



**CHEM2100J**  
**Chemistry**  
**Autumn 2024**

**Chapter 08**  
**The Second and Third Laws**  
**of Thermodynamics**

**Dr. Milias Liu**

*Assistant Teaching Professor*

UM-SJTU Joint Institute

Room 407A, Longbin Building

[milias.liu@sjtu.edu.cn](mailto:milias.liu@sjtu.edu.cn)

The **first** law of thermodynamics deals with work and heat.

The second law of thermodynamics is the tendency for chemical reactions to occur as envisioned by **Boltzmann** in a measure of disorder called **entropy**.

The third law of thermodynamics describes what happens to entropy as the temperature approaches 0 K.

# Some Things Happen Naturally, Others Don't.



Decay is natural; construction requires work.

**Water flows** downhill naturally; we have to pump it uphill.

**Hot food cools down** naturally; we have to put in energy to heat it.

**Buildings decay** is unmaintained; we have to work to build them.

What drives a reaction toward products or biological systems forward in the phenomenon we call life?

**Entropy** provides an elegant and quantitative answer to both physical and chemical changes.

First law of thermodynamics:  
The internal energy of an **isolated system** is **constant**.

The first law of thermodynamics: **if** a reaction takes place, the total **energy of the universe** remains unchanged.

But the first law does not address the questions that *lies behind* the “**if**”.

- Why do some reactions have a *tendency* to occur?
- Why does a reaction even happen?

# 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.

The reverse process does not occur.

What is the tendency?

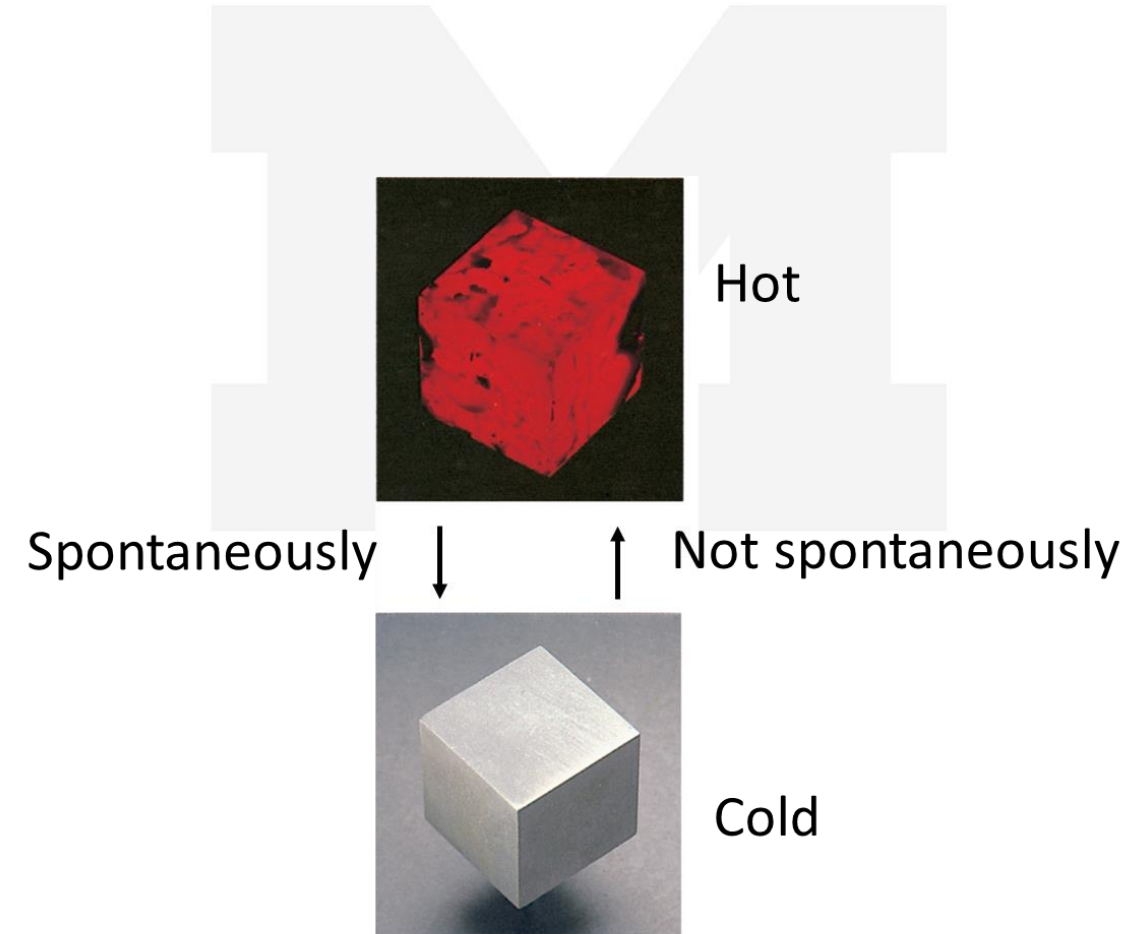


Figure 4E.1  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman photos by Ken Karp.

