

# CHEM103

## General Chemistry

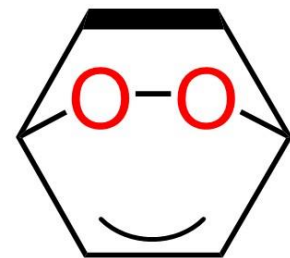
### Chapter 19: Chemical Thermodynamics

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# Homework 16-17 & Exam

## Homework 16

**Due date: 14th Dec. (Wed)**

## Homework 17

**Due date: 19th Dec. (Mon)**

**Final EXAM** (Chapters 11, 13-17, 19-20)

**10:30-12:30, 10th Jan. (Tue)**

# Review on Chapter 17

The common-ion effect

Buffer solution, Henderson–Hasselbalch equation

Solubility equilibria, solubility-product constant ( $K_{sp}$ ),  
complex ion formation, amphotericism

# Outline of Chapter 19

Spontaneous/Non-spontaneous process,  
reversible/irreversible process, entropy

The Second law of thermodynamics ( $\Delta S_{\text{univ}}$ ), The Third  
law of thermodynamics

Isothermal, statistical thermodynamics, microstate,  
Boltzmann's equation

Gibbs free energy, standard free energy change &  
equilibrium

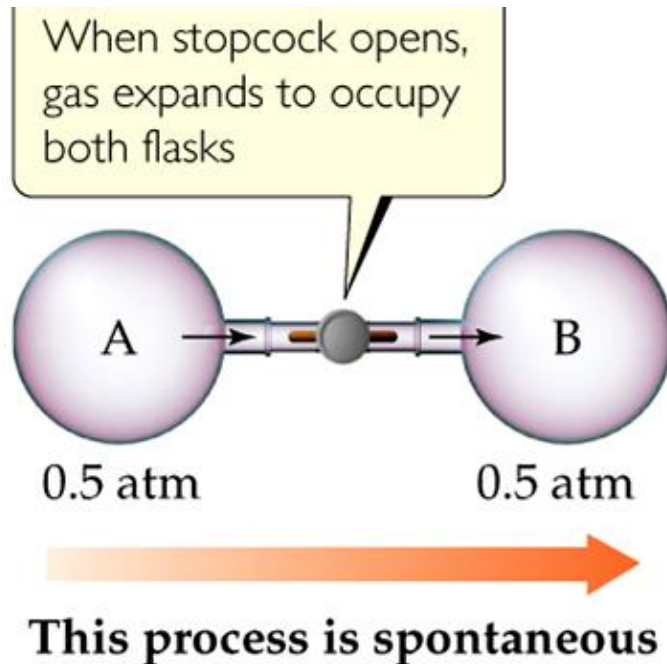
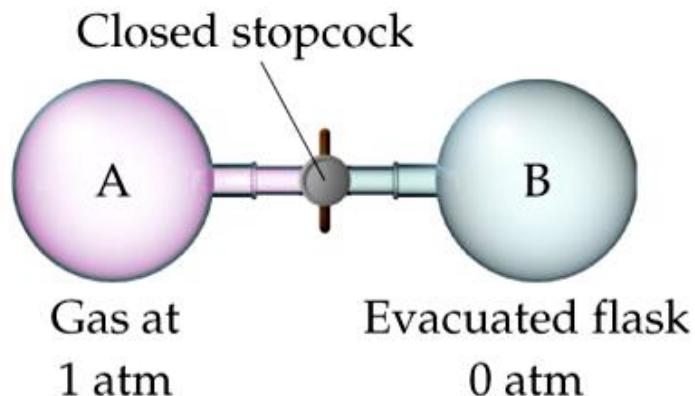
# First Law of Thermodynamics

- From Chapter 5: **energy cannot be created or destroyed.**
- Therefore, the **total energy of the universe** is a **constant.**
- Energy can, however, be **converted** from **one form to another form** or **transferred** from **a system to the surroundings or vice versa.**

# Enthalpy/Entropy

- **Enthalpy** (**H**): the **heat** absorbed by a system during a **constant-pressure** process.
- **Entropy** (**S**, 熵): a measure of the **randomness** in a system.
- Both play a role in determining whether a process is **spontaneous** (自发性).

# Spontaneous Processes

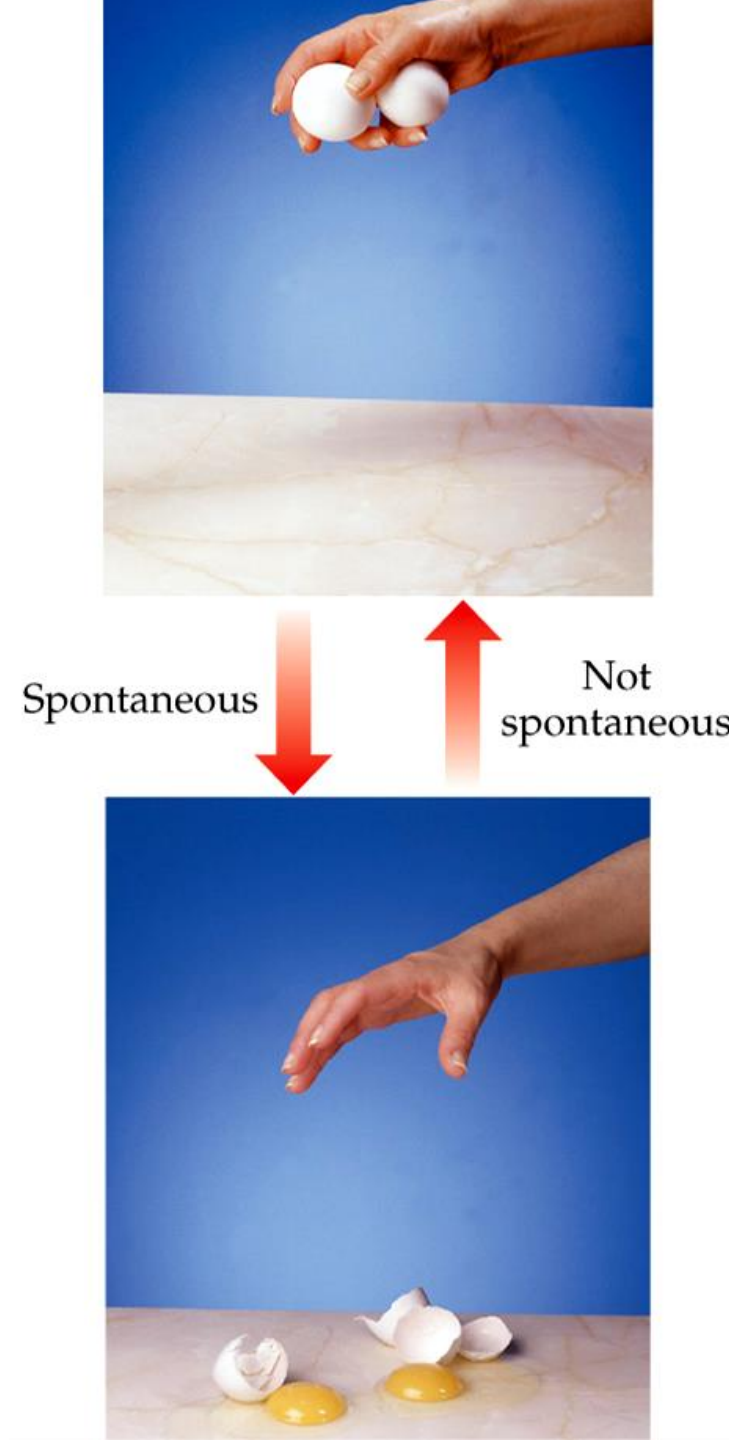


- Spontaneous processes can proceed **without** any **outside intervention or assistance**.

- The gas in vessel **A** **spontaneously** diffuse into vessel **B**. However, once the gas is in both vessels, it will *not spontaneously* return to vessel **A**.

- Processes that are **spontaneous in one direction** are **non-spontaneous in the reverse direction** (at the same conditions).

*Does the potential energy of the eggs change during this process?*





- Processes that are spontaneous at one temperature may be **non-spontaneous** at **other temperatures**.
- Above 0 °C, it is spontaneous for ice to melt.
- Below 0 °C, the reverse process is spontaneous.



Spontaneous for  $T > 0\text{ }^{\circ}\text{C}$



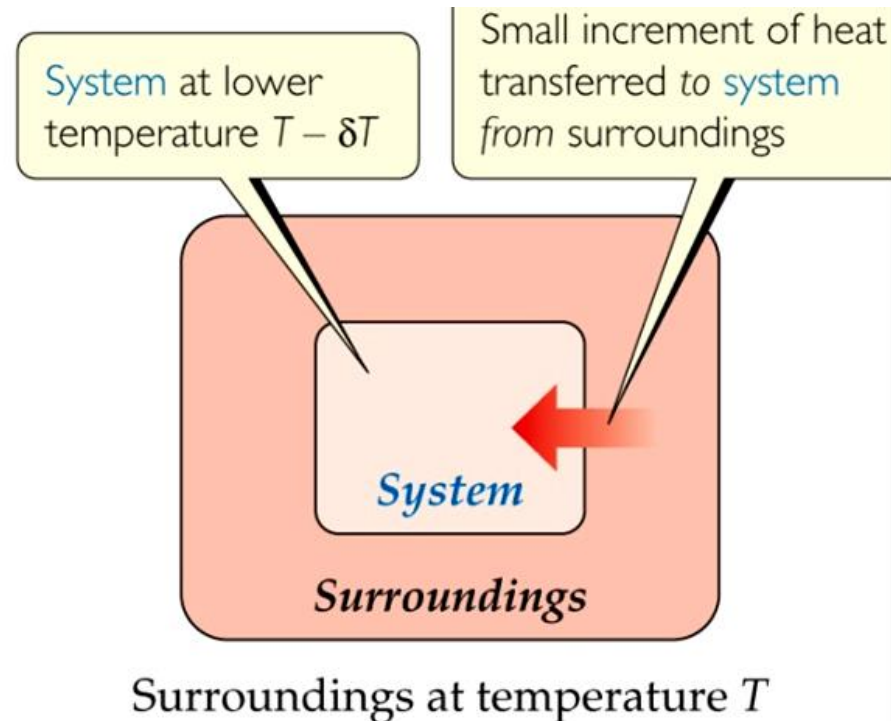
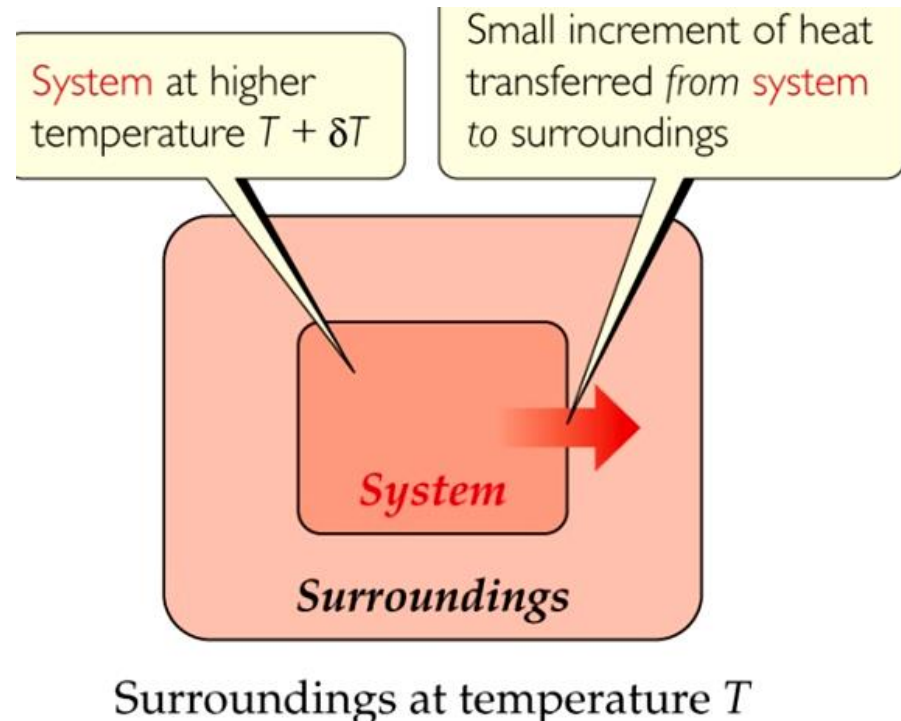
Spontaneous for  $T < 0\text{ }^{\circ}\text{C}$



- Early chemists proposed that **spontaneous** chemical reactions should occur in the direction of **decreasing energy**.
- It is true that many **exothermic** processes are **spontaneous** and that many **endothermic** reactions are **nonspontaneous**.
- However, **enthalpy change** is **NOT a sufficient criterion** for predicting spontaneous change. E.g. the dissolving of  $\text{NH}_4\text{NO}_3$ , are endothermic.

