

# Chemical Principles

## **9. Thermodynamics**

### **The second and third Laws**

# Outline

- Thermodynamic entropies
- The second law
- The third law and statistical entropies
- Molar entropies
- Gibbs free energies

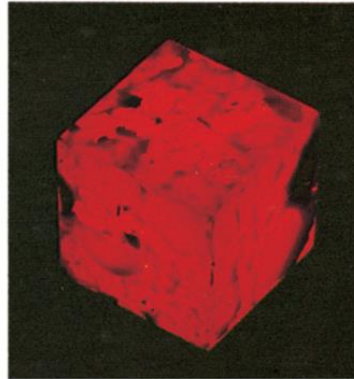
# Thermodynamics Laws

- The zeroth: If two systems are in thermal equilibrium with a third system, they are in thermal equilibrium with each other.  
Maxwell: "All heat is of the same kind"
- The first: energy conservation. The perpetual motion machines (produce work with no energy input) are impossible.
- The second: in isolated interacting system entropy always increases. The second kind of perpetual motion machines (spontaneously convert thermal energy into mechanical work) are impossible.
- The third: The entropy of a system approaches a constant value as the temperature approaches absolute zero, is equal to the natural logarithm of the number of microscopic states.

# Spontaneous Change

If no external influence drives a change (no work done on the system) the change is spontaneous.

A hot block of metal spontaneously cools to the temperature of its surroundings.



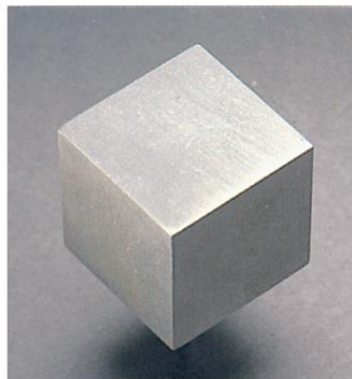
Hot

Spontaneously



Not spontaneously

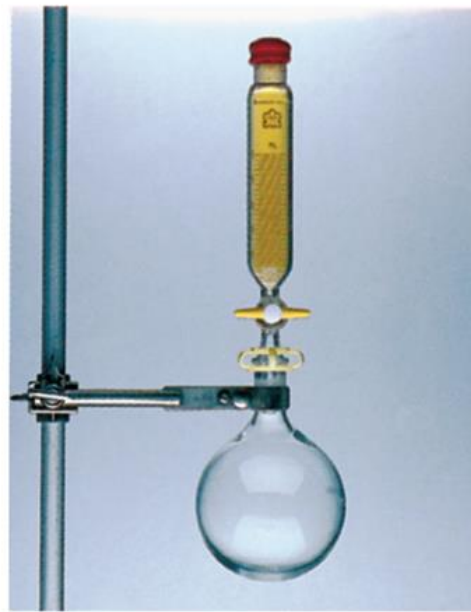
Cold



The reverse process does not occur.

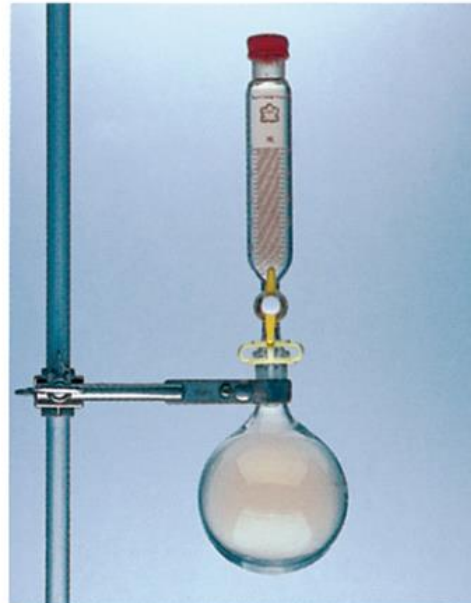
# Spontaneous Change

A spontaneous change occurs naturally without external influences.



A gas expands spontaneously into the lower evacuated flask.

Spontaneously ↓ ↑ Not spontaneously



The reverse process does not occur.

# Spontaneous Change: Tendency

The tendency is about the direction, a spontaneous process may not happen because the rate is too slow to be seen (we will discuss this as Kinetics).

e.g. A mixture of hydrogen and oxygen have a tendency to react spontaneously but can be kept safely, provided they are not ignited with a spark.

# Nonspontaneous Change

A nonspontaneous change can be made with **work**.

- **force** an electric current through a block of metal to heat it to a higher temperature.
- **drive** a gas into a smaller volume by pushing it with a piston.

# Entropy



# Entropy and Disorder

Entropy ( $S$ ) is a measure of disorder.

- Low entropy means little disorder;
- High entropy means great disorder.

*In an isolated system the **entropy increases** in the course of **any spontaneous change**.*

# How to calculate entropy

At constant temperature, in a reversible process, the entropy change of the system can be calculated as:

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

$q$  is the heat transferred reversibly,  $T$  is the absolute temperature, and typical units for entropy are  $\text{J}\cdot\text{K}^{-1}$

- If the heat **transferred**  $q_{\text{rev}} \uparrow$ , then  $\Delta S \uparrow$ .
- The lower the temperature  $T$  is, the greater the change in  $\Delta S$ .

# Entropy is a state function

Since entropy is a measure of disorder of a system, disorder is a state which does not depend on how the disorder is made, then entropy is a state function.

For a reversible process,  $\Delta S = \frac{q_{\text{rev}}}{T}$

For irreversible process, the above equation does not hold.

However, between two states, there is only one  $\Delta S$ , which can be calculated by using the equation.



# Entropy change as temperature

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

From heat capacity,  $q = C \Delta T$

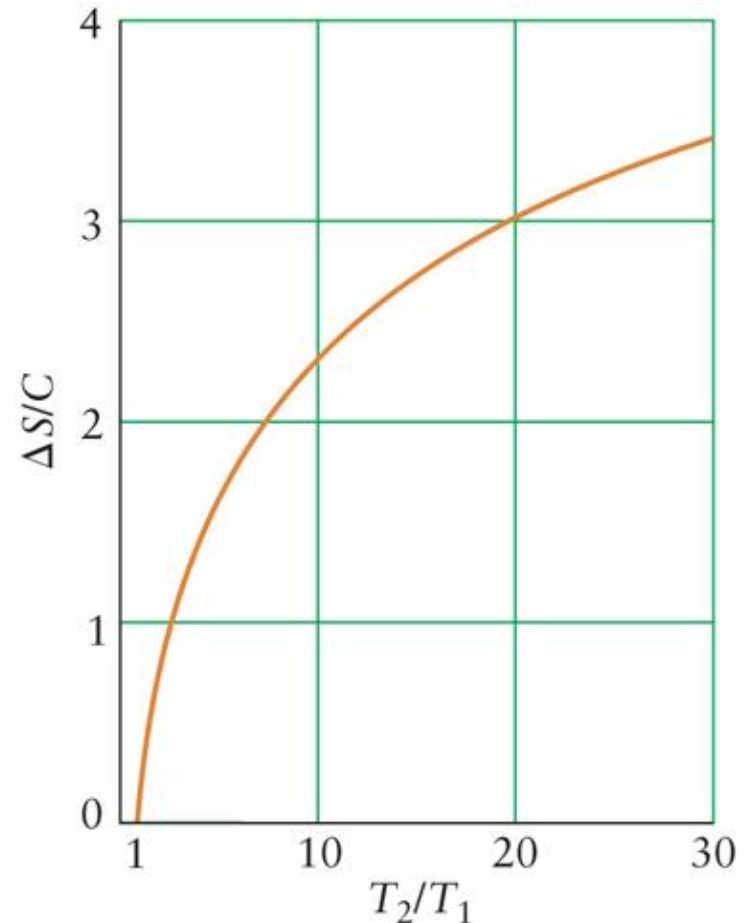
At infinitesimal change of temperature:

$$q_{\text{rev}} = C dT$$

Design a reversible process,

$$\Delta S = \int_{T_1}^{T_2} \frac{C dT}{T}$$

$$\Delta S_{1-2} = C \ln \frac{T_2}{T_1}$$



- If  $T_2/T_1 > 1$ ,  $\Delta S$  is positive.
- The greater the heat capacity the greater  $\Delta S$ .

# Entropy change as volume – ideal gases

For a reversibly isothermal ideal-gas expansion, we have ( $\Delta U=0$ )

$$q_{\text{rev}} = -w_{\text{rev}} = nRT \ln \frac{V_2}{V_1}$$

$$\Delta S_{1-2} = \frac{q_{\text{rev}}}{T} = nR \ln \frac{V_2}{V_1}$$

➤ Entropy **increase** with volume.

# Entropy change as pressure – ideal gases

For ideal gases, since  $PV = \text{constant}$ , since

$$\Delta S_{1-2} = nR \ln \frac{V_2}{V_1}$$

Then we have:

$$\Delta S_{1-2} = -nR \ln \frac{P_2}{P_1}$$

➤ Entropy **decrease** with pressure.

# Entropy depends on P, V, T

Ideal gases



$$\Delta S = C \ln \frac{T_2}{T_1}$$

C = heat capacity

**changes in  
temperature**

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

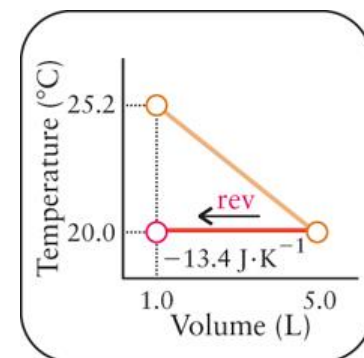
**changes in  
volume**

$$\Delta S = -nR \ln \frac{P_2}{P_1}$$

**changes in  
pressure**

Example. In an experiment, 1.00 mol Ar(g) was compressed suddenly (irreversibly) from 5.00 L to 1.00 L by driving in a piston, and in the process its temperature increased from 20.0°C to 25.2°C. What is the change in entropy of the gas? (Ar  $C_{v,m}$  is  $12.74 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ )

Although the process is irreversible, because  $S$ ,  $T$ ,  $V$  are all state functions, we do not need to worry about the real process. We can imagine two reversible processes.