# Spontaneous Change

A spontaneous change occurs naturally without external influences.

A gas expands spontaneously into the lower evacuated flask.

The reverse process does not occur.

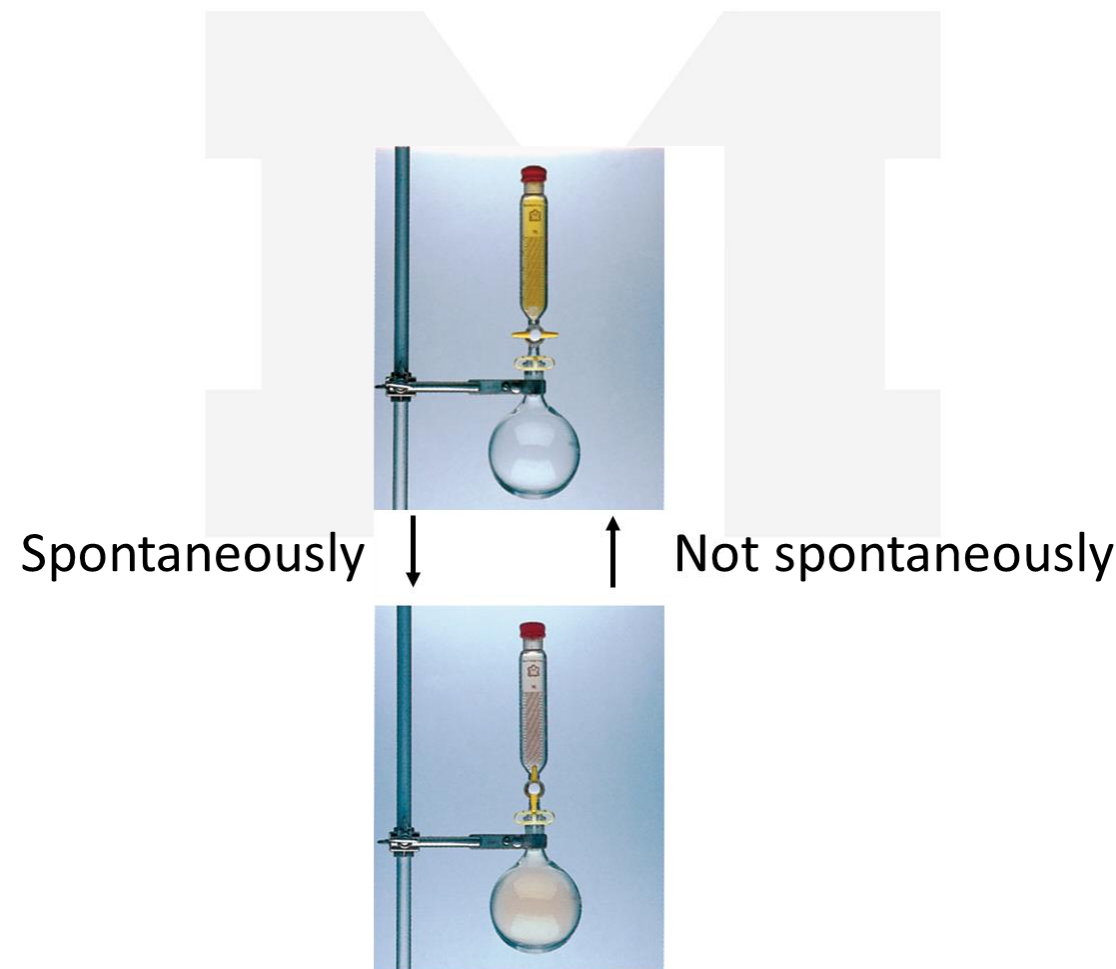


Figure 4F.2  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman photos by Ken Karp.

# Spontaneous Change: Tendency



A mixture of hydrogen and oxygen has a tendency to react spontaneously but can be kept safely for **centuries**, provided it is not ignited with a spark.

