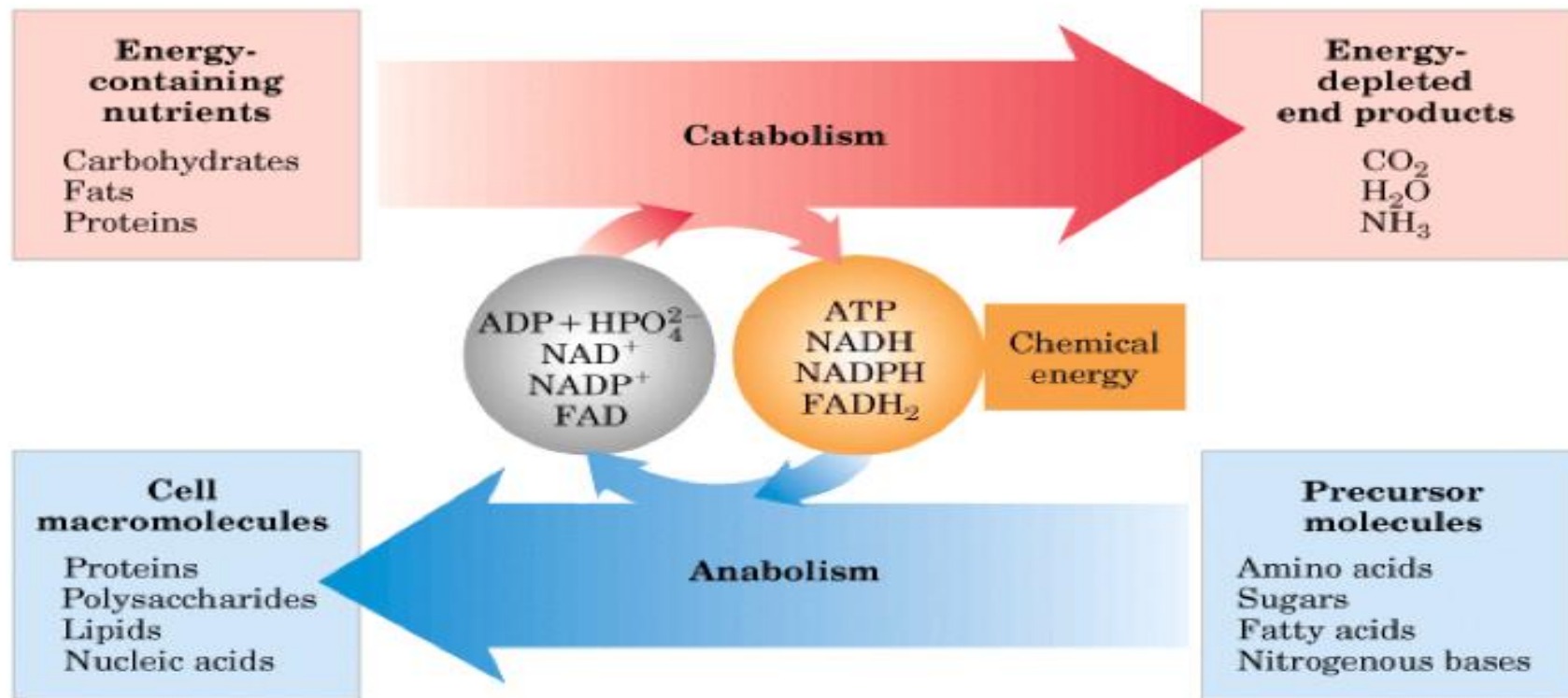
not spontaneous

The reverse will never happen. Water at 25 °C will never freeze.

The diagram illustrates the spontaneity of phase changes at 25 °C. On the left, a flask of ice is labeled 'ice'. On the right, a flask of water is labeled 'water'. A solid arrow points from ice to water, labeled 'spontaneous'. A dashed arrow points from water back to ice, labeled 'not spontaneous'. Below the flasks, text states: 'The reverse will never happen. Water at 25 °C will never freeze.'