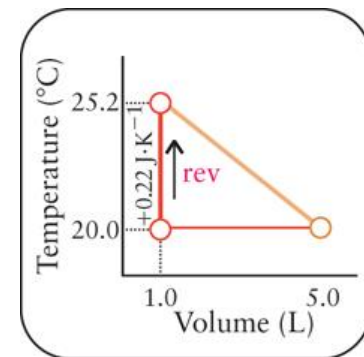


Step 1: compress the volume,

$$\Delta S = nR \ln \frac{V_2}{V_1} = R \ln \frac{1}{5} = -13.4 \text{ J}\cdot\text{K}^{-1}$$

Step 2: raise temperature at constant volume,

$$\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} = 0.22 \text{ J}\cdot\text{K}^{-1}$$



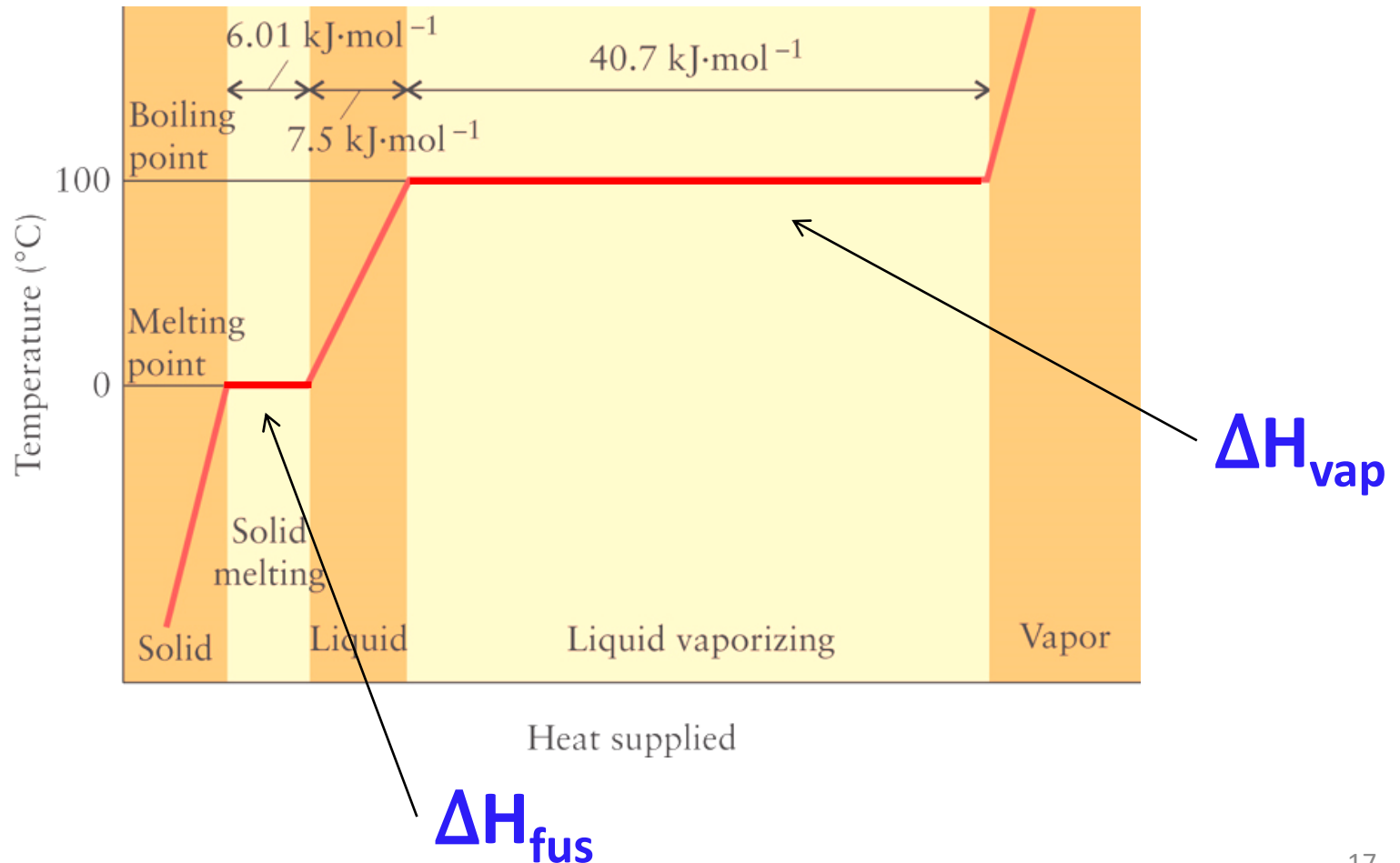
Combine both steps.

$$\Delta S = -13.4 \text{ J}\cdot\text{K}^{-1} + 0.22 \text{ J}\cdot\text{K}^{-1} = -13.2 \text{ J}\cdot\text{K}^{-1}$$



# Entropy Changes Accompanying Changes in Physical State

For molecules going through a phase change, either melting or vaporizing, entropy increases.



# Entropy Changes Accompanying Changes in Physical State

To calculate entropy  $\Delta S = \frac{q_{\text{rev}}}{T}$  we note:

- (1) the temperature remains constant as heat is added;
- (2) the heat transfer is reversible;
- (3) at constant pressure:  $q_{\text{rev}} = \Delta H$

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

$\Delta S^\circ$  can be calculated either  $\Delta H_{\text{fus}}^\circ$  or  $\Delta H_{\text{vap}}^\circ$  under standard conditions.

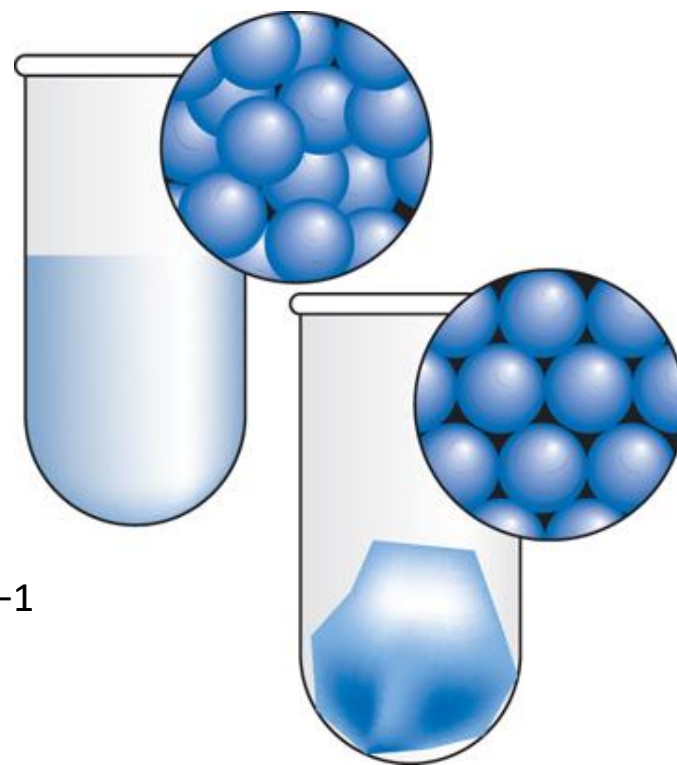
# Entropy Changes Accompanying fusion

Smaller increases in entropy occur when solids melt because liquids are only slightly more disordered than solids.

The standard entropy of fusion of benzene

From table  $\Delta H_{\text{fus}}^{\circ} = 10.59 \text{ kJ}$ , and melting point =  $5.45^{\circ}\text{C}$  or  $278.6 \text{ K}$

$$\Delta S_{\text{fus}}^{\circ} = \frac{\Delta H_{\text{fus}}^{\circ}}{T} = \frac{10,590 \text{ J}}{278.6 \text{ K}} = 38.01 \text{ J}\cdot\text{K}^{-1}$$



# Entropy Changes Accompanying vaporization

Liquid	Boiling Point (K)	$\Delta S^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$\Delta S^\circ = \frac{\Delta H_{\text{vap}}^\circ}{T}$
Helium	4.22	20	
Argon	87.3	74	
Benzene	353.2	87.2	
Ethanol	331.5	124	
Mercury	629.7	94.2	
Water	373.2	109	

$\Delta S_{\text{vap}}^\circ$  are generally larger than that of fusion.

Many values are close to 85 J·K<sup>-1</sup>·mol<sup>-1</sup>, called **Trouton's rule**.