This is different from the rates of a reaction discussed later.

# Nonspontaneous Change



Changes can be *made to happen* in an "**unnatural**" direction.

**We can force** an electric current through a block of metal to heat it to a higher temperature.

**We can drive** a gas into a smaller volume by pushing it with a piston.

These are examples of a *nonspontaneous change*: we have to force them to happen; a nonspontaneous change is done with **work**.



# The Second Law of Thermodynamics



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**.

# Entropy and Disorder: Defined



Lower Entropy



Higher Entropy

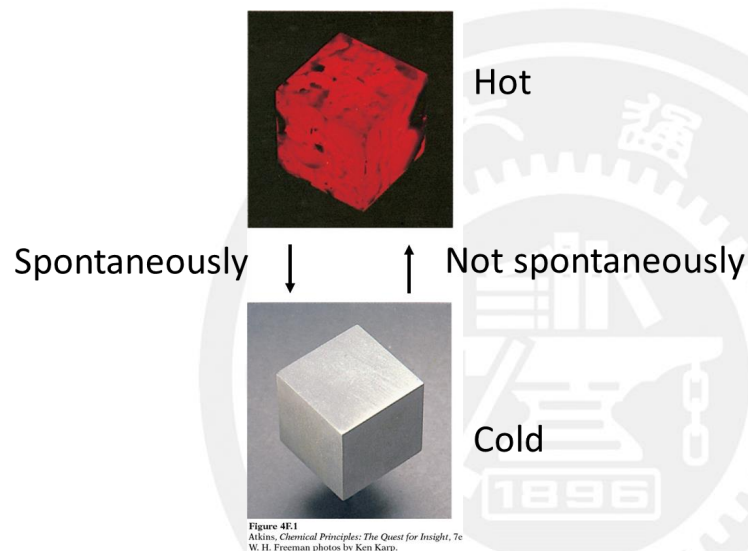
„Aufräumen ist  
thermodynamischer Unsinn.“

– W. Schattow (1944-2017)

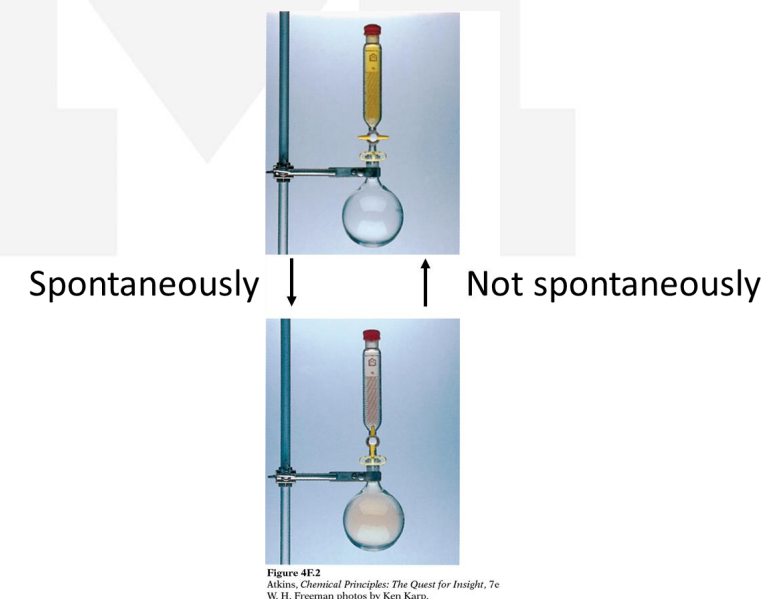
„Tidying up is thermodynamic  
nonsense.“

# Entropy and Disorder: Defined

As metal cools, **entropy increases** as **energy spreads** into the **surroundings**.



As gases expand, **entropy increases** as the **molecules spread** through the container.



**Energy and Matter  
disperse.**

# Entropy and Disorder: Quantitative



The **natural progression** of a system and its surroundings is **from order to disorder**, **from lower to higher entropy**.

To quantify entropy, we take a thermally insulated, sealed calorimeter, to measure and make precise predictions about disorder.

An entropy change in a system is calculated as:

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

$Q$  is energy transferred, “rev” means energy must be transferred reversibly, **infinitesimal change**,  $T$  is the absolute temperature, and the typical unit for entropy is  $\text{J}\cdot\text{K}^{-1}$ .