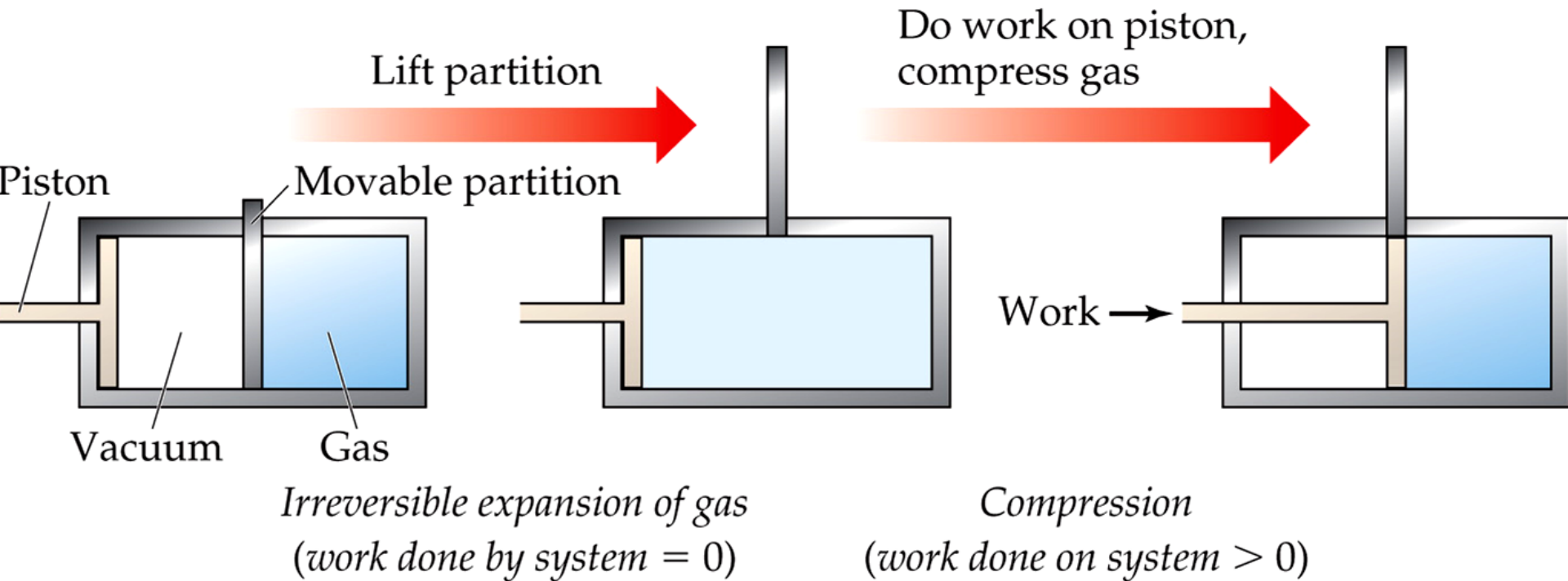
# Reversible Processes

- If the flow of heat into or out of the system is to be reversible, what must be true of  $\delta T$  (*a very small difference in temperature*)?



- The system changes so that **the system & surroundings** can be **returned** to the **original state** by **exactly reversing the process**.

# Irreversible Processes



- Irreversible processes **cannot be undone by exactly reversing** the change to the system or cannot have the process exactly followed in reverse.
- **Spontaneous** processes are **irreversible**.

# Entropy

- A term coined by Rudolph Clausius in the 19th century.
- A measure of the **randomness** of a system.
- Related to **various modes of motion** in **molecules**.
- The significance of the **ratio of heat delivered** and the **temperature** at which it is delivered,  $\frac{q}{T}$ .

- Like total energy ( $E$ ), and enthalpy ( $H$ ), **entropy ( $S$ )** is a **state function**.
- So, the change in entropy:

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

- For a process occurring at **constant temperature** (an **isothermal** process), the **change in entropy** is equal to the **heat** that would be transferred if the **process** were **reversible** **divided by** the **temperature**:

$$\Delta S = q/T$$

# Second Law of Thermodynamics

- The **entropy of the universe** does **not change** for **reversible** processes:

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

- The **entropy of the universe increases** in any **spontaneous (irreversible)** processes:

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

- **All spontaneous change leads to an increase in the entropy of the world (universe).**
- There are many common instances in which there is a **clear decrease** in entropy, such as the **freezing of a liquid**, the **formation of a precipitate**, or the **growth of an organism**.
- but it's the entropy of the system *plus* surroundings that counts!



If a process is nonspontaneous, does that mean the process cannot occur under any circumstances?

A. Yes. Nonspontaneous processes can never occur under any circumstances.

B. No. Nonspontaneous processes can occur with some continuous external assistance.

All spontaneous processes are

- a. reversible.
- b. irreversible.
- c. isothermal.
- d. exothermic.

How do we reconcile the fact that  $S$  is a state function but  $\Delta S$  depends on  $q$ , which is not a state function?

A. The value of  $\Delta S$  is a state function because  $q$  is constant for a specified  $T$  irrespective of the path chosen.

B.  $\Delta S$  depends not merely on  $q$  but on  $q_{\text{rev}}$ . There is only one reversible isothermal path between two states regardless of the number of possible paths.

C.  $\Delta S$  has negligible dependence on  $q$  and thus  $q$  does not affect the state function properties of  $S$  or  $\Delta S$ .

D.  $\Delta H = q_p$ .  $\Delta H$  is directly related to  $q$ .  $\Delta H$  is a state function; thus,  $\Delta S$  is also a state function.

Which process is spontaneous, spontaneous in the reverse direction, or in equilibrium: **(a)** Water at 40°C gets hotter when a piece of metal heated to 150°C is added. **(b)** Water at room temperature decomposes into  $\text{H}_2(g)$  and  $\text{O}_2(g)$ . **(c)** Benzene vapor,  $\text{C}_6\text{H}_6(g)$ , at a pressure of 1 atm condenses to liquid benzene at the normal boiling point of benzene, 80.1°C.

Entropy is a measurement of the \_\_\_\_\_ of a system.

- a. randomness
- b. internal energy
- c. temperature
- d. polarity

Entropy (S) is a state function, so the change in entropy is given by  $S_{\text{final}}$  \_\_\_\_\_  $S_{\text{initial}}$ .

- a. +
- b. −
- c. ×
- d. /

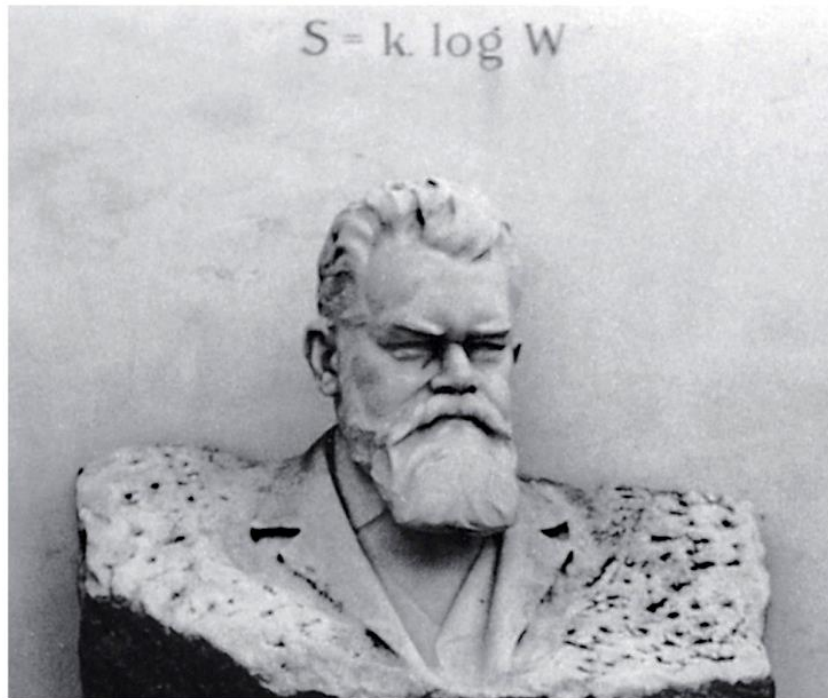
Elemental mercury is a silver liquid at room temperature. Its normal freezing point is  $-38.9\text{ }^{\circ}\text{C}$ , and its molar enthalpy of fusion is  $\Delta H_{\text{fusion}} = 2.29\text{ kJ/mol}$ . What is the entropy change of the system when 50.0 g of  $\text{Hg}(l)$  freezes at the normal freezing point?

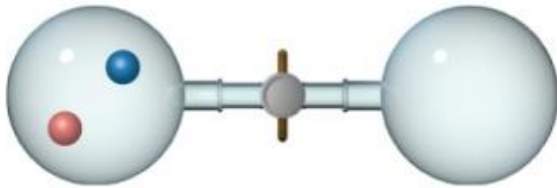
The rusting of iron is spontaneous and is accompanied by a decrease in the entropy of the system (the iron and oxygen). What can we conclude about the entropy change of the surroundings?

- A. We need to know if the change involves a closed or open system to make a conclusion.
- B. The entropy of the surroundings must increase by the same amount as the entropy decrease of the system.
- C. The entropy of the surroundings must increase by a greater amount than the entropy decrease of the system.
- D. The entropy of the surroundings must decrease by a smaller amount than the entropy decrease of the system.

# Entropy on the Molecular Scale

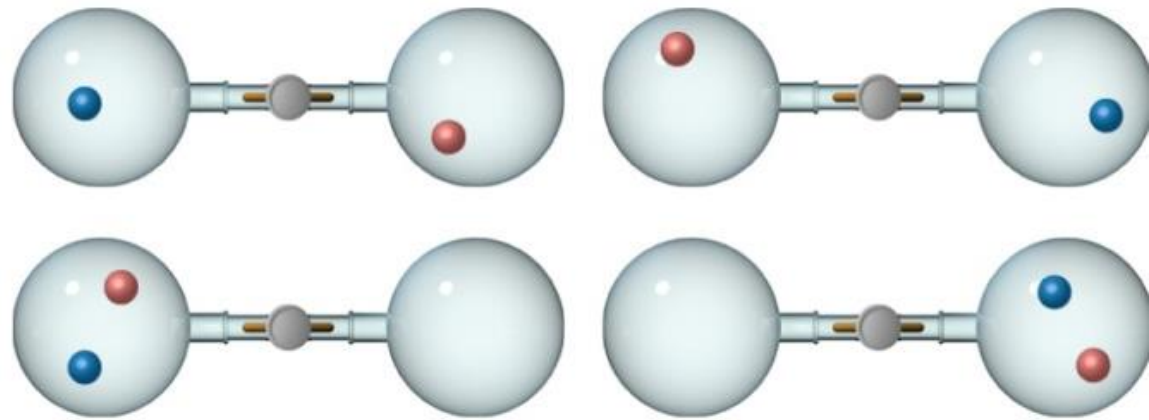
- Ludwig Boltzmann described the concept of entropy on the **molecular level**.
- **Temperature**: a measure of the **average kinetic energy of the molecules** in a sample.





(a)

The two molecules are colored red and blue to keep track of them.