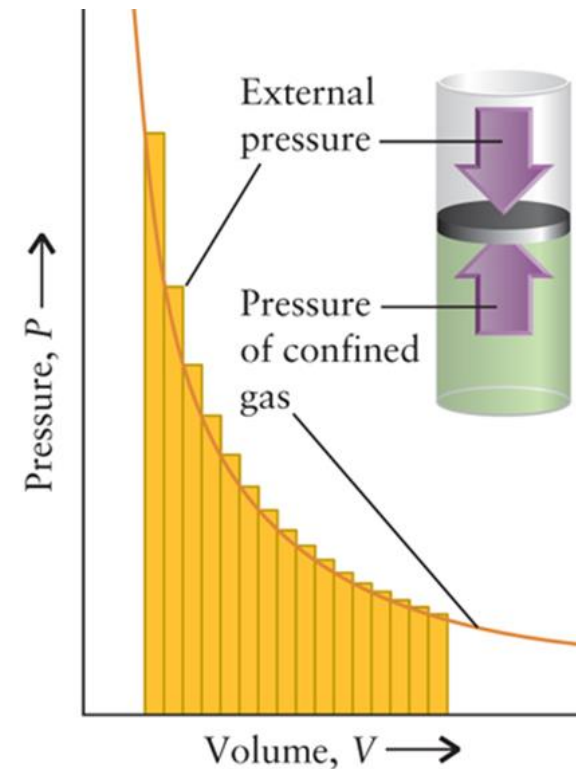
- Approximately the same increase in disorder occurs when any liquid is converted into vapor.

# The Second Law

# Maximum work is produced by reversible process

This can be seen by using the isothermal expansion of ideal gases as an example.

- In an isothermal reversible expansion, at each point  $P = P_{\text{ex}}$ , so the work =  $RT \ln V_2/V_1$ .
- If  $P_{\text{ex}} = 0$ , the expansion is irreversible,  $w = 0$
- At any point, if  $P_{\text{ex}}$  is lower than  $P$ , the system makes less work. If  $P_{\text{ex}}$  is greater than  $P$ , the system will be compressed (negative work).



$$w = -nRT \ln \frac{V_f}{V_i}$$

# Clausius Inequality

Focus on the system. Work is related to heat by

$$\Delta U = q + w.$$

Since  $w_{\text{rev}}$  is more negative than  $w_{\text{irrev}}$ , then  $q_{\text{rev}}$  is more positive than  $q_{\text{irrev}}$ . Therefore, for any  $\Delta U$ , we have

$$\Delta S = \frac{q_{\text{rev}}}{T} \geq \frac{q_{\text{irrev}}}{T}$$

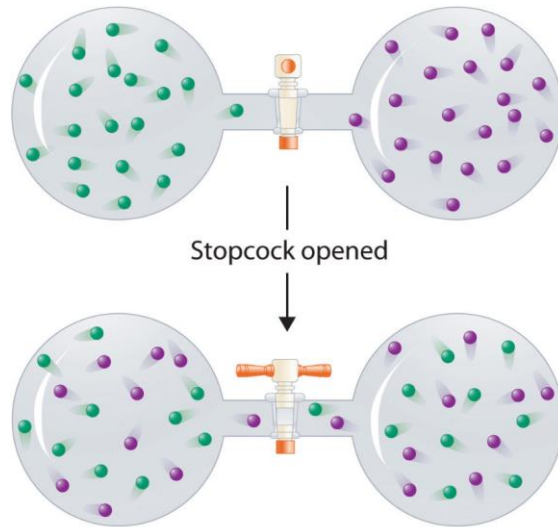
Generally, we have

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

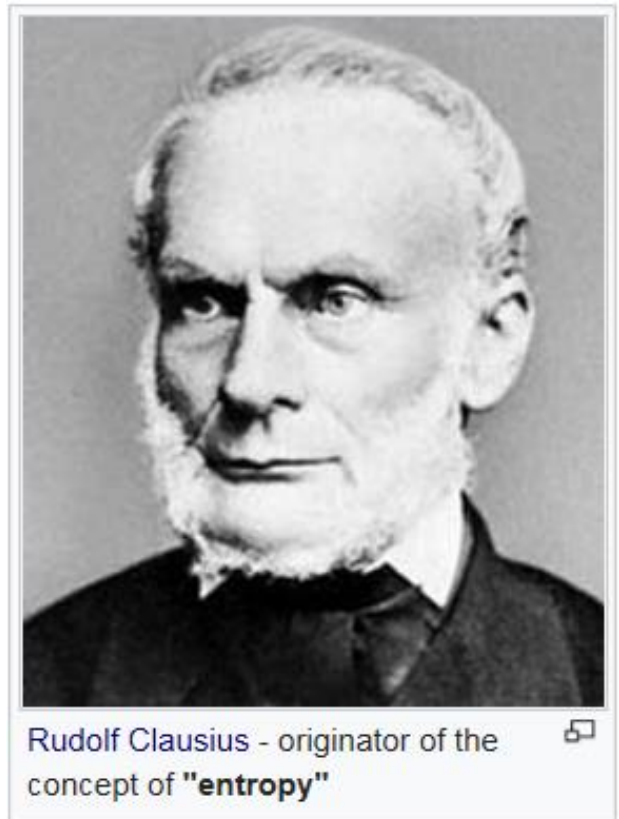
In an isolated system  $q = 0$  so  $\Delta S \geq 0$

# What is the cause of a spontaneous process

Clausius: in an isolated system, a spontaneous process is a process that changes toward more disorder state.



Mixing of two ideal gases in an isolated system (no energy and matter changes), the system moves toward more disordered state spontaneously.





# The second law of thermodynamics

Since disorder is measured by entropy, a spontaneous process in an isolate system increases the system's entropy.

If the process is reversible, we have

$$\Delta S = Q/T$$

then for an irreversible, spontaneous process

$$\Delta S > Q/T$$

Since isolated system means ( $Q = 0$ ), *we have*

$$\Delta S \geq 0 \quad (\text{Clausius inequality})$$

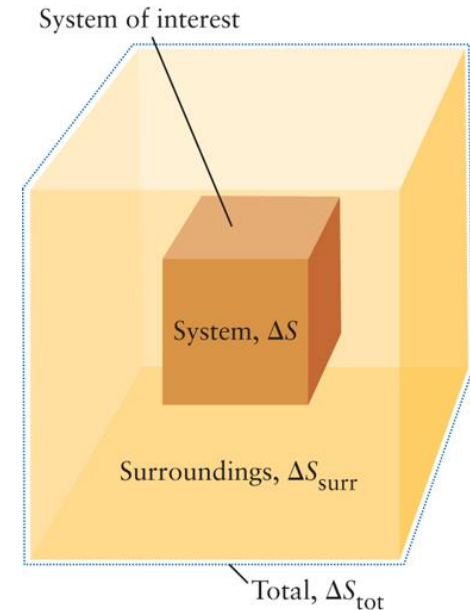
**The second Law: in isolated interacting system entropy always increases.**

# Global Changes in Entropy: Total

To use the second law, we need to consider isolated system.

An isolated system can be constructed by considering system and surroundings

Total Entropy  $\Delta S$  (total) are the system and surroundings.

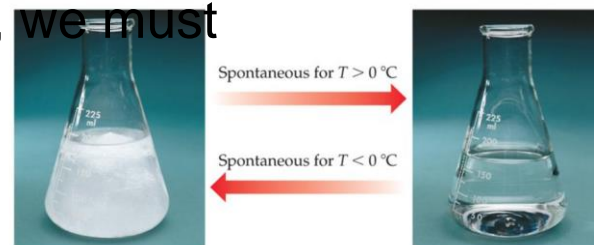


$$\Delta S (\text{total}) = \Delta S (\text{system}) + \Delta S (\text{surroundings})$$

# An example – ice to water

Since an isolated system = system + surrounding, we must calculate the total entropy change

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$



The Entropy change of system can be calculated using the standard entropies

$$\text{H}_2\text{O (l)} \quad 65.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\text{H}_2\text{O (s)} \quad 43.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta S_{sys} = 22.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The process releases  $6.0 \text{ kJ}\cdot\text{mol}^{-1}$ . Since the surrounding is very large, the heat transferred won't change its temperature, we can use  $\Delta S = Q_{surr}/T$ ,  $Q_{surr} = -\Delta H_{sys}$ , to calculate the entropy change.

$$-10\text{C}^0 \quad \Delta S_{surr} = -\frac{\Delta H_{sys}}{T} = \frac{6.0 \times 10^3}{263} = -23 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} ;$$

$$\Delta S_{total} = 22-23 = -1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$0\text{C}^0 \quad \Delta S_{surr} = -\frac{\Delta H_{sys}}{T} = \frac{6.0 \times 10^3}{273} = -22 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} ;$$

$$\Delta S_{total} = 22-22 = 0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$10\text{C}^0 \quad \Delta S_{surr} = -\frac{\Delta H_{sys}}{T} = \frac{6.0 \times 10^3}{283} = -21 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} ;$$

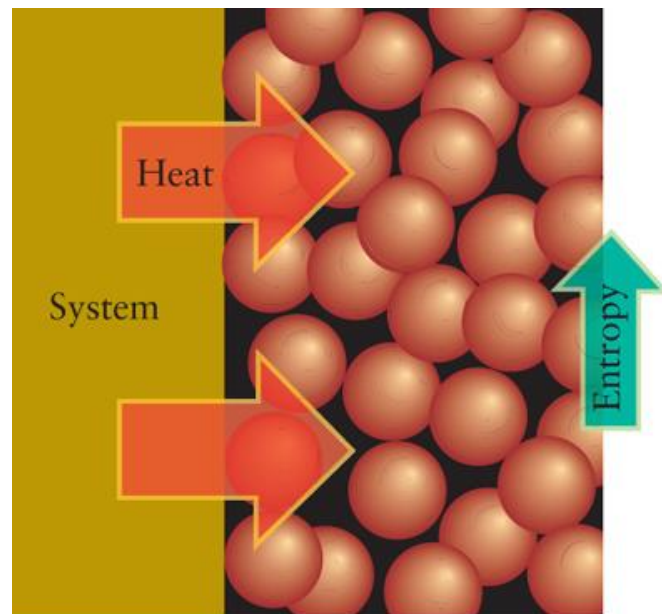
$$\Delta S_{total} = 22-21 = 1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