# Entropy and Disorder: Quantitative



$$\text{Interpreting } \Delta S = \frac{Q_{\text{rev}}}{T}$$

(a) If heat is **transferred** ( $Q_{\text{rev}} \uparrow$ ) then entropy increases,  $\Delta S \uparrow$ . This can happen from the system to the surroundings or from the surroundings into the system, as long as the system is not isolated.

(b) The lower the temperature,  $T$ , the greater the change in  $\Delta S$ .

As an analogy, talking in a quiet library will attract attention, but talking in a noisy street may pass unnoticed.



Figure 4A.8  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman photo by Ken Karp

# Entropy: A State Function



Changes in entropy of a system are independent of the path **between its initial and final states**, so for a reversible process we use  $\Delta S = \frac{Q_{rev}}{T}$ .

Other *state functions*:

(determined by knowing the difference between final and initial state)

Mass ( $m$ )

Internal energy ( $U$ )

Entropy ( $S$ )

Temperature ( $T$ )

Chemical composition

Density ( $\rho$ )

Enthalpy ( $H$ )

Gibbs free energy ( $G$ )

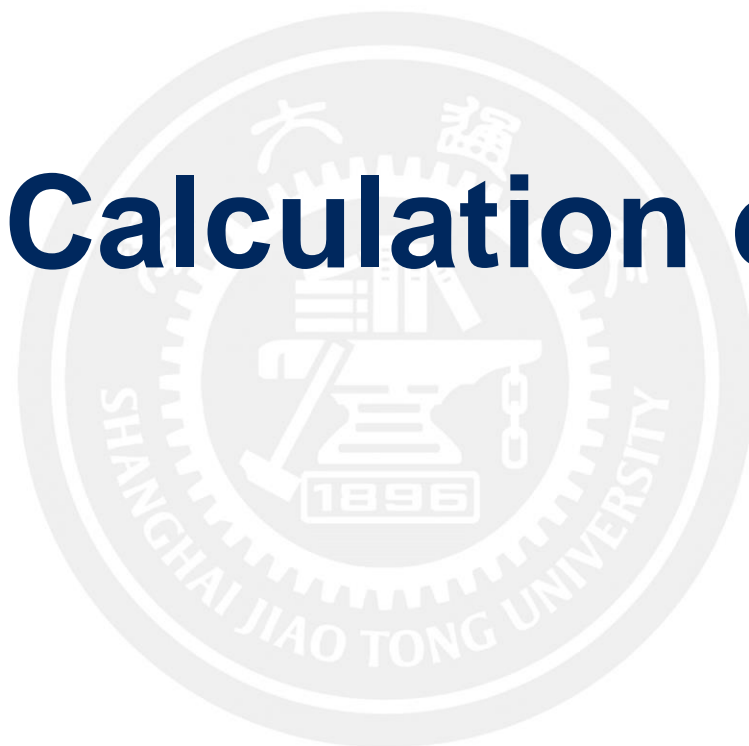
Pressure ( $p$ )

Volume ( $V$ )

Specific volume ( $v$ )

Altitude ( $h$ )

# Calculation of Change in Entropy



# Deriving a Change in Entropy



A dispersion of molecules is a form of positional disorder.

Changes can occur by either a change in **temperature**, **volume**, or **pressure**.

On the right are the expressions derived over the next few slides.

## Changes in temperature

$$\Delta S = C \cdot \ln \left( \frac{T_2}{T_1} \right)$$

$C$ : heat capacity

## Changes in volume

$$\Delta S = nR \cdot \ln \left( \frac{V_2}{V_1} \right)$$

$n$ : amount

$R$ : gas constant

## Changes in pressure

$$\Delta S = nR \cdot \ln \left( \frac{p_1}{p_2} \right)$$

Note  $p_1$  and  $p_2$



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

From our definition of heat capacity:

$$C = \frac{Q}{\Delta T}$$

Energy added as heat reversibly, so that the temperature changes infinitesimally:

$$Q_{rev} = C \cdot dT$$

(reversible or an infinitesimal change, so either at constant volume  $C_V$  or constant pressure  $C_P$ )

# Changes in Temperature



Substituting  $Q_{rev} = C \cdot dT$  into  $\Delta S = \frac{Q_{rev}}{T}$  yields:

$$dS = \frac{C \cdot dT}{T}$$

The change in entropy between temperatures  $T_1$  to  $T_2$  is the sum of all entropy changes, so we integrate:

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

Assuming that  $C$  is temperature-independent:

$$\Delta S = C \cdot \ln\left(\frac{T_2}{T_1}\right)$$

- If  $\frac{T_2}{T_1} > 1$ , the logarithm is positive, so  $\Delta S$  is positive.
- The greater the heat capacity, the greater  $\Delta S$ .