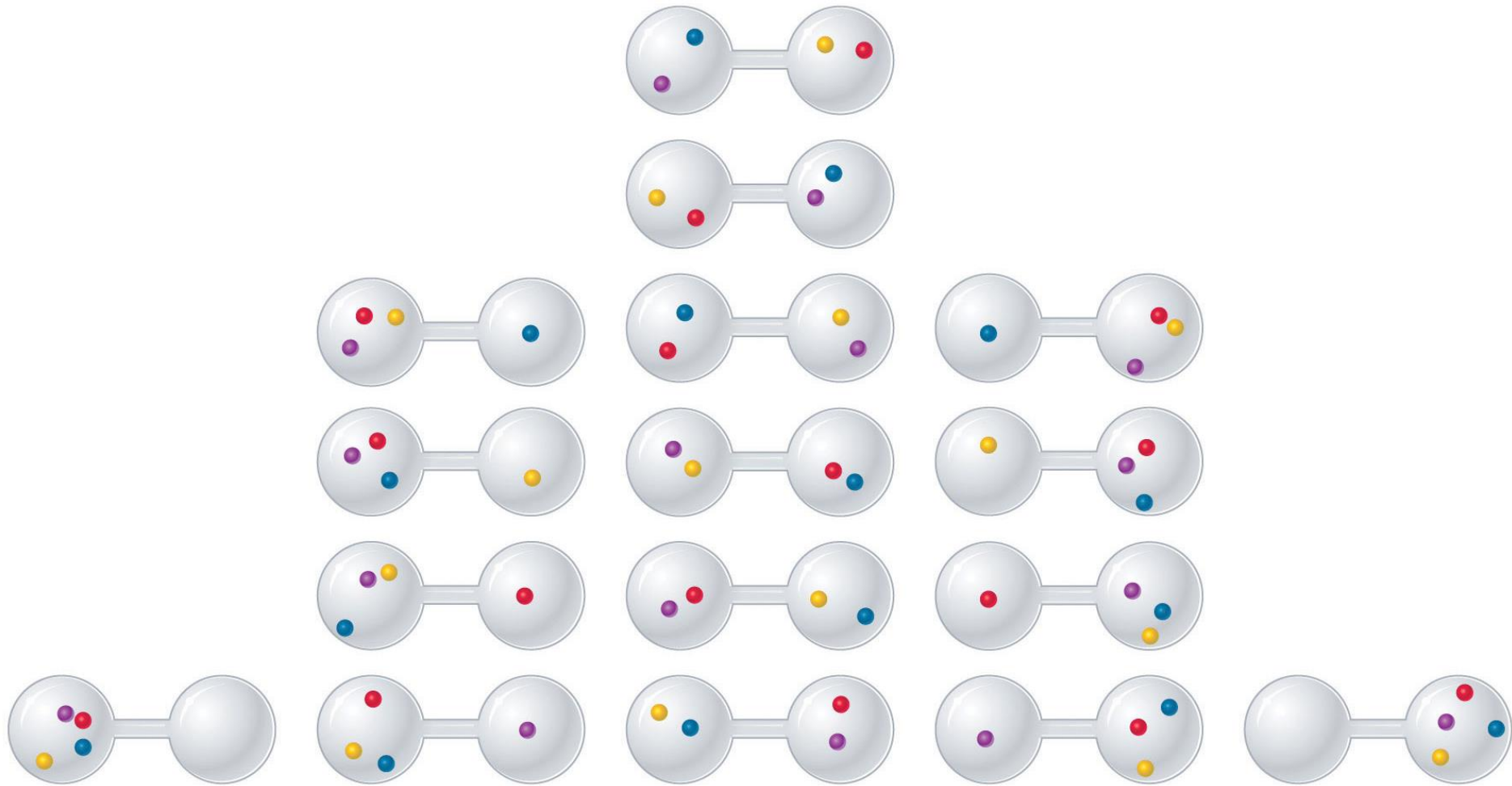


(b)

Four possible arrangements (microstates) once the stopcock is opened.

- Gas molecule expansion: two molecules are in the apparatus above; both start in one side.
- What is the **likelihood** they both will end up there?  $(1/2)^2$
- If one mole is used?  $(1/2)^{6.02 \times 10^{23}}$ ! (No chance!)





- Gases spontaneously expand to fill the volume given.
- **Most probable arrangement** of molecules: **approximately equal** molecules in **each side**.

# Statistical Thermodynamics

- **Thermodynamics** looks at **bulk** properties of substances (the *big* picture).
- We have seen what happens on the **molecular** (small) scale. How do they relate?
- We use **statistics (probability)** to relate them. The field is called **statistical thermodynamics**.
- **Microstate**: a **single possible arrangement** of **position and kinetic energy** of molecules

- Because there are so many possible microstates, we can't look at every picture generally.
- **W** represents the *number of microstates*.
- **Entropy**: a measure of a specific **number of microstates** are associated with a **particular macroscopic state**. The connection between the number of microstates and the entropy of the system (**Boltzmann's equation**):

$$S = k \ln W$$

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

# Entropy Change

- The change in entropy for a process:

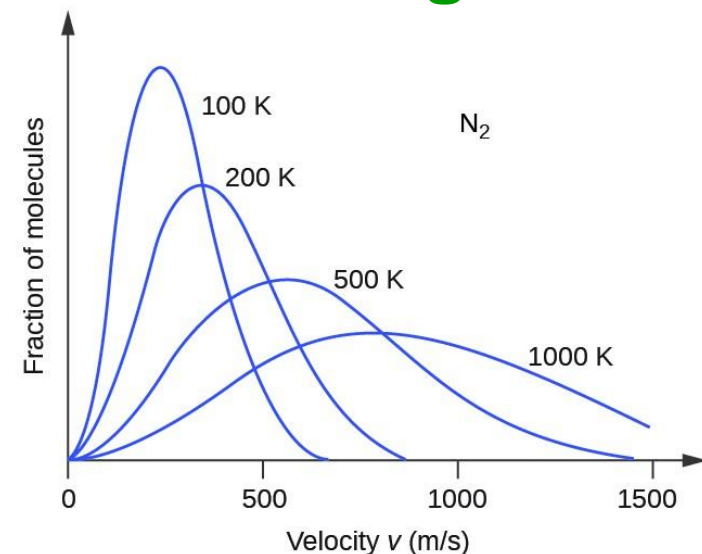
$$\Delta S = k \ln W_{\text{final}} - k \ln W_{\text{initial}} = k \ln \frac{W_{\text{final}}}{W_{\text{initial}}}$$

- Entropy **increases with the number of microstates** in the system (more **disorder**).

- The number of microstates and, therefore, the entropy, tends to **increase** with increases in
  - ❖ Temperature
  - ❖ Volume
  - ❖ The number of independently moving molecules.

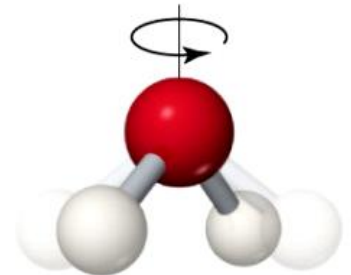
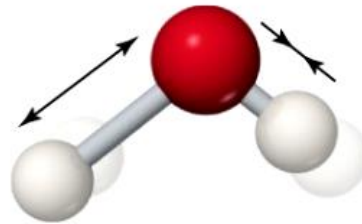
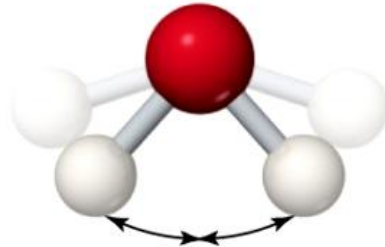
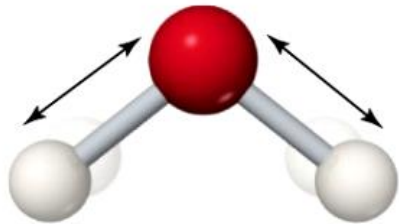
# Effect of Volume and Temperature Change on the System

- If we **increase volume**, there are **more positions** possible for the molecules. This results in **more microstates**, so **increased entropy**.
- If we **increase temperature**, the **average kinetic energy** increases. This results in a **greater distribution of molecular speeds**. Therefore, there are **more possible kinetic energy values**, resulting in **more microstates**, **increasing entropy**.



# Molecular Motions

- Molecules exhibit several types of motion (more atoms: more microstates & more possible molecular motions):
  - ❖ **Translational**: Movement of the entire molecule from one place to another.
  - ❖ **Rotational**: Rotation of the molecule about an axis or rotation about  $\sigma$  bonds.
  - ❖ **Vibrational**: Periodic motion of atoms within a molecule.

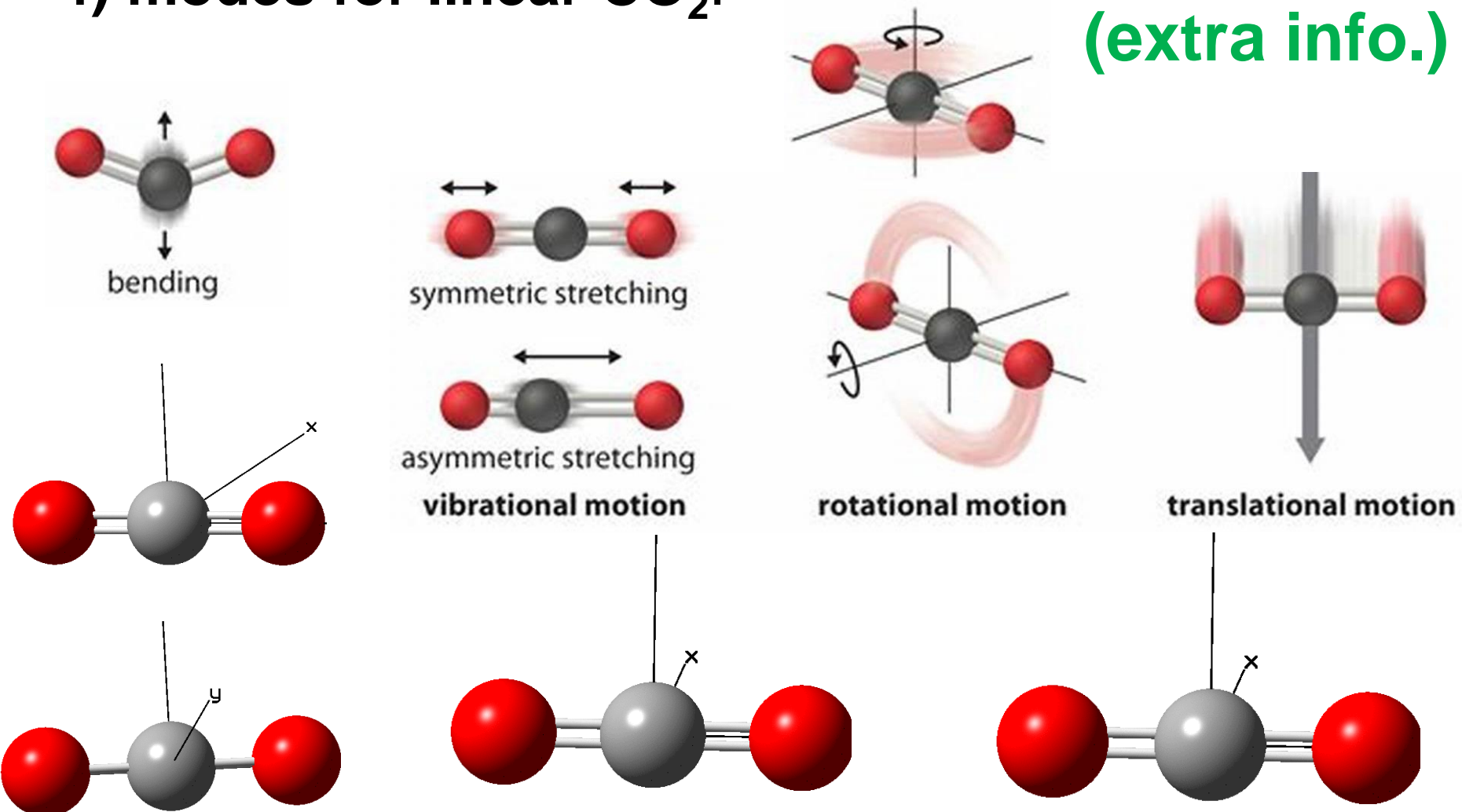


Vibrations

Rotation

- Generally, molecules have  $3N-6$  vibrational modes except  $3N-5$  for linear molecules.

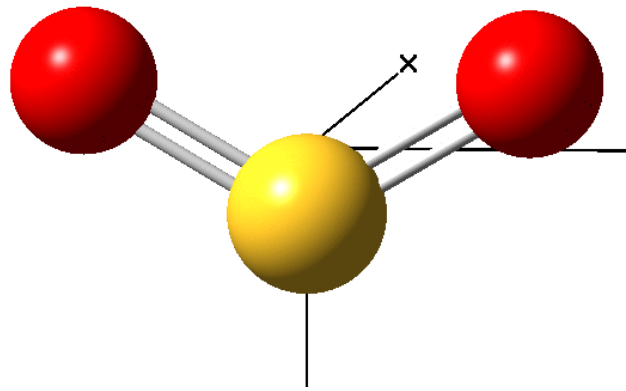
**Translational (3) + Rotational (2) + Vibrational ( $3 \times 3 - 5 = 4$ ) modes for linear  $\text{CO}_2$ :**