# Lower temperature causes larger change of entropy

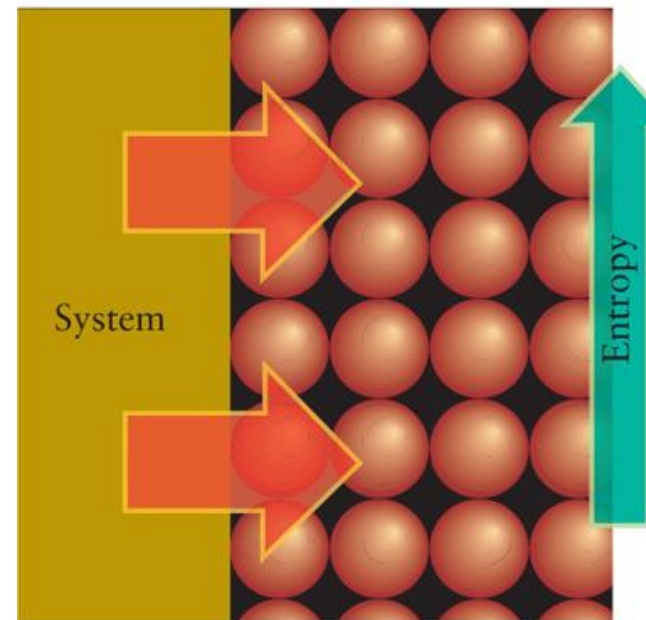
Because of

$$\Delta S = - \frac{\Delta H}{T}$$

At low temperatures,  $T$ , there is a greater effect on  $\Delta S$



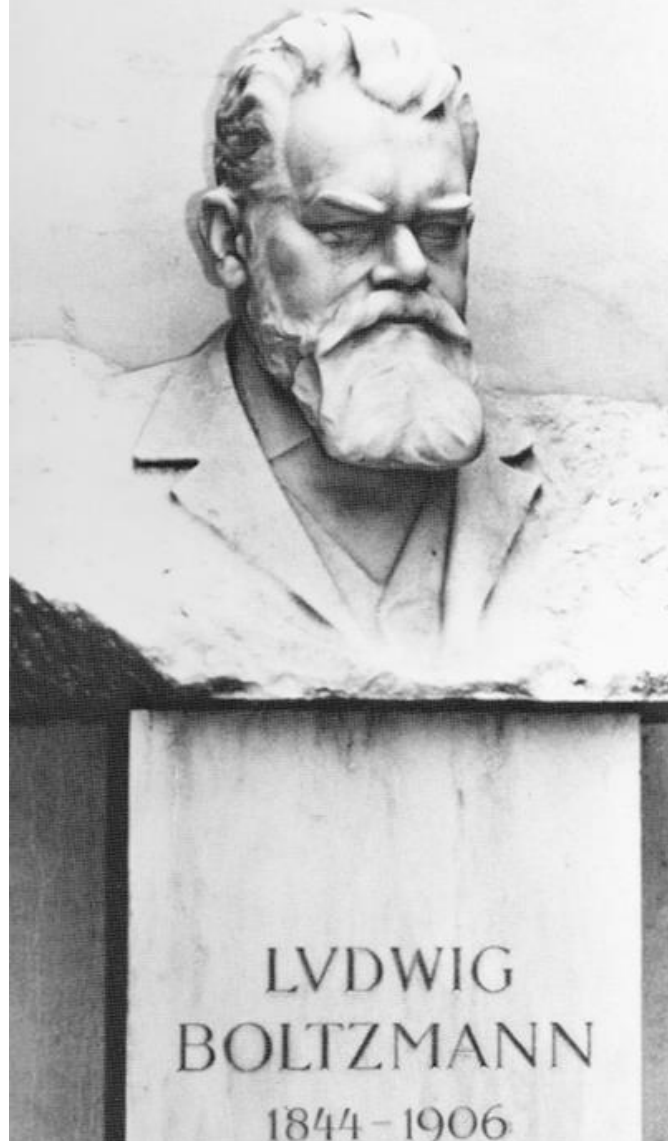
(a) Warm



(b) Cool

# The Third Law

$$S = k \cdot \log W$$



Austrian physicist Ludwig Boltzmann (1877) proposed a molecular definition of entropy.

The Boltzmann formula, as seen on his epitaph,

$$S = k \ln W$$

An absolute scale of entropy at any temperature.

$$k = 1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1} \quad (R = k N_A)$$

$W$  = the number of microstates

# The third law of thermodynamics

The entropy of a system approaches a constant value as the temperature approaches absolute zero, is equal to the natural logarithm of the number of microscopic states.

$$S = k \ln W$$

- A "perfect crystal" has no positional disorder,  $W=1$ ,  $S=0$
- The entropy of any substance is greater than zero above  $T = 0$ .

# Essential Concepts

A microscopic state is an arrangement of the positions and velocities of all atoms as well as the energy levels of all electrons.

The number of microstates,  $W$ , is the number of different arrangements. It can be a huge number (considering  $N_A$  molecules). Only at  $T$  approaches 0K and for perfect crystals, the number of microstates may be small.

If all microstates have the same energy (isolated), then

$$S = k \ln W$$

is called **statistical entropy**.



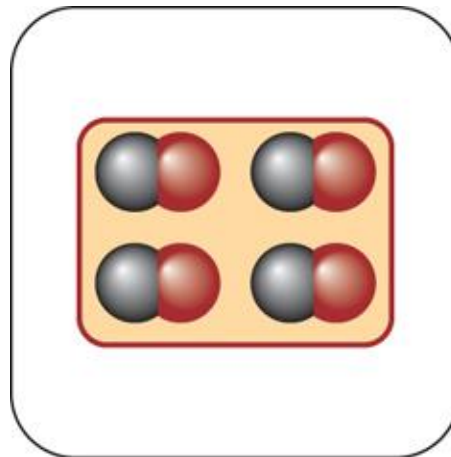
Calculate the entropy of a tiny solid made up of four diatomic molecules of a compound such as carbon monoxide, CO, at  $T = 0$  when

- (a) the four molecules have formed a perfectly ordered crystal
- (b) the four molecules lie in random orientations, but parallel.

- a) If all four molecules are pointing in one direction, there is only one arrangement,

$$W = 1,$$

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

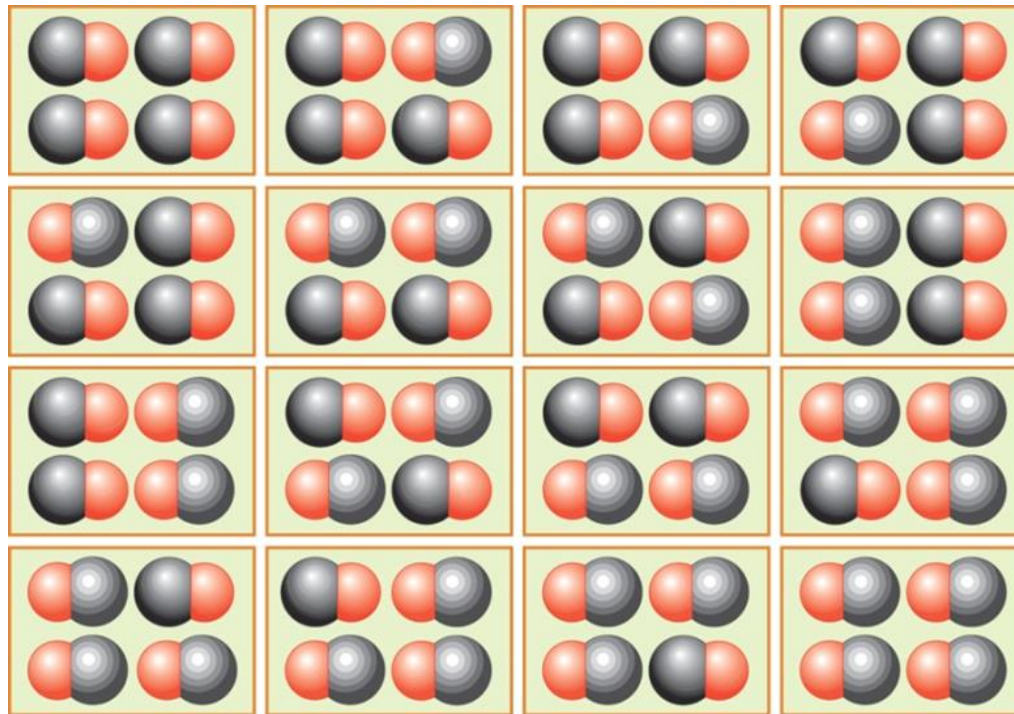


(b) The four molecules lie in random but parallel orientations. Because each molecule has 2 different orientations and there are 4 molecules, the number of arrangements is:

$$W = 2 \times 2 \times 2 \times 2 = 2^4 = 16$$

Then:

$$S = (1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}) \times \ln 16 = 3.8281 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$$



# Entropy and dipole moments

For 1 mol of CO crystal, at 0K, using the same model

$$\begin{aligned}\text{From } S &= k \ln W \quad \text{and} \quad W = 2^{6.02 \times 10^{23}} \\ S &= k \ln 2^{6.02 \times 10^{23}} \\ &= (1.3807 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}) \times (6.02 \times 10^{23}) \times \ln 2 \\ &= 5.76 \text{ J} \cdot \text{K}^{-1}\end{aligned}$$

The experimentally measured entropy of 1 mol CO at  $T = 0$ ,  
 **$4.6 \text{ J} \cdot \text{K}^{-1}$ .**

This is called residual entropy arising from positional disorder of the CO.