# Changes in Volume



For the change in entropy of an ideal gas for changes in volume during an isothermal (temperature remains constant) expansion (reversible) at constant  $T$ , we use  $\Delta S = \frac{Q_{rev}}{T}$ .

# Changes in Volume



For a reversible expansion of an ideal gas,  $Q_{rev} = -W_{rev}$ , therefore:

$$Q_{rev} = -W_{rev} = -nRT \cdot \ln \frac{V_2}{V_1}$$

$$\Delta S = \frac{Q_{rev}}{T} = \frac{-W_{rev}}{T} = \frac{nRT \cdot \ln \left( \frac{V_2}{V_1} \right)}{T}$$

$$\Delta S = nR \cdot \ln \left( \frac{V_2}{V_1} \right)$$

# Changes in Pressure



$$pV = nRT = \text{const.}$$

For a constant temperature  $\frac{V_2}{V_1} = \frac{p_1}{p_2}$  where  $p_1$  is the initial pressure and  $p_2$  is the final pressure.

Applying  $\frac{V_2}{V_1} = \frac{p_1}{p_2}$  to  $\Delta S = nR \cdot \ln \left( \frac{V_2}{V_1} \right)$ :

$$\Delta S = nR \cdot \ln \left( \frac{p_1}{p_2} \right)$$

# Example



In an experiment, 1.00 mol  $O_2(g)$  was compressed suddenly (and irreversibly) from 5.00 L to 1.00 L by driving in a piston (like a big bicycle pump), and in the process, its temperature increased from 20.0 °C to 25.2 °C. What is the change in entropy of the gas?  $\left(C_{V,m,O_2} = 20.79 \frac{J}{mol \cdot K}\right)$

This problem is solved in 2 steps:

Step 1: find the effect from the change in volume

Step 2: find the effect from the change in temperature

Combine both steps.

# Example



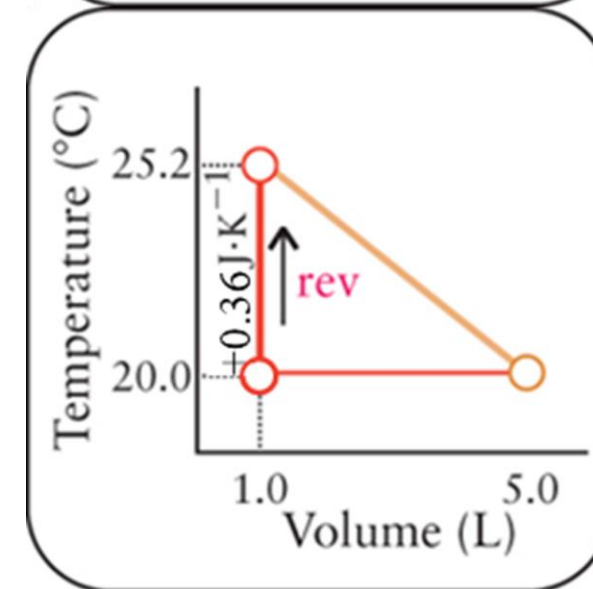
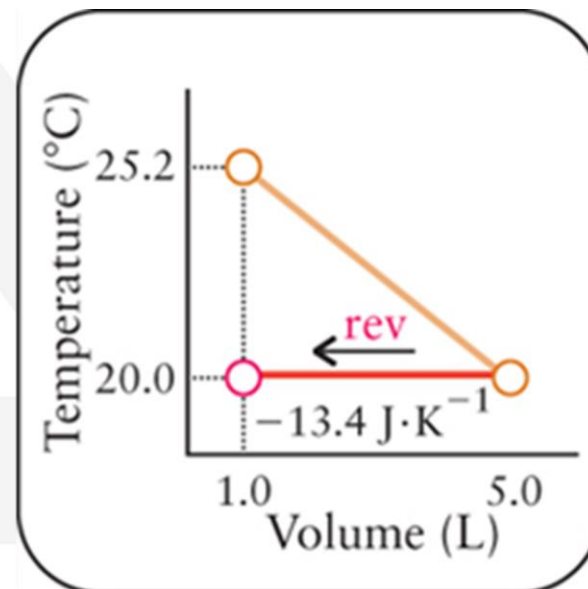
In an experiment, 1.00 mol  $\text{O}_2(g)$  was compressed suddenly (and irreversibly) from 5.00 L to 1.00 L by driving in a piston (like a big bicycle pump), and in the process, its temperature increased from 20.0 °C to 25.2 °C. What is the change in entropy of the gas? ( $C_{V,m,\text{O}_2} = 20.79 \frac{\text{J}}{\text{mol}\cdot\text{K}}$ )