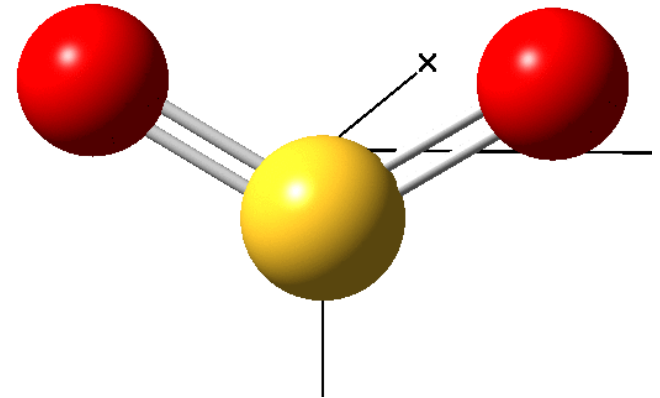


**Translational (3) + Rotational (3) + Vibrational ( $3 \times 3 - 6 = 3$ ) modes for bent  $\text{SO}_2$ :**

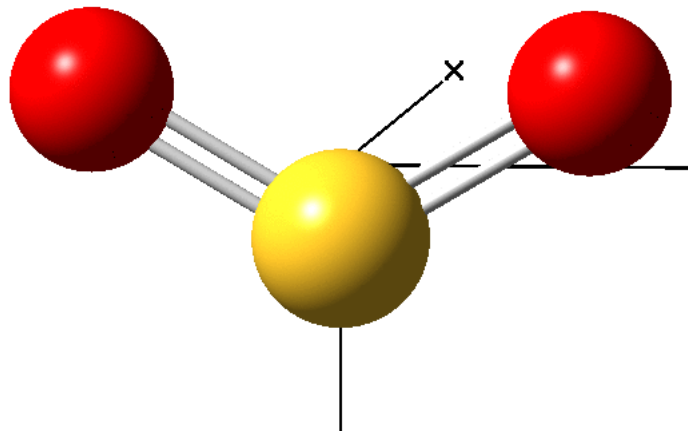
symmetric stretching



asymmetric stretching



bending



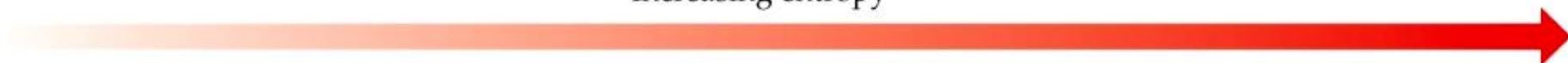
**(extra info.)**

# Entropy and Physical States

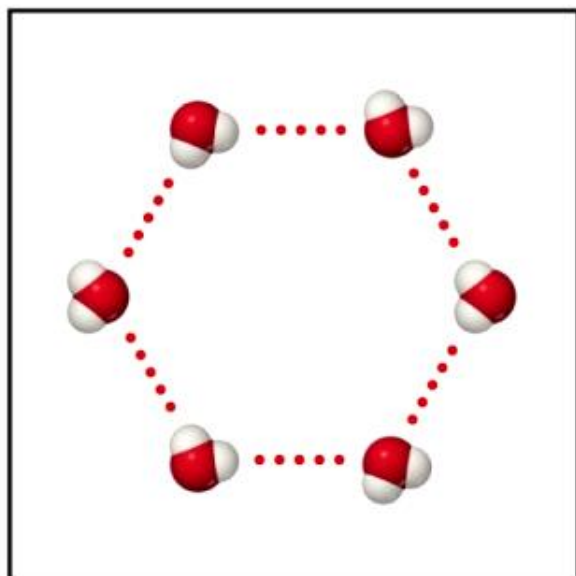
- Entropy increases with the **freedom of motion of molecules**.

$$S(g) > S(l) > S(s)$$

Increasing entropy

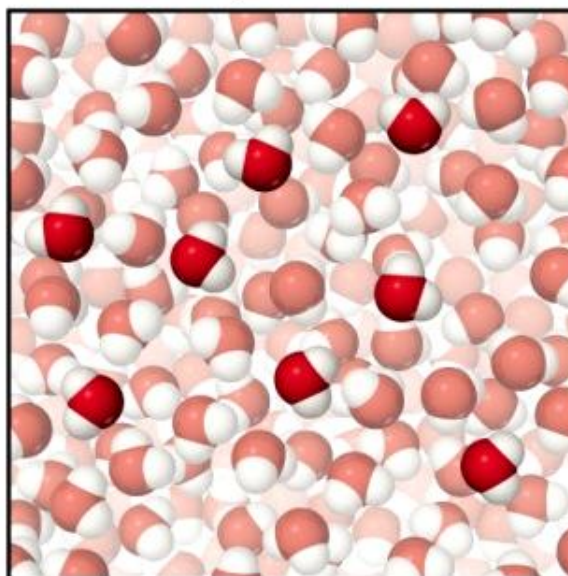


Ice



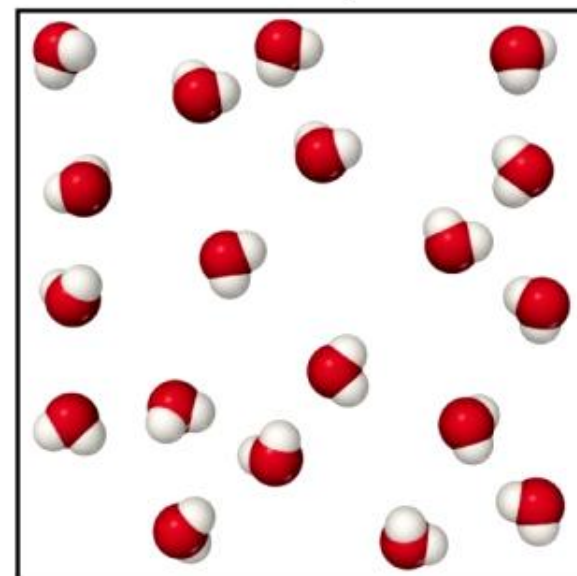
Rigid, crystalline structure  
Motion restricted to **vibration** only  
Smallest number of microstates

Liquid water



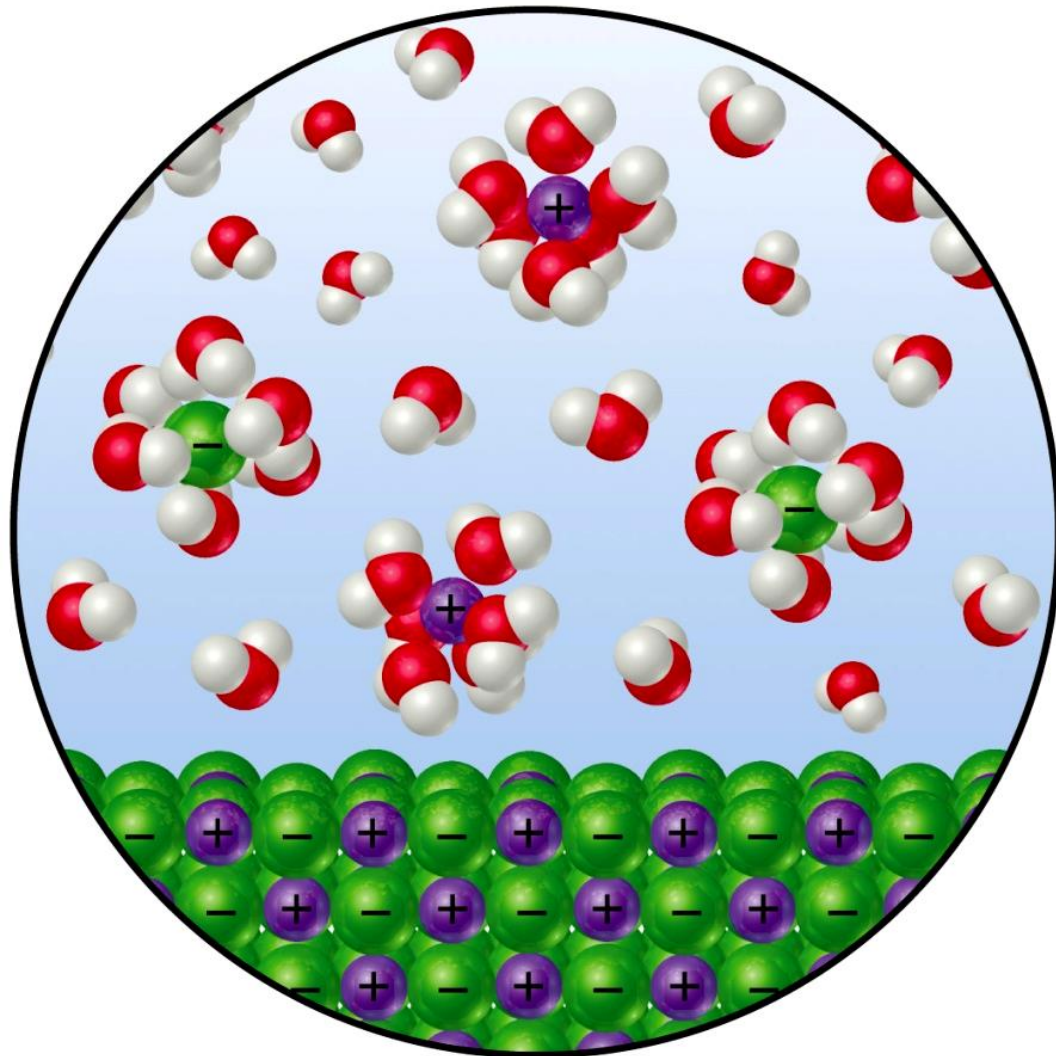
Increased freedom with respect to **translation**  
Free to **vibrate** and **rotate**  
Larger number of microstates

Water vapor



Molecules spread out, essentially independent of one another  
Complete freedom for **translation, vibration, and rotation**  
Largest number of microstates

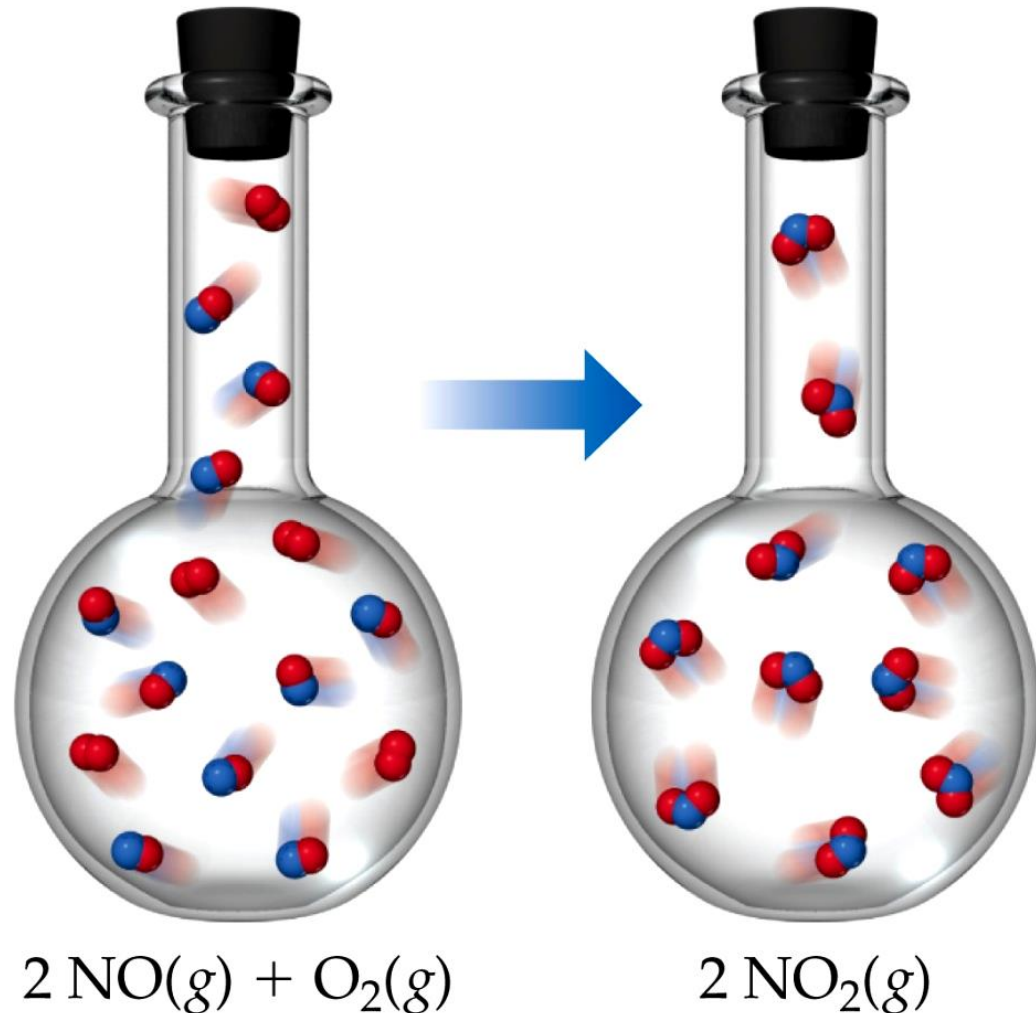
# Solutions



- The dissolving of a salt involves both a disordering process (the ions become less confined) & an ordering process (some water molecules become more confined in hydrated ions).
- Generally, when a **solid is dissolved** in a solvent, **entropy increases**.