**Q:** What causes the small difference? How may be possible to improve the calculations?

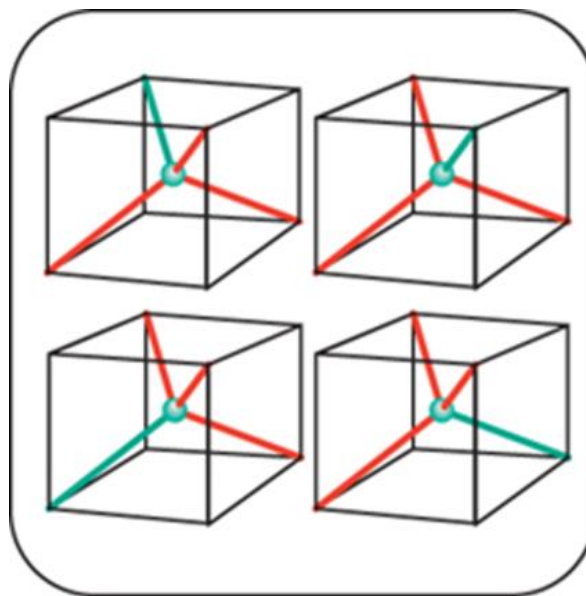
# Entropy and dipole moments

For molecule with strong dipole, like HCl, the same experimental measurements give  $S = 0$  close to  $T = 0$ .

This indicates a bigger dipole moment for HCl, *the molecules arrange themselves* into head-to-tail fashion so there is **no positional disorder**.

Example 9.8 The entropy of 1.00 mol  $\text{FCIO}_3$  (s) at  $T = 0$  is  $10.1 \text{ J}\cdot\text{K}^{-1}$ . Suggest an interpretation.

An  $\text{FCIO}_3$  (s) molecule is tetrahedral, and so we can expect it to be able to take up any of 4 orientations in a crystal



$$W = 4^{6.022 \times 10^{23}}$$

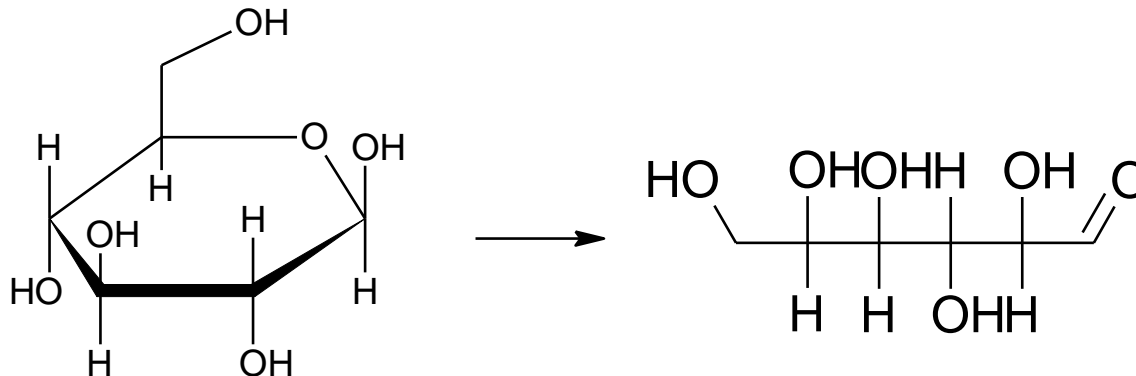
$$S = k \ln W$$

$$S = (1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}) \times 6.022 \times 10^{23} \ln 4 = 11.5 \text{ J}\cdot\text{K}^{-1}$$

# Entropy change can be estimated by disorderness

The ring opening of the glucose molecule is

- A. entropy disfavored, or  $-S$ .
- B. entropy neutral, or  $S = 0$ .
- C. entropy favored, or  $+S$ .
- D. Temperature is unknown.

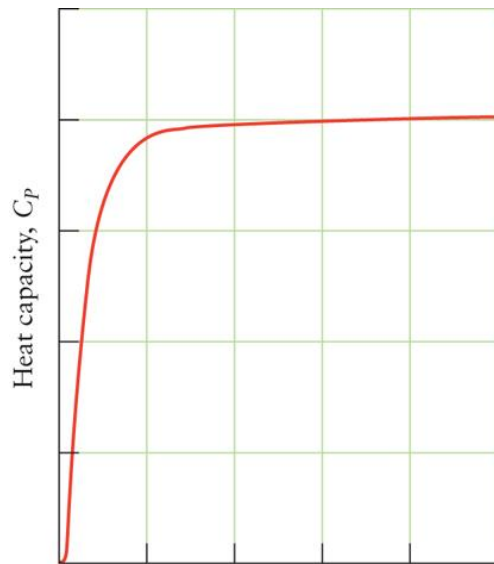


Ring molecules are more rigid than chain molecules that are allowed to twist and flex.

# Calculate of entropy using the third law

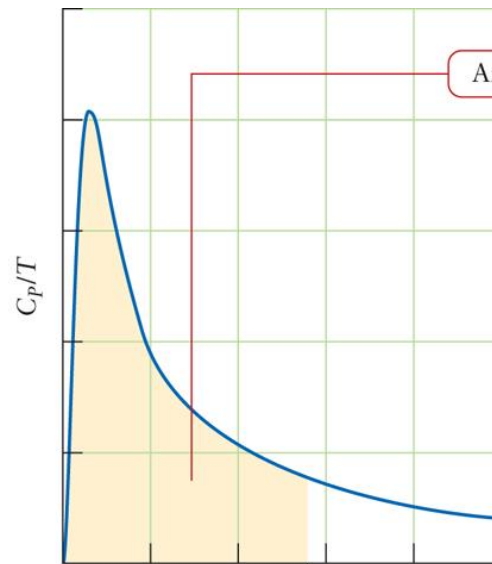
Since the third law gives  $S(0)$  at  $T=0$ ,  $S(T)=S(0)+\Delta S(T)$  at any temperatures can be calculated using (at constant pressure).

$$\Delta S(T) = \int_0^T \frac{C_p dT}{T}$$



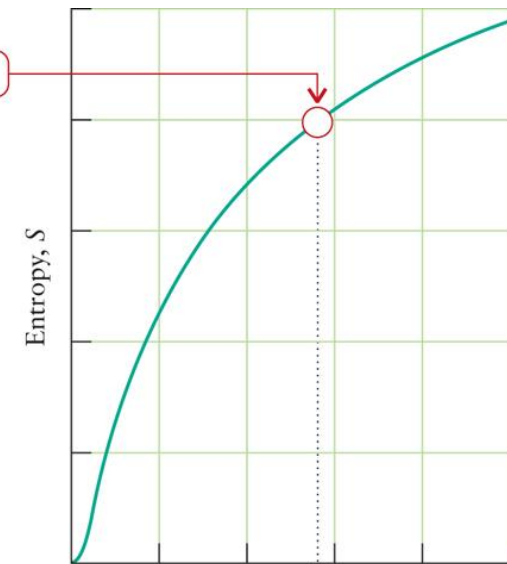
Temperature

$C_p$



Temperature

$C_p/T$



Temperature

$\Delta S(T)$

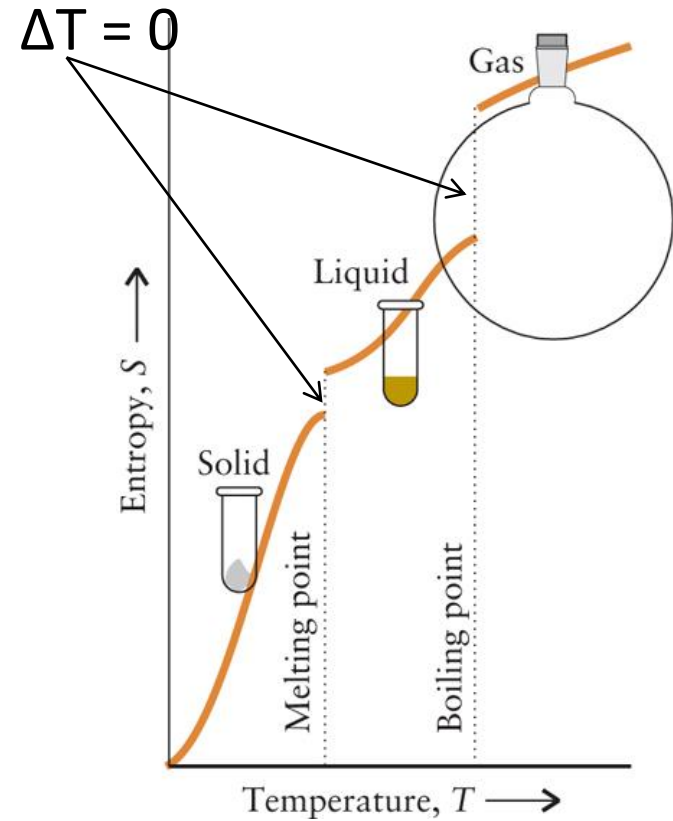
# In case of phase transition

1. For  $\Delta S$  between  $T_1$  to  $T_2$ .

$$\Delta S = \int_{T_1}^{T_2} \frac{C dT}{T}$$

2. At phase transition

$$\Delta S_{\text{fus}}^{\circ} = \frac{\Delta H_{\text{fus}}^{\circ}}{T}$$





# Equivalencies of Statistical and Thermodynamic Entropies

The thermodynamic and statistical entropies are:

$$\Delta S = \frac{q_{\text{rev}}}{T} \qquad \Delta S = k \ln \frac{W_f}{W_i}$$

We have just seen one example of agreement between the two entropies.