Step 1: find the effect from the change in volume:

$$\Delta S = nR \cdot \ln\left(\frac{V_2}{V_1}\right) = 1.00 \text{ mol} \times 8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \times \ln\left(\frac{1.00 \text{ L}}{5.00 \text{ L}}\right) = -13.4 \frac{\text{J}}{\text{K}}$$

Step 2: find the effect from the change in temperature:

$$\Delta S = nC_{V,m} \cdot \ln\left(\frac{T_2}{T_1}\right) = 1.00 \text{ mol} \times 20.79 \frac{\text{J}}{\text{mol}\cdot\text{K}} \times \ln\left(\frac{298.4 \text{ K}}{293.2 \text{ K}}\right) = +0.36 \frac{\text{J}}{\text{K}}$$



# Example

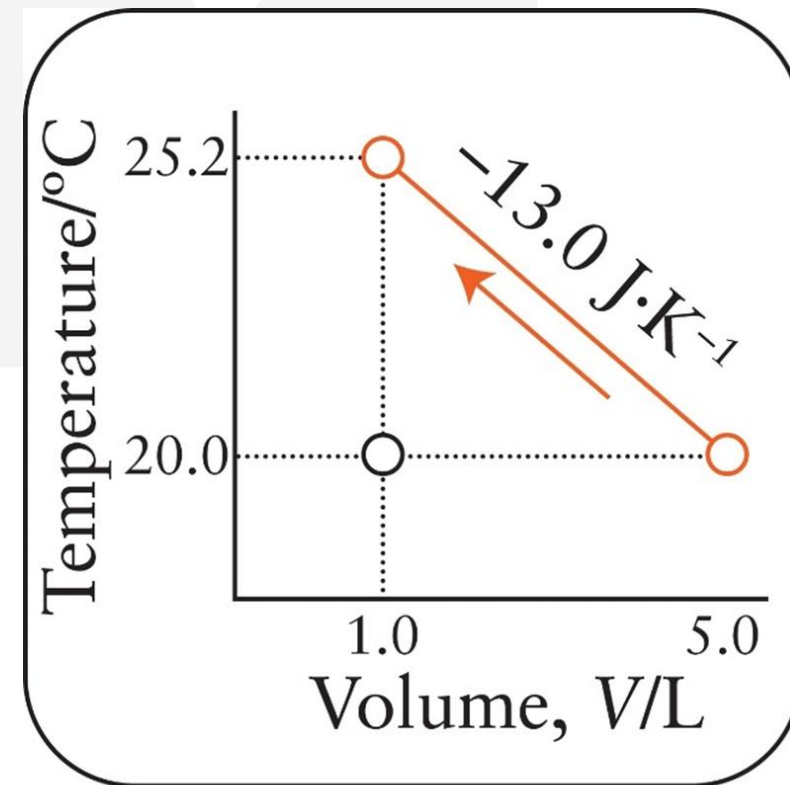


In an experiment, 1.00 mol  $\text{O}_2(g)$  was compressed suddenly (and irreversibly) from 5.00 L to 1.00 L by driving in a piston (like a big bicycle pump), and in the process, its temperature increased from 20.0 °C to 25.2 °C. What is the change in entropy of the gas? ( $C_{V,m,\text{O}_2} = 20.79 \frac{\text{J}}{\text{mol}\cdot\text{K}}$ )

Combine both steps.

$$\Delta S = -13.4 \frac{\text{J}}{\text{K}} + 0.36 \frac{\text{J}}{\text{K}} = -13.0 \frac{\text{J}}{\text{K}}$$

The 5-fold effect of compression is greater than a small rise in temperature.



Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman



# Example



Calculate the change in entropy when the pressure of 23.5 g of oxygen gas is increased from 2.00 kPa to 8.00 kPa while the temperature increases from 240 K to 360 K. Assume ideal behavior.

$$\left( C_{p,m,O_2} = 29.099 \frac{\text{J}}{\text{mol} \cdot \text{K}}, M_{O_2} = 32.00 \frac{\text{g}}{\text{mol}} \right)$$

Step 1: find the effect from change in pressure:

$$\Delta S = nR \cdot \ln \left( \frac{p_1}{p_2} \right) = \frac{23.5 \text{ g}}{32.00 \frac{\text{g}}{\text{mol}}} \times 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times \ln \left( \frac{2.00 \text{ kPa}}{8.00 \text{ kPa}} \right) = -8.46 \frac{\text{J}}{\text{K}}$$

# Example



Calculate the change in entropy when the pressure of 23.5 g of oxygen gas is increased from 2.00 kPa to 8.00 kPa while the temperature increases from 240 K to 360 K. Assume ideal behavior.

$$\left( C_{p,m,O_2} = 29.099 \frac{\text{J}}{\text{mol} \cdot \text{K}}, M_{O_2} = 32.00 \frac{\text{g}}{\text{mol}} \right)$$

Step 2: find the effect from the change in temperature:

$$\Delta S = n C_{p,m} \cdot \ln \left( \frac{T_2}{T_1} \right) = \frac{23.5 \text{ g}}{32.00 \frac{\text{g}}{\text{mol}}} \times 29.099 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times \ln \left( \frac{360 \text{ K}}{240 \text{ K}} \right) = +8.61 \frac{\text{J}}{\text{K}}$$

Combine both steps.

$$\Delta S = -8.46 \frac{\text{J}}{\text{K}} + 8.61 \frac{\text{J}}{\text{K}} = \mathbf{0.15 \frac{J}{K}}$$