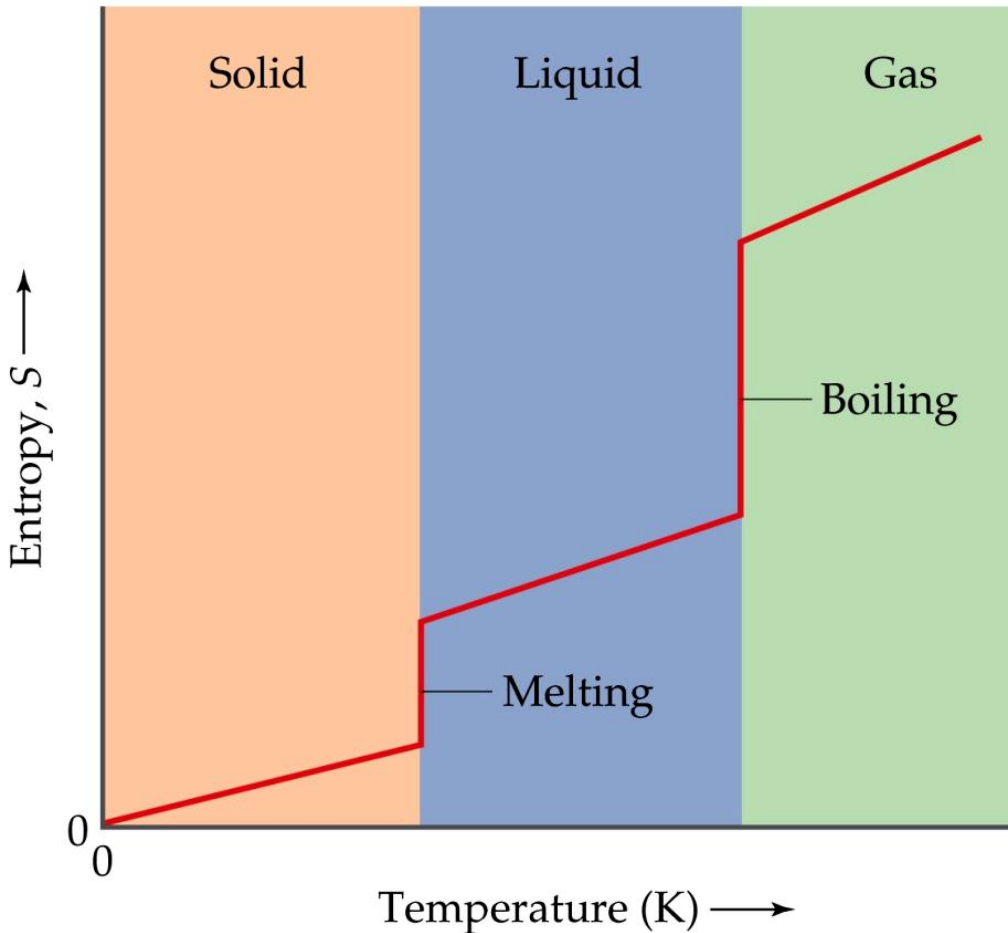
# Chemical Reaction

- In general, entropy increases,
  - 1) when gases are formed from liquids and solids;
  - 2) when liquids or solutions are formed from solids;
  - 3) when the **number of gas molecules** (or moles) **increases**.



*What major factor leads to a decrease in entropy as the reaction shown takes place?*

# Third Law of Thermodynamics



- The **entropy** of a **pure crystalline substance** at absolute zero (**0 K**) is **0**.

- Consider all atoms or molecules in the perfect lattice at 0 K; there will **only** be **one microstate**.

- $$S = k \ln W = k \ln 1 = 0$$

*Why does the plot show vertical jumps at the melting and boiling points?*



# Standard Molar Entropies

Table 19.1 Standard Molar Entropies of Selected Substances at 298 K

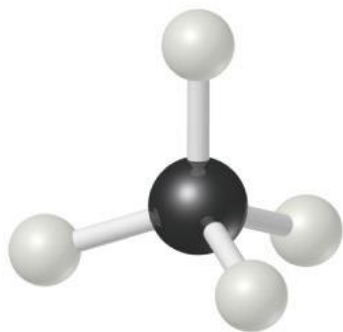
Substance	$S^\circ$ (J/mol-K)
$\text{H}_2(\text{g})$	130.6
$\text{N}_2(\text{g})$	191.5
$\text{O}_2(\text{g})$	205.0
$\text{H}_2\text{O}(\text{g})$	188.8
$\text{NH}_3(\text{g})$	192.5
$\text{CH}_3\text{OH}(\text{g})$	237.6
$\text{C}_6\text{H}_6(\text{g})$	269.2
$\text{H}_2\text{O}(\text{l})$	69.9
$\text{CH}_3\text{OH}(\text{l})$	126.8
$\text{C}_6\text{H}_6(\text{l})$	172.8
$\text{Li}(\text{s})$	29.1
$\text{Na}(\text{s})$	51.4
$\text{K}(\text{s})$	64.7
$\text{Fe}(\text{s})$	27.23
$\text{FeCl}_3(\text{s})$	142.3
$\text{NaCl}(\text{s})$	72.3

- As reference for entropy is **0 K** (vs. **H & G at 298.15 K**), the values for elements are **not 0 J/mol K at 298.15 K**.

- Molar entropy values of substances in their standard states.

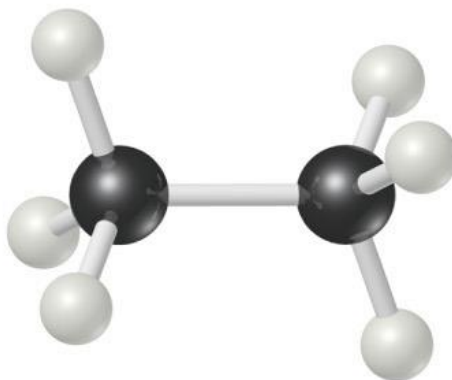
- Generally, standard molar entropy: gases > liquids & solids.

- Standard molar entropies **increase with molar mass**.



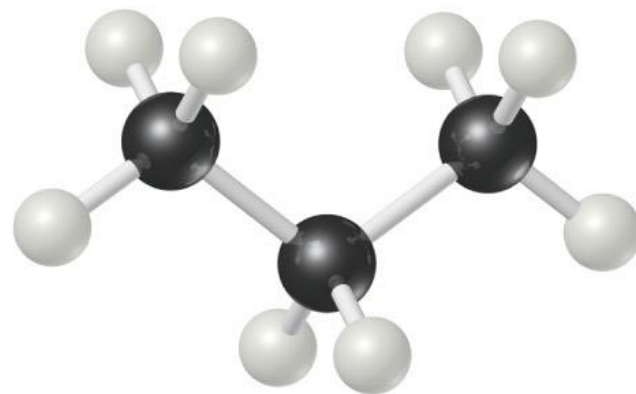
Methane, CH<sub>4</sub>

$S^\circ = 186.3 \text{ J/mol-K}$



Ethane, C<sub>2</sub>H<sub>6</sub>

$S^\circ = 229.6 \text{ J/mol-K}$



Propane, C<sub>3</sub>H<sub>8</sub>

$S^\circ = 270.3 \text{ J/mol-K}$

- Standard molar entropies increase with number of atoms in a formula of a substance.

# Entropy Changes of a Reaction

- Entropy changes for a reaction:

$$\Delta S^{\circ} = \Sigma nS^{\circ}(\text{products}) - \Sigma mS^{\circ}(\text{reactants})$$

where  $n$  and  $m$  are the coefficients in the balanced chemical equation.



# Entropy Changes in Surroundings

- **Heat** that **flows** into or out of the system **changes** the **entropy of the surroundings**.
- For an **isothermal** process:

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

- At **constant pressure**,  $q_{\text{sys}}$  is simply  $\Delta H^\circ$  for the system.

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \quad [\text{at constant } P]$$

# Entropy Change in the Universe

- The universe is composed of the system and the surroundings. So,

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

- For **spontaneous processes**:  $\Delta S_{\text{universe}} > 0$
- Multiplying  $(-T)$  on both sides:

$$-T\Delta S_{\text{universe}} = -T\Delta S_{\text{system}} - T\Delta S_{\text{surroundings}}$$

An **isothermal** process & constant pressure:

$$-T\Delta S_{\text{universe}} = -T\Delta S_{\text{system}} + \Delta H_{\text{system}}$$

# Gibbs Free Energy (G)

- For isothermal process at the constant pressure:

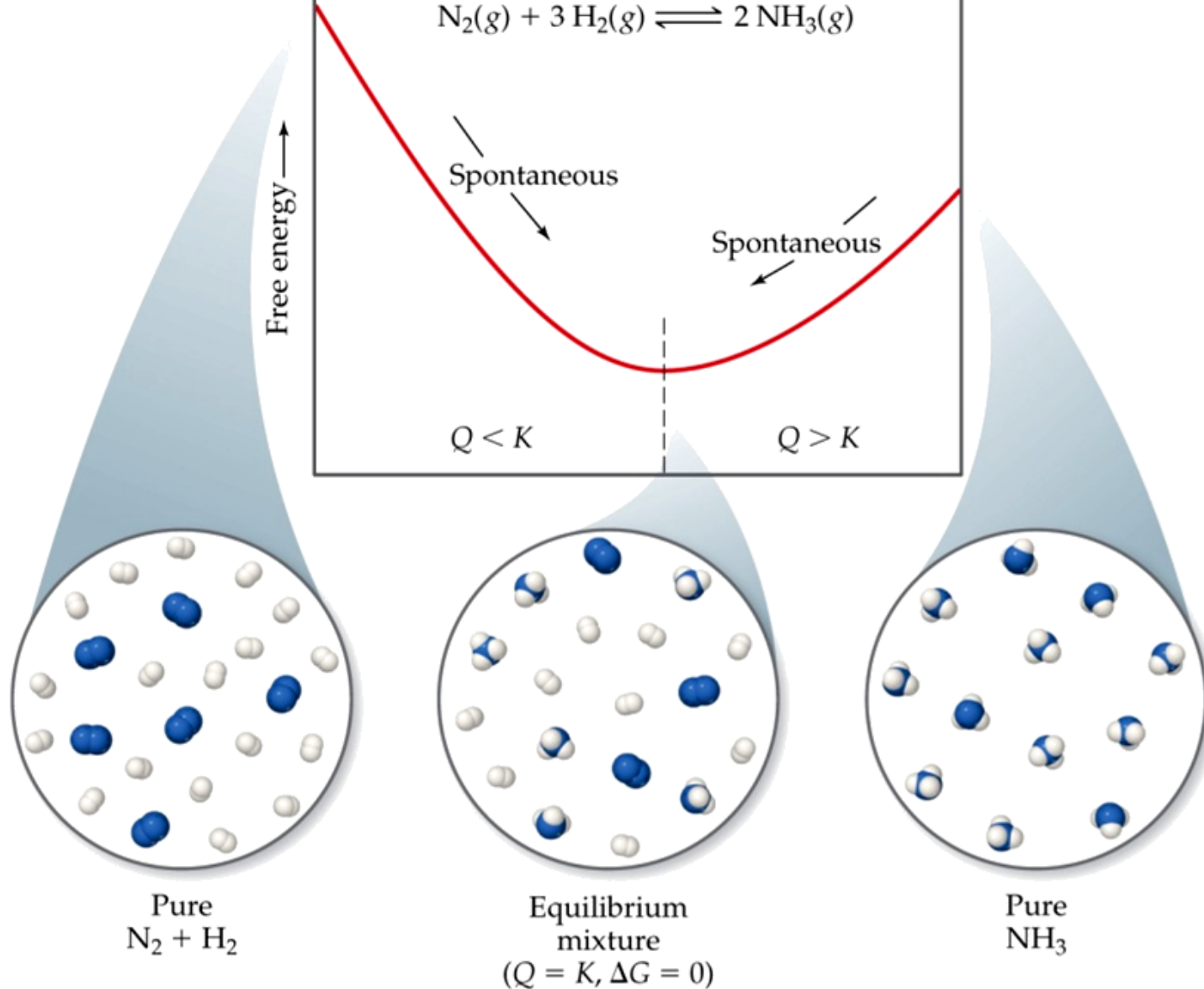
$$-T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

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

$$G = H - TS$$



- When  $\Delta S_{\text{universe}} > 0$ ,  $\Delta G < 0$ . Therefore, when  $\Delta G < 0$ , a process is **spontaneous**.