There are many agreements between two entropies.

Although to calculate the entropies are too involved, we can see the trends qualitatively in this course.



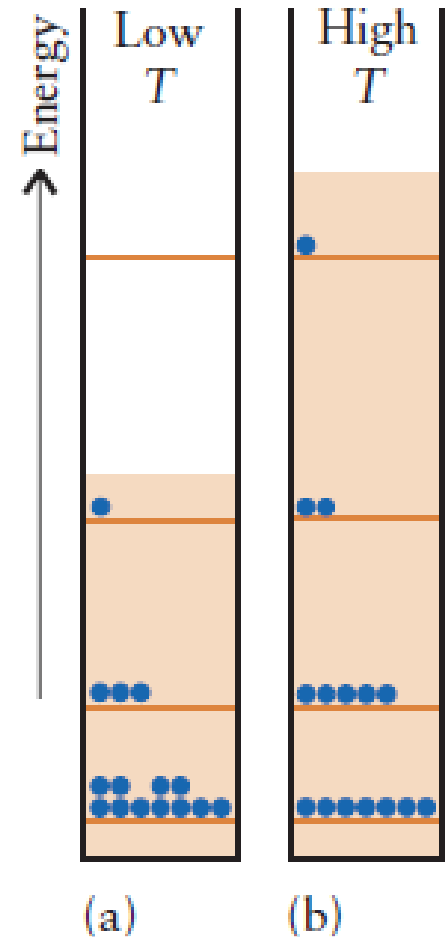
# Temperature dependence

At  $T = 0$ , if only the lowest energy level is occupied, then  $W = 1$  and the entropy is zero.

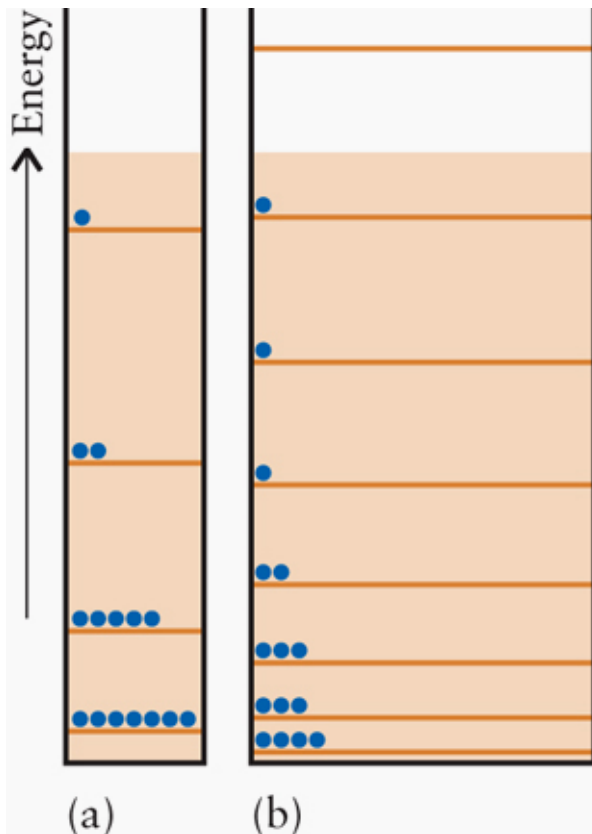
As temperature increases, more energy levels are occupied, the number of microstates increases, so the entropy increases.

Raising temperature creates more microstates, high entropy, consistent with:

$$\Delta S = C_{vm} \ln \frac{T_2}{T_1}$$



# Volume dependence



As volume increases, more energy levels are accessible at given temperature,

The number of microstates increases in the same energy range.

The entropy increases. Expansion creates more microstates, higher entropy, consistent with

$$\Delta S = R \ln \frac{V_2}{V_1}$$

# Standard Molar Entropies

# Standard Molar Entropies: $S_m^\circ$

As a state function, molar entropies at standard condition can be tabulated, as follows:

Gases	$S_m^\circ$	Liquids	$S_m^\circ$	Solids	$S_m^\circ$
ammonia, $\text{NH}_3$	192.4	benzene, $\text{C}_6\text{H}_6$	173.3	calcium oxide, $\text{CaO}$	39.8
carbon dioxide, $\text{CO}_2$	213.7	ethanol, $\text{C}_2\text{H}_5\text{OH}$	160.7	calcium carbonate, $\text{CaCO}_3^\dagger$	92.9
hydrogen, $\text{H}_2$	130.7	water, $\text{H}_2\text{O}$	69.9	diamond, $\text{C}$	2.4
nitrogen, $\text{N}_2$	191.6			graphite, $\text{C}$	5.7
oxygen, $\text{O}_2$	205.1			lead, $\text{Pb}$	64.8

- **All are positive** because of  $S = k \ln W$  ( $W > 1$ )
- **Gases** have the most freedom (more **W**'s). Liquids have a greater freedom of movement than solids.
- **More complex** molecules have a greater freedom of movement.
- **Heavier** atoms have more energy levels available than lighter ones.
- **Polar** molecules have *lower* entropy values.

# Standard reaction entropies

It can be used in the same way as standard molar enthalpies, to calculate the change in entropy in a reaction,

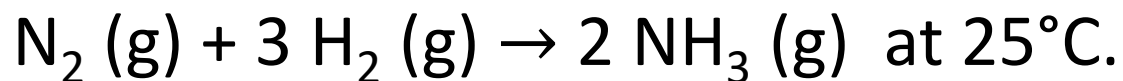
$$\Delta S (\text{system}) = \sum n S_{\text{m}}^{\circ} (\text{products}) - \sum n S_{\text{m}}^{\circ} (\text{reactants})$$

$n$  = stoichiometric coefficients

$S_{\text{m}}^{\circ}$  = standard molar entropies

## Example Calculating the standard reaction entropy

Calculate the standard reaction entropy of



$$S_{\text{m}}^\circ \text{N}_2 (\text{g}) = 191.6 \text{ J}\cdot\text{K}^{-1}$$

$$S_{\text{m}}^\circ \text{H}_2 (\text{g}) = 130.7 \text{ J}\cdot\text{K}^{-1}$$

$$S_{\text{m}}^\circ \text{NH}_3 (\text{g}) = 192.4 \text{ J}\cdot\text{K}^{-1}$$

$$\Delta S = 2 S_{\text{m}}^\circ(\text{NH}_3(\text{g})) - [S_{\text{m}}^\circ(\text{N}_2(\text{g})) + 3 S_{\text{m}}^\circ(\text{H}_2 (\text{g}))]$$

$$\Delta S = \{2 (192.4 \text{ J}\cdot\text{K}^{-1})\} - \{(191.6 \text{ J}\cdot\text{K}^{-1}) + 3(130.7 \text{ J}\cdot\text{K}^{-1})\}$$

$$\Delta S = -198.9 \text{ J}\cdot\text{K}^{-1}$$

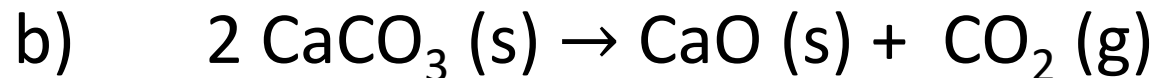
## Quick Estimate

Because gases have much larger entropies, without any calculations, we can estimate the sign of the entropy change for a reaction.

For examples



The entropy change is negative because there is a net decrease in the number of moles of gas molecules.



The entropy change is positive because net results is producing a gas from a solid.



# Gibbs Free Energy

# Gibbs Free Energy

The Clausius inequality  $\Delta S_{\text{tot}} \geq 0$  is not convenient to use, as we must carefully analyze how surrounding changes.

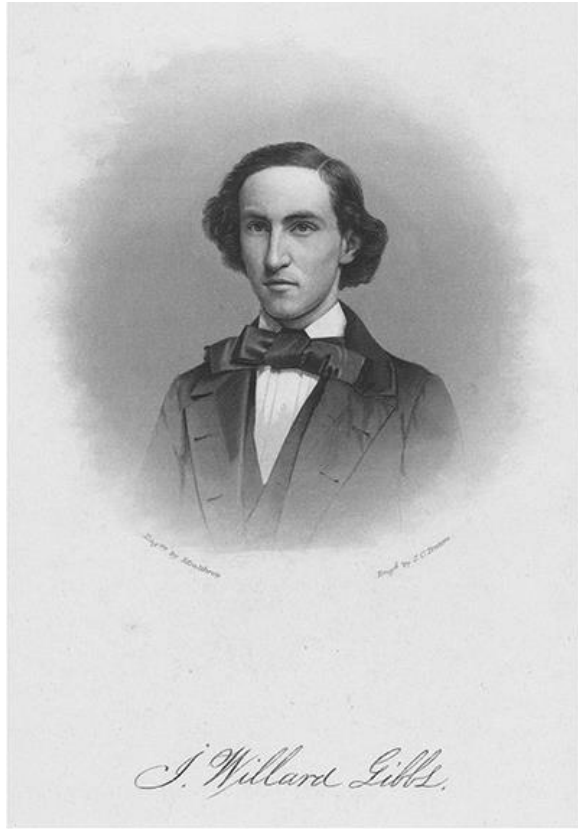
For chemistry, **constant pressure** is a very common condition, and the surrounding is infinitely large so that the temperature is constant, therefore we have:

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} - \Delta H_{\text{sys}}/T$$

Which is:

$$-T\Delta S_{\text{tot}} = -T\Delta S_{\text{sys}} + \Delta H_{\text{sys}}$$

# Gibbs Free Energy



Define the Gibbs free energy difference for the system:

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

$G = H - TS$  is Gibbs free energy, another state function.