Exergonic and Endergonic Reactions in Metabolism



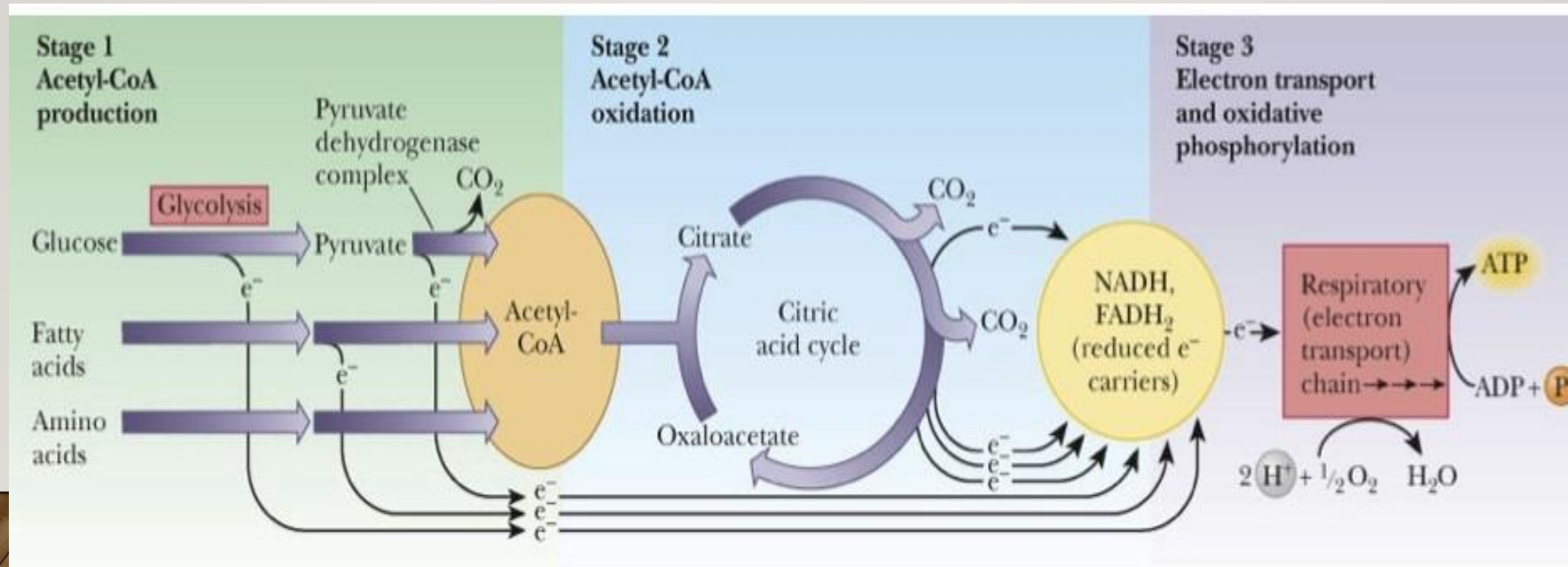


How cells stay out of equilibrium

- If a cell were an isolated system, its chemical reactions would reach equilibrium, which would not be a good thing. If a cell's reaction reached equilibrium, the cell would die because there would be no free energy left to perform the work needed to keep it alive.
- Cells stay out of equilibrium by manipulating (controlling) concentrations of reactants and products to keep their metabolic reactions running in the right direction.

For instance: 1-They may use energy to import reactant molecules (keeping them at a high concentration).

2-They may use energy to export product molecules (keeping them at a low concentration)



Units

٤٦

- (ΔG) J/mol
+ nonspontaneous , - spontaneous
- (ΔH) KJ/mol
- + endothermic , - exothermic
- ΔS J/k.mol
- + increase entropy , - decrease in entropy

REFERENCES

1. Van Holde, K.E., Johnson, W.C., Ho, P.S. (2006) Principles of Physical Biochemistry (2nd edition). Pearson Education, Inc., USA.
2. Sheehan, D. (2009) Physical Biochemistry: Principles and Applications (2nd edition). Wiley-Blackwell, Chichester, UK.
3. Principles and Applications in Biological Sciences
Tinoco and others Fourth Edition-2002
4. Dillon, P. F. (2012). *Biophysics: a physiological approach*. Cambridge University Press.