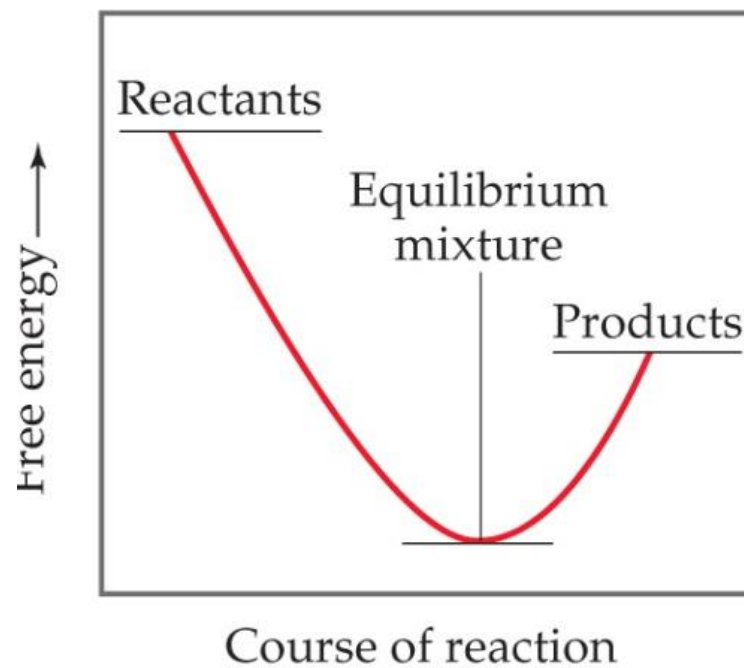
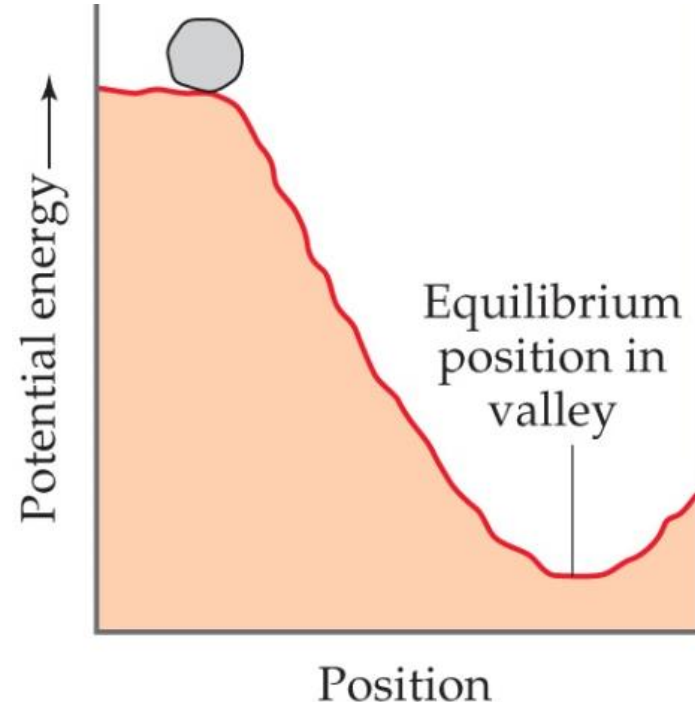
1. If  $\Delta G < 0$ , the **forward** reaction is **spontaneous**.
2. If  $\Delta G = 0$ , the system is at **equilibrium**.
3. If  $\Delta G > 0$ , the **reverse** reaction is **spontaneous**.

# Standard Free Energy Change ( $\Delta G^\circ$ )

- $\Delta G^\circ$  of a reaction: the free energy change when reactants and products are in their standard states **at 298.15 K**.

$$\Delta G^\circ = \sum G^\circ_{\text{(products)}} - \sum G^\circ_{\text{(reactants)}}$$

- The **standard free energy of formation,  $\Delta G_f^\circ$** : the free energy change for the formation of **1 mol** of a substance in its standard state from the elements in their standard states **at 298.15 K**.



## Table 19.2 Conventions Used in Establishing Standard Free Energies

State of Matter	Standard State
Solid	Pure solid
Liquid	Pure liquid
Gas	1 atm pressure
Solution	1 <i>M</i> concentration
Element	$\Delta G_f^\circ = 0$ for element in standard state

Analogous to standard enthalpies of formation, standard free energies of formation,  $\Delta G_f^\circ$ :

$$\Delta G^\circ = \Sigma n G_f^\circ (\text{products}) - \Sigma m G_f^\circ (\text{reactants})$$

where  $n$  and  $m$  are the stoichiometric coefficients.

# Free Energy Changes and Temperature

- There are two parts to the free energy equation:

the enthalpy term:  $\Delta H^\circ$

the entropy term:  $-T\Delta S^\circ$

- The **temperature dependence** of free energy then comes from the **entropy term**.
- Since reactions are spontaneous if  $\Delta G < 0$ , the sign of enthalpy and entropy and the magnitude of the temperature matters to spontaneity



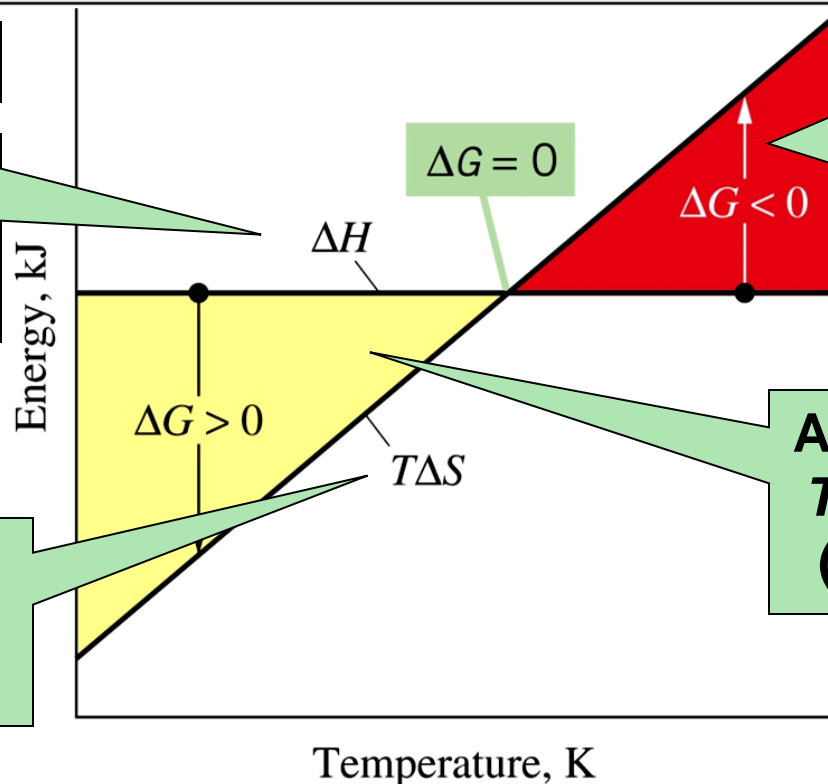
$$\Delta G = \Delta H - T\Delta S$$

Case	$\Delta H$	$\Delta S$	$\Delta G$	Result	Example
1	—	+	—	Spontaneous at all $T$	$2 \text{ O}_3(\text{g}) \longrightarrow 3 \text{ O}_2(\text{g})$
2	{ — —	{ — —	—	Spontaneous at low $T$	$\text{N}_2(\text{g}) + 3 \text{ H}_2(\text{g}) \longrightarrow 2 \text{ NH}_3(\text{g})$
			+	Nonspontaneous at high $T$	
3	{ + +	{ + +	+	Nonspontaneous at low $T$	$2 \text{ H}_2\text{O}(\text{g}) \longrightarrow 2 \text{ H}_2(\text{g}) + \text{O}_2(\text{g})$
			—	Spontaneous at high $T$	
4	+	—	+	Nonspontaneous at all $T$	$2 \text{ C}(\text{graphite}) + 2 \text{ H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_4(\text{g})$

### Case 3 illustrated

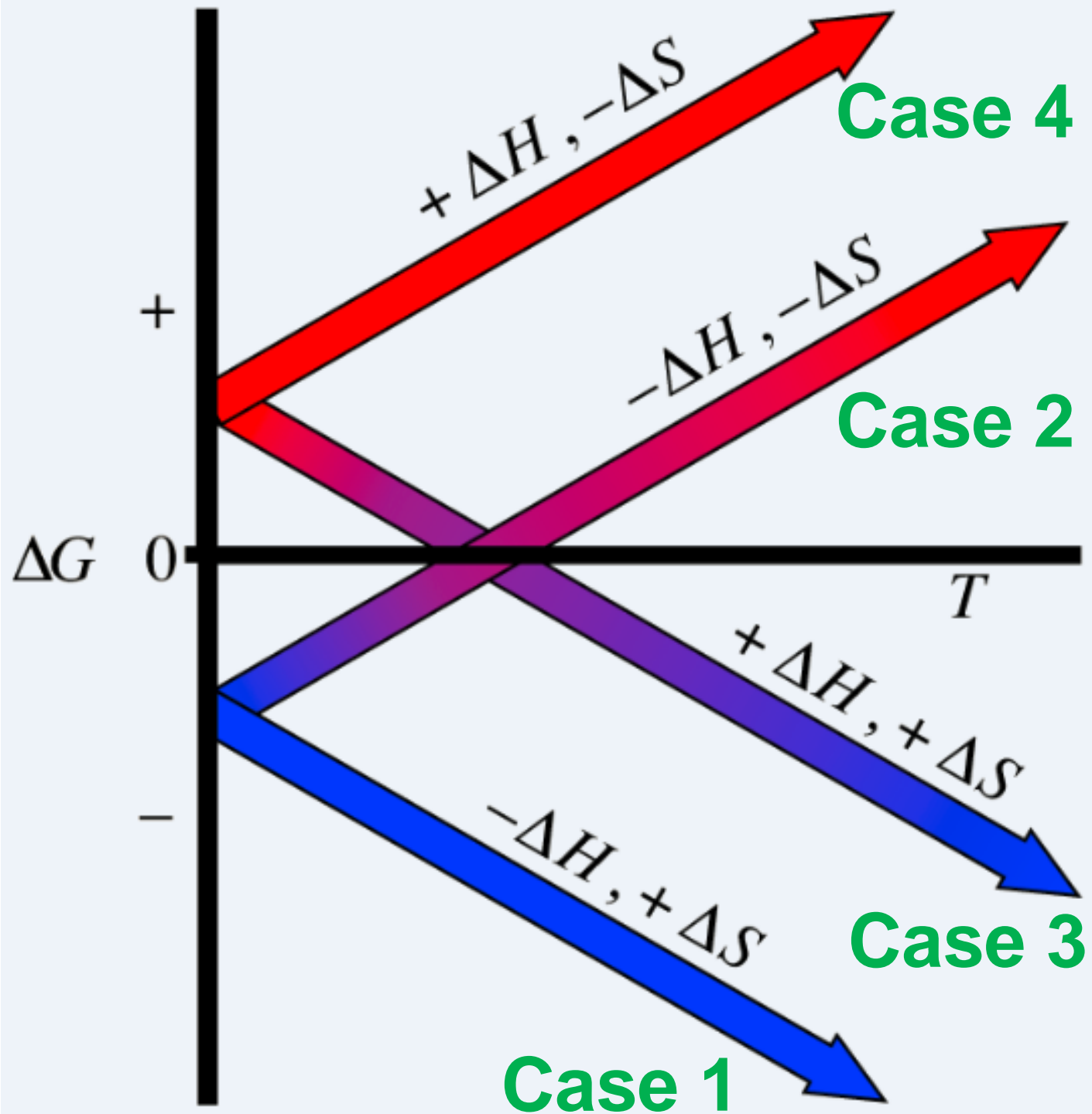
$\Delta H$  is (+) and is more-or-less constant with  $T$ .

Since  $\Delta S$  is (+), the slope  $T\Delta S$  is also (+).



At high  $T$ , the size of  $T\Delta S$  is large, &  $-\Delta S$  predominates.

At low  $T$ , the size of  $T\Delta S$  is small, &  $\Delta H$  (+) predominates.



# Free Energy (G) and Equilibrium (K)

- Under any conditions, standard or nonstandard, the free energy change can be found this way:

$$\Delta G = \Delta G^\circ + RT^*\ln Q$$

(Under **standard conditions**, **all concentrations are 1 M**, so  $Q = 1$  and  $\ln Q = 0$ ; the last term drops out.)