The Clausius inequality  $\Delta S_{\text{tot}} \geq 0$  now becomes:  $\Delta G \leq 0$

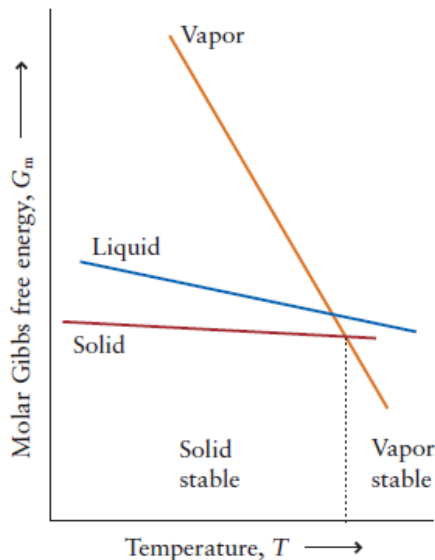
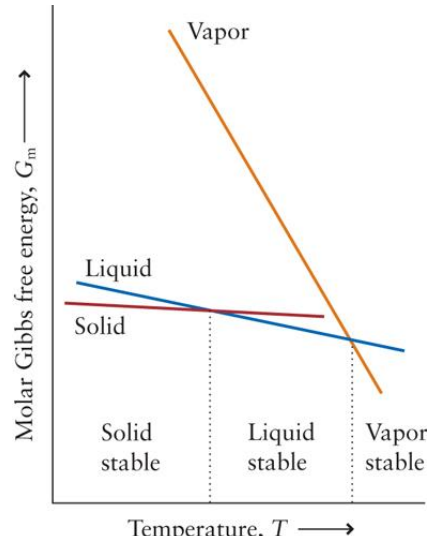
It is much more convenient because we can focus on the system only.

# Gibbs Free Energy

$$G = H - TS$$

G decreases as the temperature increases because **S is always positive**.

G decreases with temperature faster for larger S (the slop: gas > liquid > solid).



At any temperature, the lower free energy corresponds to the more stable state. The cross point is equilibrium (phase transition point)

In some systems the sublimation occurs because the solid is more stable than liquid.

# Gibbs free energy change

Using Gibbs free energy formula,  $\Delta G = \Delta H - T\Delta S$  to find spontaneity.

Since  $\Delta G = \Delta H - T\Delta S$ ,  $\Delta H$  and  $\Delta S$  influence the change together.

Enthalpy change	Entropy change	Spontaneous?
exothermic ( $\Delta H < 0$ )	increase ( $\Delta S > 0$ )	yes, $\Delta G < 0$
exothermic ( $\Delta H < 0$ )	decrease ( $\Delta S < 0$ )	yes, if $ T\Delta S  <  \Delta H $ , $\Delta G < 0$
endothermic ( $\Delta H > 0$ )	increase ( $\Delta S > 0$ )	yes, if $T\Delta S > \Delta H$ , $\Delta G < 0$
endothermic ( $\Delta H > 0$ )	decrease ( $\Delta S < 0$ )	no, $\Delta G > 0$

Example Calculate the change in molar Gibbs free energy,  $\Delta G_m$ , for the process  $\text{H}_2\text{O (s)} \rightarrow \text{H}_2\text{O (l)}$  at 1 atm and (a)  $10.^\circ\text{C}$ ; (b)  $0.0^\circ\text{C}$ . Decide for each temperature whether melting is spontaneous or not. Treat  $\Delta H_{\text{fus}}$  and  $\Delta S_{\text{fus}}$  as independent of temperature.

The enthalpy of fusion ( $\Delta H_{\text{fus}}$ ) is  $6.01 \text{ kJ}\cdot\text{mol}^{-1}$  and the entropy of fusion ( $\Delta S_{\text{fus}}$ ) is  $22.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . These values are almost independent of temperature over the temperature range considered.

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

$10.^\circ\text{C}$

$$\Delta G = \Delta H - T\Delta S = 6.01 \text{ kJ}\cdot\text{mol}^{-1} - (273.15 + 10.^\circ\text{C})\text{K} \times 22.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -0.22 \text{ kJ}\cdot\text{mol}^{-1}$$

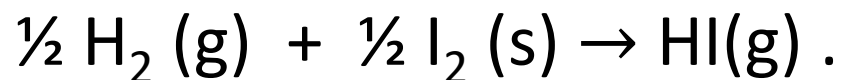
$0.0^\circ\text{C}$

$$\Delta G = \Delta H - T\Delta S = 6.01 \text{ kJ}\cdot\text{mol}^{-1} - 273.15\text{K} \times 22.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 0.0 \text{ kJ}\cdot\text{mol}^{-1}$$

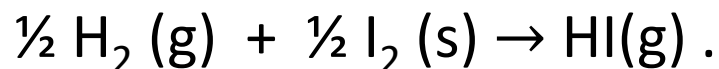
# Standard Gibbs Free Energy of Formation

The Standard Gibbs free energy of formation,  $\Delta G_f$ , of a substance is the standard Gibbs free energy of reaction per mole for the formation of a compound from its elements in their most stable form.

The standard Gibbs free energy of formation of hydrogen iodide gas at 25°C is the standard Gibbs free energy of reaction for:



**Example** Calculate the standard Gibbs free energy of formation of HI(g) at 25°C from its standard molar entropy and standard enthalpy of formation.



We can use  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  , where  $\Delta G^\circ = \Delta G_f^\circ$

From table,  $\Delta H_f^\circ (\text{HI}, \text{g}) = +26.48 \text{ kJ}$

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

$$\begin{aligned} & \Delta S_m^\circ (\text{HI}, \text{g}) - \left\{ \frac{1}{2} \Delta S_m^\circ (\text{H}_2, \text{g}) + \frac{1}{2} \Delta S_m^\circ (\text{I}_2, \text{s}) \right\} \\ &= 203.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - \{130.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} + 116.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\} \\ &= +0.0832 \text{ kJ}\cdot\text{K}^{-1} \end{aligned}$$

$$\Delta G^\circ = +26.48 \text{ kJ} - 298 \text{ K} \times 0.0832 \text{ kJ}\cdot\text{K}^{-1} = +1.69 \text{ kJ}$$



# Standard Gibbs Free Energy for Formation

Gases	$\Delta G_f^\circ$	Liquids	$\Delta G_f^\circ$	Solids	$\Delta G_f^\circ$
ammonia, $\text{NH}_3$	-16.45	benzene, $\text{C}_6\text{H}_6$	+124.3	Calcium	-1128.8
carbon dioxide, $\text{CO}_2$	-394.4	ethanol, $\text{C}_2\text{H}_5\text{OH}$	-174.8	carbonate, $\text{CaCO}_3^\dagger$	
nitrogen dioxide, $\text{NO}_2$	+51.3	water, $\text{H}_2\text{O}$	-237.1	silver chloride, $\text{AgCl}$	-109.8
water, $\text{H}_2\text{O}$	-228.6				

\*Additional values are given in Appendix 2A.

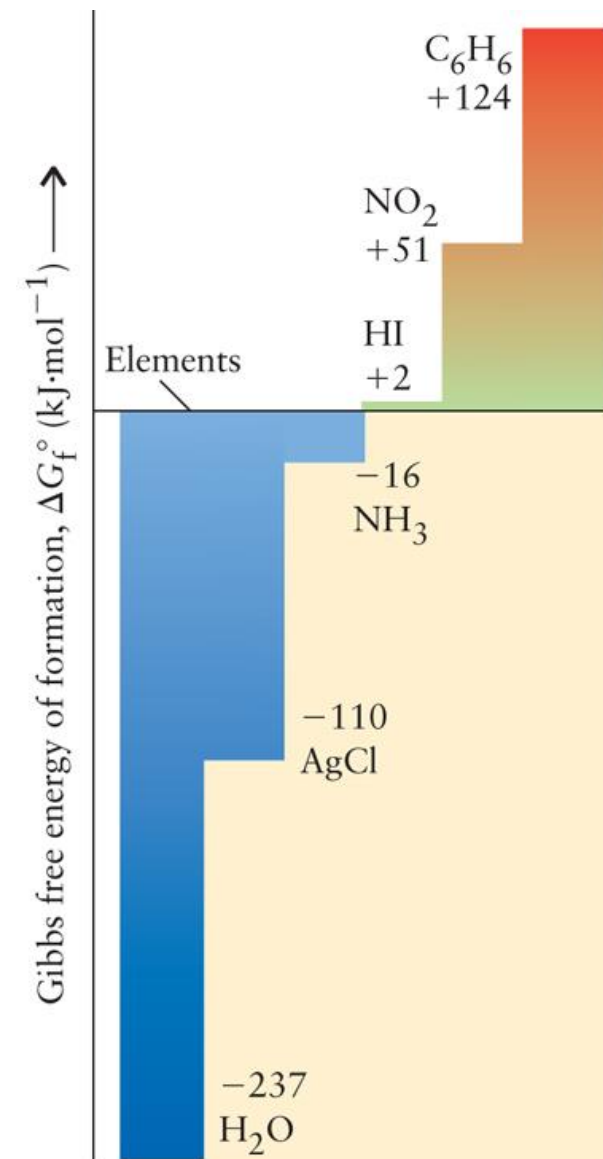
$^\dagger$ Calcite.