- At equilibrium,  $Q = K$ , and  $\Delta G = 0$ .
- The equation becomes

$$0 = \Delta G^\circ + RT^*\ln K$$

$$\Delta G^\circ = -RT^*\ln K$$

or

$$K = e^{-\Delta G^\circ/RT}$$

- $\Delta G = 0$  is a criterion for **equilibrium at any temperature**.
- $\Delta G^\circ = 0$  is a criterion for equilibrium at a **single temperature (298.15 K)**, that temperature at which the equilibrium state has all reactants and products in **their standard states**.
- $\Delta G$  and  $\Delta G^\circ$  are related through the **reaction quotient, Q** (chapter 15):

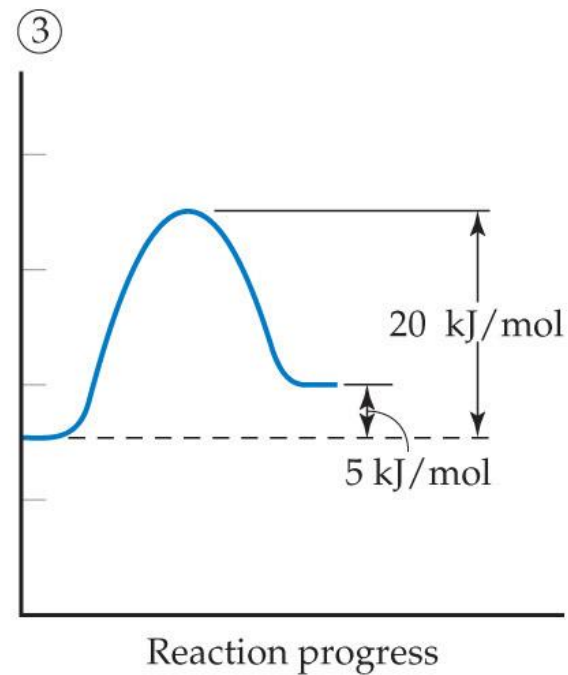
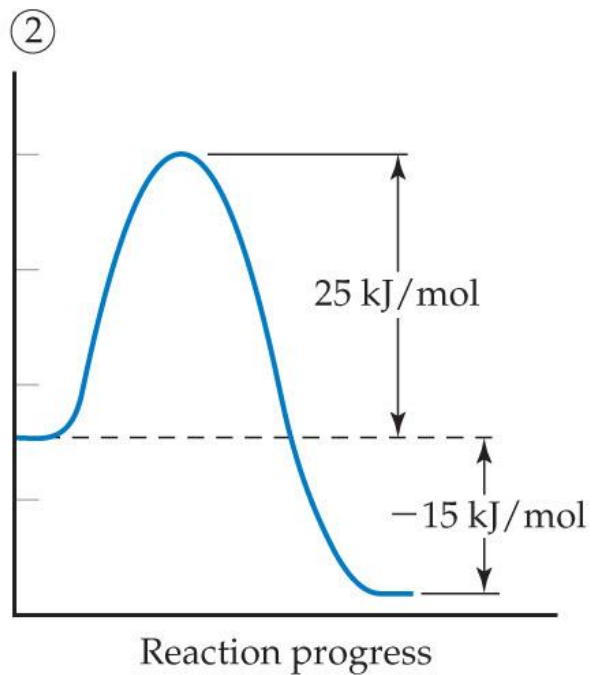
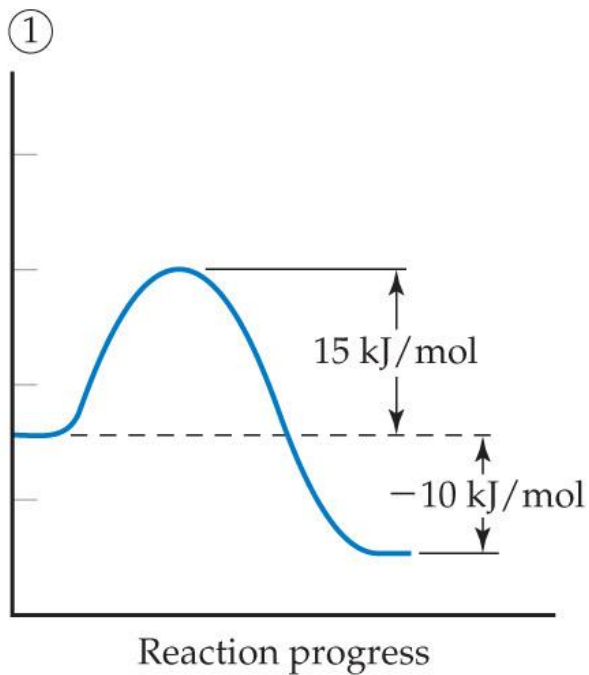
$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$Q = \frac{\text{activities of products}}{\text{activities of reactants}}$$



$$Q_c = \frac{[D]^d [E]^e}{[A]^a [B]^b}$$

$$Q = \prod_j a_j^{\nu_j}$$



$$K = e^{-\Delta G^\circ/RT}$$

# Arrhenius Equation (Chapter 14)

$$k = Ae^{-E_a/RT}$$

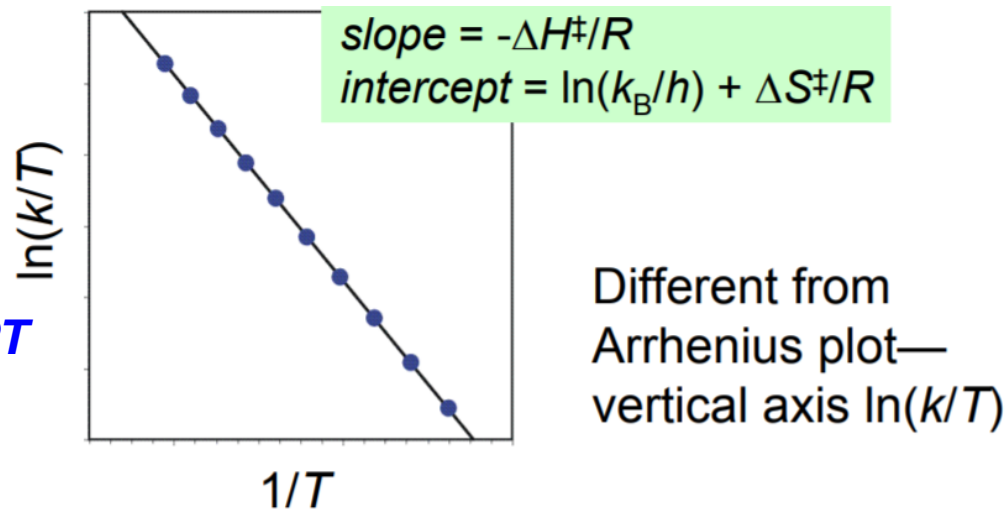
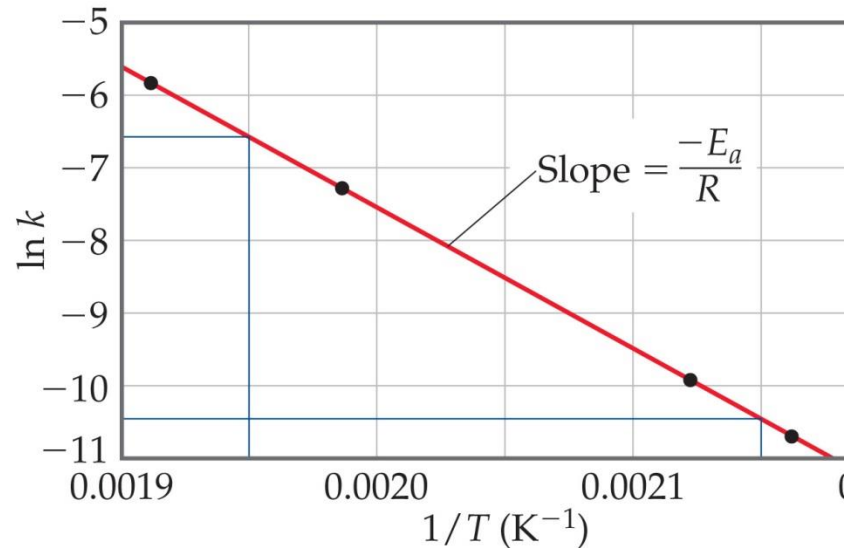
$$\ln(k) = -E_a/RT + \ln(A)$$

(extra info.)

## Eyring Equation

$$k = (k_B T/h) e^{-G_a/RT}$$

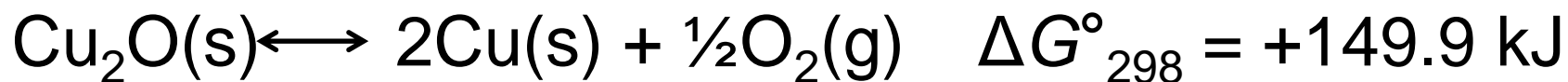
$$k = (k_B T/h) e^{S_a/R} * e^{-H_a/RT}$$



$$\ln(k/T) = -H_a/RT + \{\ln(k_B/h) + S_a/R\}$$

# Coupled Reactions

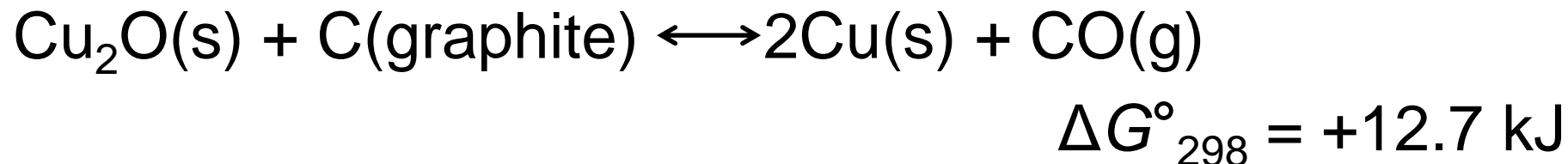
- A **nonspontaneous** reaction may be ***coupled*** with a **spontaneous** reaction. E.g. the decomposition of copper(I) oxide is quite nonspontaneous at room temperature:



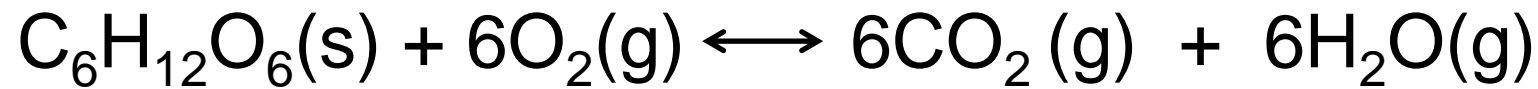
- By coupling this with the formation of CO from carbon,



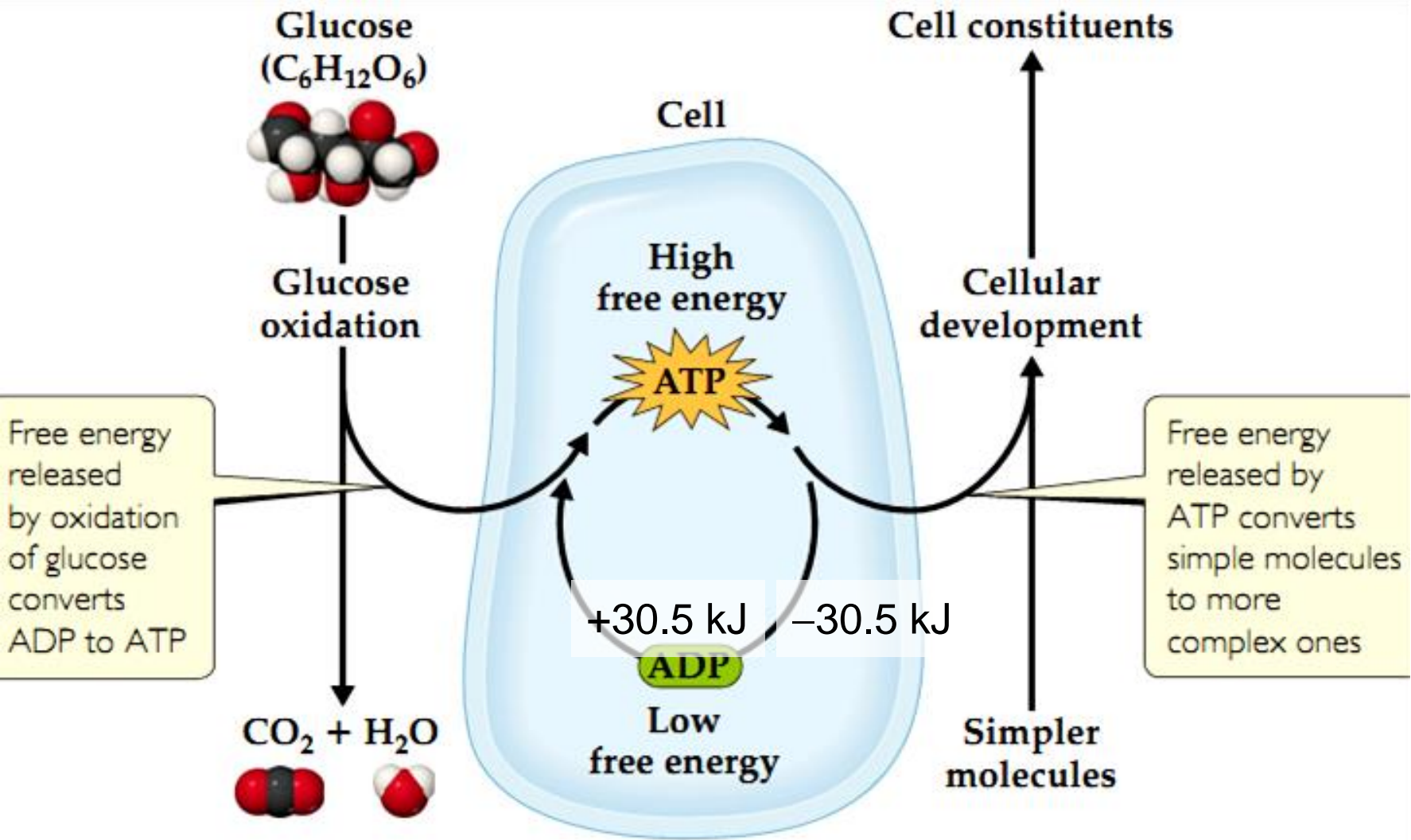
reduce the nonspontaneity of  $\text{Cu}_2\text{O}$  and make the overall reaction occur slightly above room temperature:



- Biological systems employ the same way to drive nonspontaneous ones.



$$\Delta G^\circ = -2880 \text{ kJ}$$





The Second Law of Thermodynamics says that the entropy of the universe \_\_\_\_\_ whenever a spontaneous process occurs.

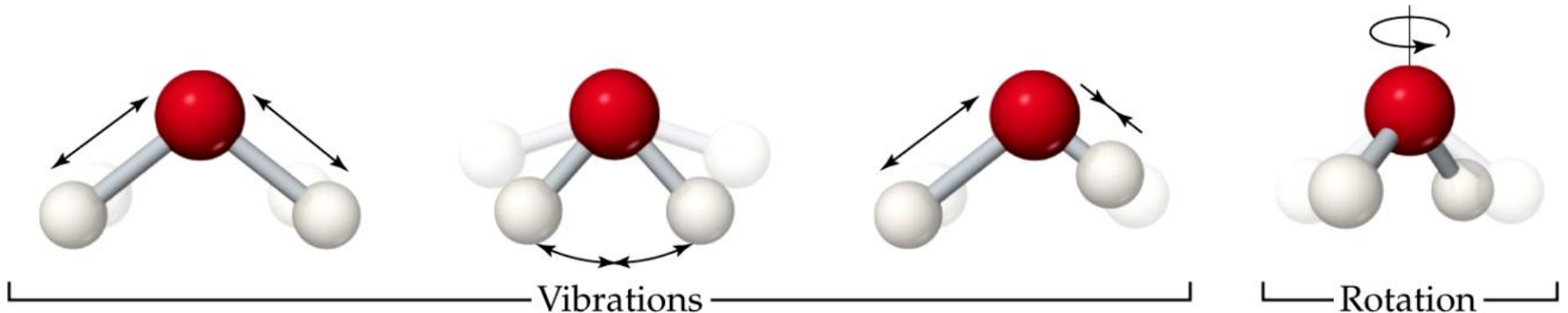
- a. increases
- b. decreases
- c. remains unchanged
- d. reaches equilibrium

An automobile being driven from west to east is experiencing \_\_\_\_\_ motion.

- a. kinetic
- b. translational
- c. vibrational
- d. rotational

What kinds of motion can a molecule undergo that a single atom cannot?

- A. Molecules and single atoms experience the same types of motion.
- B. A molecule can vibrate and rotate; a single atom undergoes neither.
- C. A molecule can undergo translational motion and rotate; a single atom undergoes neither.
- D. A molecule can vibrate and undergo translational motion; a single atom undergoes neither.



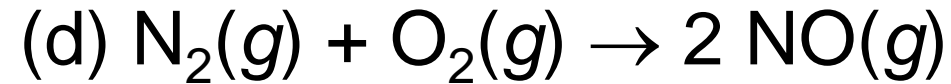
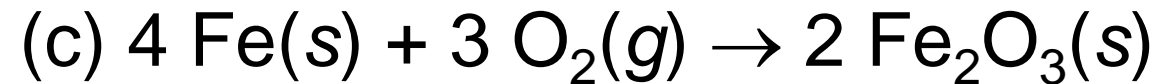
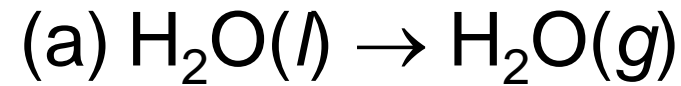
Changes in a molecule's bond lengths or bond angles are examples of \_\_\_\_\_ motion.

- a. kinetic
- b. translational
- c. vibrational
- d. rotational

When a molecule spins, it is undergoing \_\_\_\_\_ motion.

- a. translational
- b. vibrational
- c. rotational
- d. the loco-

Predict whether  $\Delta S$  is positive or negative for each process, assuming each occurs at constant temperature:



$k$  = Boltzmann's constant.  $W$  = the number of microstates.  $S$  = entropy. Which is true?

a.  $S = k \times W$

b.  $S = k / W$

c.  $S = k \ln W$

d.  $S = k^W$

Entropy decreases when

a. a liquid becomes a gas.

b. a solid becomes a liquid.

c. a gas becomes a solid.

d. the number of moles of gas increases.

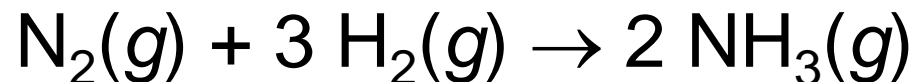
What is the entropy of a system that has only a single microstate?

- A.  $S = 0$
- B.  $S = 1$
- C.  $S > 0$
- D.  $S < 0$

Which process does **not** illustrate a decrease in entropy?

- a.  $\text{Na(s)} + \text{Br}_2(\text{l}) \rightarrow 2 \text{NaBr(s)}$
- b.  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO(s)} + \text{CO}_2(\text{g})$
- c.  $\text{NH}_3(\text{aq}) + \text{H}_2\text{S(g)} \rightarrow (\text{NH}_4)_2\text{S(aq)}$
- d.  $\text{AgNO}_3(\text{aq}) + \text{KCl(aq)} \rightarrow \text{AgCl(s)} + \text{KNO}_3(\text{aq})$

Calculate the change in the standard entropy of the system,  $\Delta S^\circ$ , for the synthesis of ammonia from  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$  at 298 K:



Substance	$S^\circ$ (J/mol-K)
$\text{H}_2(\text{g})$	130.6
$\text{N}_2(\text{g})$	191.5
$\text{O}_2(\text{g})$	205.0
$\text{H}_2\text{O}(\text{g})$	188.8
$\text{NH}_3(\text{g})$	192.5
$\text{CH}_3\text{OH}(\text{g})$	237.6
$\text{C}_6\text{H}_6(\text{g})$	269.2
$\text{H}_2\text{O}(\text{l})$	69.9
$\text{CH}_3\text{OH}(\text{l})$	126.8
$\text{C}_6\text{H}_6(\text{l})$	172.8
$\text{Li}(\text{s})$	29.1
$\text{Na}(\text{s})$	51.4
$\text{K}(\text{s})$	64.7
$\text{Fe}(\text{s})$	27.23
$\text{FeCl}_3(\text{s})$	142.3
$\text{NaCl}(\text{s})$	72.3

If a process is exothermic, does the entropy of the surroundings (1) always increase, (2) always decrease, or (3) sometimes increase and sometimes decrease, depending on the process?

$$\frac{-q_{\text{system}}}{T}$$

- A. Always increase
- B. Always decrease
- C. Sometimes increases and sometimes decreases, depending on the process

The notation, pressure, temperature, and units for reporting *Standard Molar Entropies* are

- a.  $S_{\text{std}}$ ; 1 atm; 0° C; kJ/mol-°C.
- b.  $S^{\circ}$ ; 1 atm; 298 K; J/mol-K.
- c.  $\Delta S^{\circ}$ ; 0 atm; 298 K; J/mol-K.
- d.  $\Delta S^{\circ}_{\text{f}}$ ; 1 atm; 0° C; kJ/°C.



What are the criteria for spontaneity

- a. in terms of entropy and
- b. in terms of free energy?

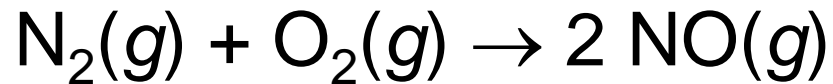
A. (a) The entropy of the universe increases and (b) the free energy of a system decreases at constant temperature.

B. (a) The entropy of the system decreases and (b) the free energy of the universe increases at constant temperature.

C. (a) The entropy of the system increases and (b) the free energy of the universe decreases at constant temperature.

D. (a) The entropy of the universe decreases and (b) the free energy of a system increases at constant temperature.

Calculate the standard free-energy change for the formation of  $\text{NO}(g)$  from  $\text{N}_2(g)$  and  $\text{O}_2(g)$  at 298 K:



given that  $\Delta H^\circ = 180.7 \text{ kJ}$  and  $\Delta S^\circ = 24.7 \text{ J/K}$ . Is the reaction spontaneous under these conditions?

The normal boiling point of benzene is 80 °C. At 100 °C and 1 atm, which term is greater in magnitude for the vaporization of benzene,  $\Delta H$  or  $T\Delta S$ ?

A.  $\Delta H = T\Delta S$

B.  $\Delta H < T\Delta S$

C.  $\Delta H > T\Delta S$

D. Cannot determine without additional information

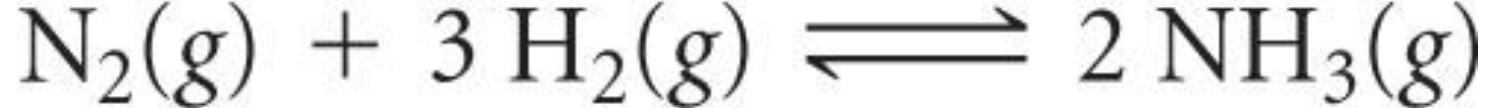
At equilibrium, the value of the free energy change ( $\Delta G$ ) is

a. positive.

b. negative.

c. fluctuating.

d. zero.



Assume that  $\Delta H^\circ$  and  $\Delta S^\circ$  for this reaction do not change with temperature. (a) Predict the direction in which  $\Delta G^\circ$  for the reaction changes with increasing temperature. (b) Calculate  $\Delta G^\circ$  at  $25^\circ \text{C}$  and  $500^\circ \text{C}$ , given that  $\Delta H^\circ = -92.38 \text{ kJ}$  and  $\Delta S^\circ = -198.3 \text{ J/K}$ .

The Third Law of Thermodynamics says that the entropy of a pure, perfect crystal is \_\_\_\_\_ at absolute zero (zero Kelvins).

- a. increasing
- b. decreasing
- c. infinite
- d. zero

G = the Gibbs free energy. H = enthalpy. S = entropy.  
T = the Kelvin temperature.

Which is true?

- a.  $G = H + TS$
- b.  $G = H - TS$
- c.  $G = H \times TS$
- d.  $G = H / TS$

If the enthalpy change is positive and the entropy change is negative, the reaction is

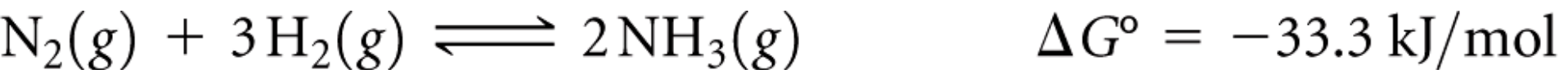
- a. spontaneous at all temperatures.
- b. non-spontaneous at all temperatures.
- c. spontaneous at low temperatures.
- d. spontaneous at high temperatures.

If the enthalpy change is negative and the entropy change is positive, the reaction is

- a. spontaneous at all temperatures.
- b. non-spontaneous at all temperatures.
- c. spontaneous at low temperatures.
- d. spontaneous at high temperatures.

What does the superscript  $^\circ$  indicate when associated with a thermodynamic quantity, as in  $\Delta H^\circ$ ,  $\Delta S^\circ$ , or  $\Delta G^\circ$ ?

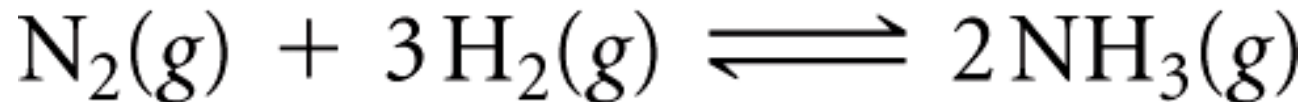
- A. It indicates the process is spontaneous under standard conditions.
- B. It indicates the process has taken place under standard conditions.
- C. It indicates the process has taken place at 273 K and 1 torr.
- D. It indicates the process has taken place at 1 atm and 0 K.



Use this value of  $\Delta G^\circ$  to calculate the equilibrium constant for the process at 25 °C.



Calculate  $\Delta G$  at 298 K for a mixture of 1.0 atm  $\text{N}_2$ , 3.0 atm  $\text{H}_2$ , and 0.50 atm  $\text{NH}_3$  being used in the Haber process:



# Key Summary

Spontaneous/Non-spontaneous process,  
reversible/irreversible process, entropy

The Second law of thermodynamics ( $\Delta S_{\text{univ}}$ ), The Third  
law of thermodynamics

Isothermal, statistical thermodynamics, microstate,  
Boltzmann's equation

Gibbs free energy, standard free energy change &  
equilibrium

**Thank You for Your  
Attention!  
Any Questions?**