**Gibbs Free Energy of Reaction,  $\Delta G$ , can be calculated from the Standard Molar Gibbs Free Energy of Formation**

$$\Delta G = \sum n_P \Delta G_f^\circ (P) - \sum n_R \Delta G_f^\circ (R)$$

$n_P$ ,  $n_R$  are the stoichiometric coefficients

# Compounds verses Elements



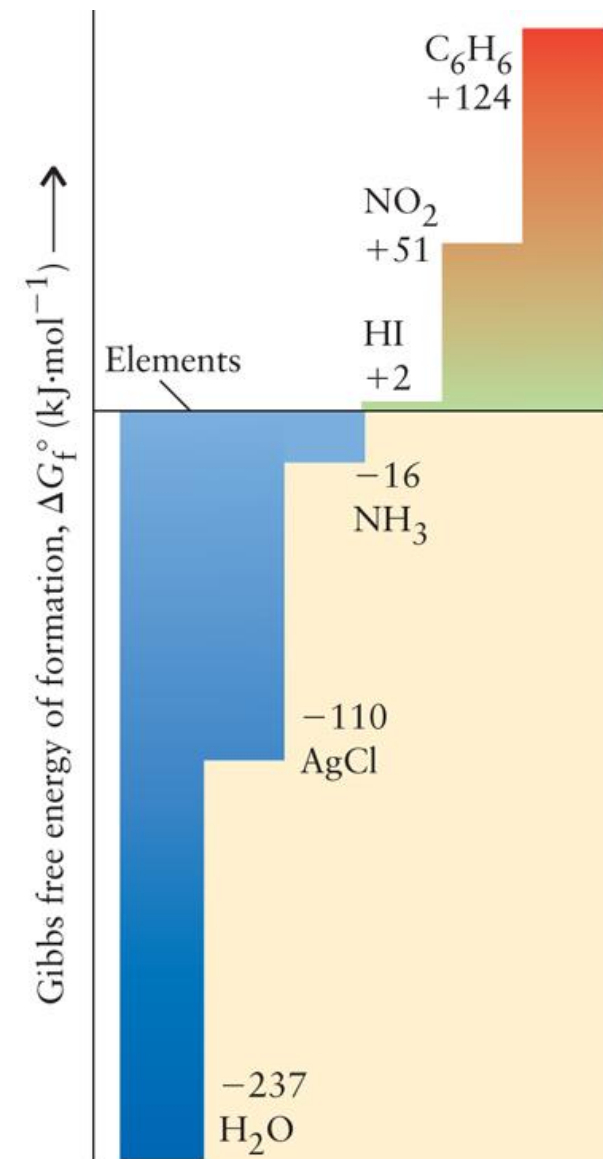
Standard Gibbs free energy of formation is an indication of a compound's stability.

If  $\Delta G_f^\circ < 0$ , the compound is more stable than the elements.

If  $\Delta G_f^\circ > 0$ , the elements in most common states are more stable

For example, the  $\Delta G_f^\circ$  of benzene is +124 kJ·mol<sup>-1</sup> at 25°C, so benzene is unstable and is **poised to decompose spontaneously** into its pure element states.

# Labile verses inert



The tendency may not be realized in practice, because the decomposition may be very slow. *Benzene can, in fact, be kept indefinitely without decomposing at all.*

Substances that are thermodynamically unstable but survive for long periods are called **inert**. So benzene is thermodynamically unstable but inert.

Substances that decompose or react rapidly are called **labile**.

Why the Gibbs free energy is called *free energy*.

Gibbs free energy is the **energy free to do non-expansion work** at constant pressure and temperature.

# The Gibbs Free Energy and Nonexpansion Work

$$G = H - TS$$

$$\Delta G = \Delta U + P\Delta V - T\Delta S$$

$$= q + w + P\Delta V - T\Delta S$$

$$= q - P\Delta V + w' + P\Delta V - T\Delta S$$

$$= q - T\Delta S + w'$$

$$\Delta G + T\Delta S - q = w'$$

reversible process

$$T\Delta S - q = 0, \Delta G = w'$$

generally :

$$T\Delta S - q \geq 0, \Delta G \leq w'$$

The decrease of Gibbs free energy (negative) is the maximum nonexpansion work (negative) the system can produce. Irreversible system has energy lost.

# The Gibbs Free Energy and Nonexpansion Work

How much nonexpansion work is done in our body in the oxidation of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s, glucose}) + 6 \text{O}_2(\text{g}) \rightarrow 6 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l})$  to make peptide chains.

We calculated Gibbs free energy of reaction is -2879 kJ per mol or 180.0 g of glucose.

It takes 17 kJ of work to build 1 mol of peptide links (a link between amino acids) in a protein.

So 1 mole of glucose or of 180. g of glucose can build about  $(2879 \text{ kJ}) / (17 \text{ kJ}) = 170$  moles of peptide links.

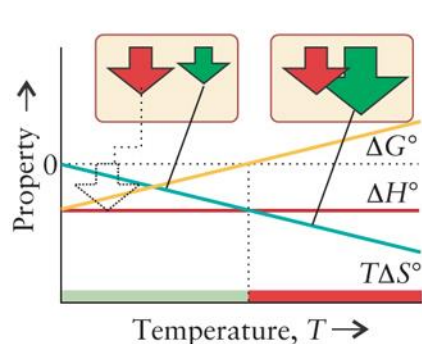
A typical protein has several hundred peptide links, and so several glucose molecules must be sacrificed to build one protein molecule.

# The temperature effect on free energy change

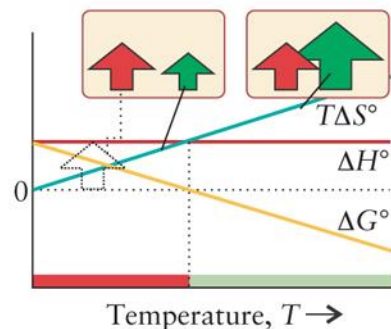
Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature, then  $\Delta G^\circ$  depend on temperature by  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ .

There are four circumstances to be considered:

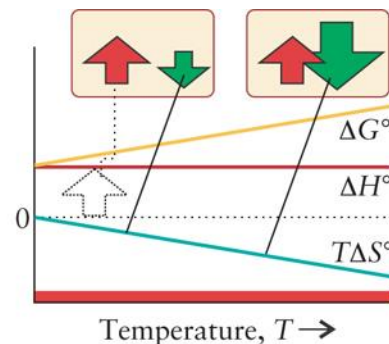
- $\Delta H^\circ < 0$ ,  $\Delta S^\circ < 0$ , low-T spontaneous
- $\Delta H^\circ > 0$ ,  $\Delta S^\circ > 0$ , high-T spontaneous
- $\Delta H^\circ > 0$ ,  $\Delta S^\circ < 0$ , never spontaneous
- $\Delta H^\circ < 0$ ,  $\Delta S^\circ > 0$ , always spontaneous



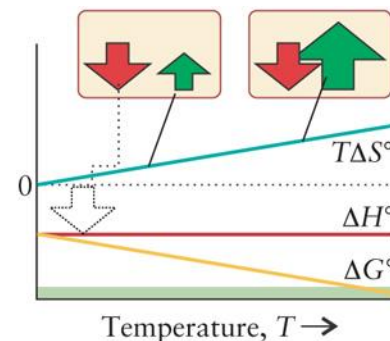
(a)  $\Delta H^\circ < 0$   $\Delta S^\circ < 0$



(b)  $\Delta H^\circ > 0$   $\Delta S^\circ > 0$

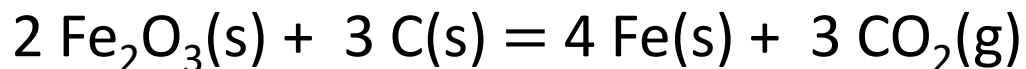


(c)  $\Delta H^\circ > 0$   $\Delta S^\circ < 0$



(d)  $\Delta H^\circ < 0$   $\Delta S^\circ > 0$

Estimate the temperature at which it is thermodynamically possible for carbon to reduce iron(III) oxide to iron under standard conditions by the endothermic reaction



Find thermodynamic data on table

$S_{\text{m}}^{\circ} \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$ :	87.4	5.7	27.3	213.7
$\Delta H_{\text{f}}^{\circ} \text{ kJ}\cdot\text{mol}^{-1}$ :	-824.2	0	0	-393.5

It is likely an endothermic  $\Delta H^{\circ} > 0$ , and entropy increase  $\Delta S^{\circ} > 0$  reaction. If the T is high enough,  $\Delta G^{\circ}$  will be negative so that the reaction will be spontaneous.

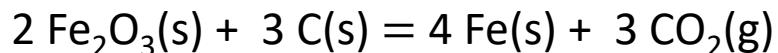
We need to find out at what temperature

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = 0,$$

Since,  $\Delta H^{\circ} = T\Delta S^{\circ}$ ,

$$\text{then } T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}}$$





$S_m^\circ \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$ :	87.4	5.7	27.3	213.7
$\Delta H_f^\circ \text{ kJ}\cdot\text{mol}^{-1}$ :	-824.2	0.0	0.0	-393.5

$$\begin{aligned}\Delta S^\circ &= [(4 \times 27.3 + 3 \times 213.7) - (2 \times 87.4 + 3 \times 5.7)] \times 10^{-3} \\ &= 0.5584 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta H^\circ &= (4 \times 0 + 3 \times -393.5) - (2 \times -824.2 + 3 \times 0) \\ &= 467.9 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{+467.9 \text{ kJ}}{+0.5584 \text{ kJ}\cdot\text{K}^{-1}} = 838\text{K},$$

Temperature above 838K, the reaction is spontaneous

# Thanks!



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