# Entropy Changes and Phase Changes



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

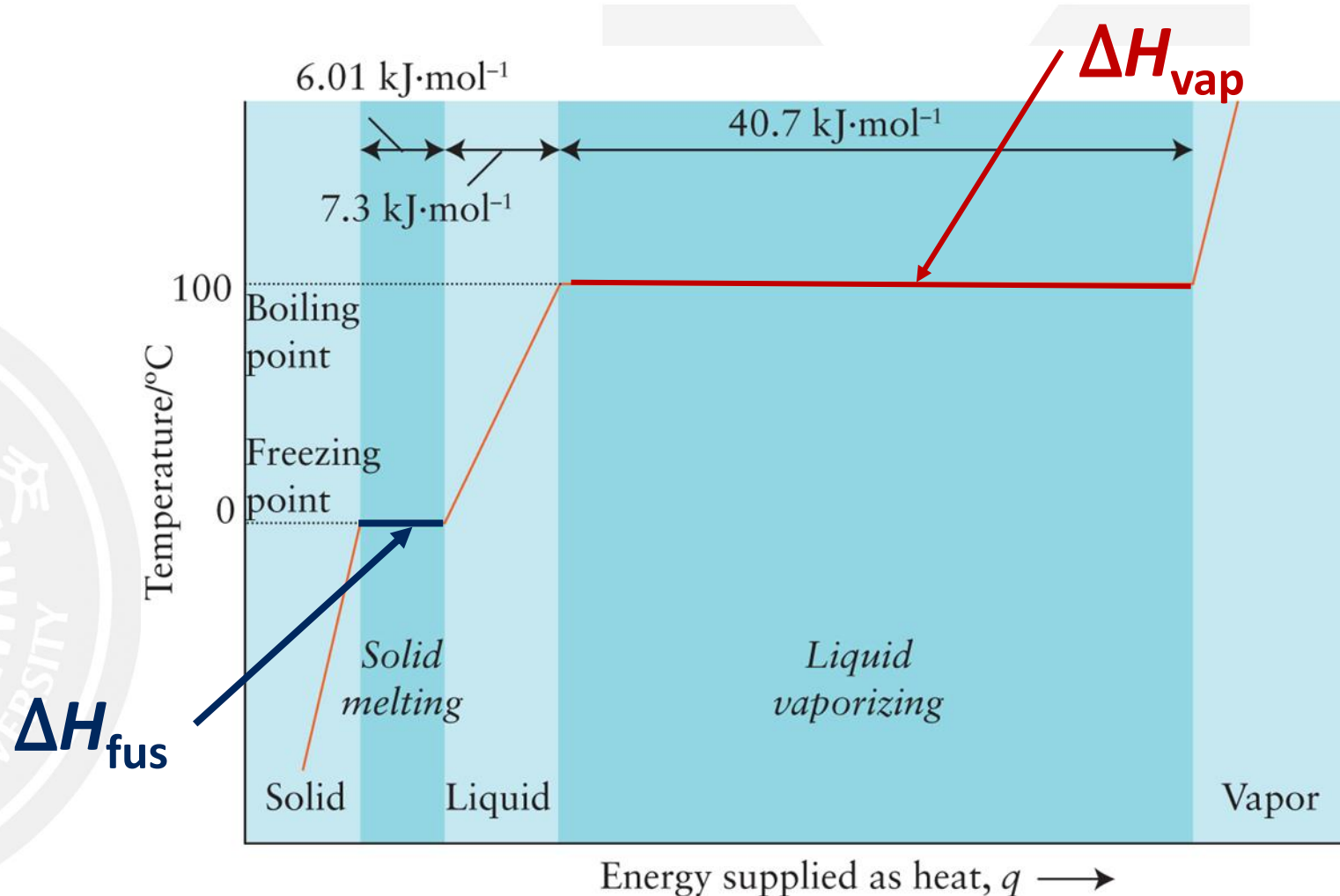


Figure 4C.9

Atkins, *Chemical Principles: The Quest for Insight*, 7e

W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

# Entropy Changes and Phase Changes



Phase changes occur at constant temperature.

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

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

This means for  $\Delta S^\circ$ :

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

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

Under standard conditions!

# A Molecular Interpretation of Entropy



We've only calculated **changes** in entropy  $\Delta S = \frac{Q_{rev}}{T}$ .

What exactly is entropy measuring the disorder of?

**Here we imagine entropy from an atomic view** as a perfectly ordered state of matter with neither positional nor thermal disorder.

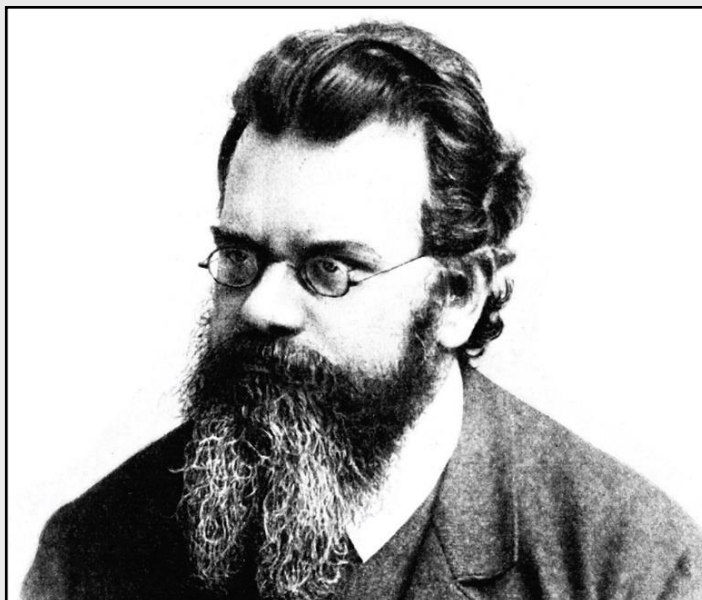
This is a state where entropy is zero, a state of perfect order.

This is the absolute scale of entropy, just as Kelvin is the absolute scale of temperature. *This is the third law of thermodynamics.*

*The entropies of all perfect crystals approach zero as the absolute temperature approaches zero.*

In a **perfect crystal**  $S \rightarrow 0$  as  $T \rightarrow 0$ , implying a perfectly ordered array, and so no positional or thermal disorder.

We expect the entropy of any substance to be greater than zero for  $T > 0$ .



Ludwig  
Boltzmann

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

The Boltzmann formula, as seen on his epitaph is:

$$S = k_B \cdot \ln(W)$$

An **absolute scale of entropy** at any temperature.

$$k_B = 1.381 \times 10^{-23} \frac{\text{J}}{\text{K}}$$

**$W$**  is the number of positions atoms or molecules can arrange into and are called **microstates**.



A microstate lasts only for an instant; so, when we measure bulk properties, we are measuring an average taken over many microstates. That's why the Boltzmann formula is called **statistical entropy**,  $S = k_B \cdot \ln(W)$ .

We imagine a box, called a microstate, where molecules are distributed. Every time we change the position of a molecule it represents a different microstate. Each microstate has the same total energy. This collection is called an ensemble.

If there is only one microstate, then all molecules are in exactly the same energy level,  $W = 1$ , and the total system has zero entropy ( $\ln(1) = 0$ ) and zero disorder.



# Example

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 in which all molecules are aligned with their C atoms on the left (top-left image) and (b) the four molecules lie in random orientations (but parallel) (bottom-right image).

If all four molecules are pointing in one direction (as in the top left or bottom right image), the entropy of the solid is zero.

The entropy is greater than zero when the molecules become disordered and adopt different orientations.

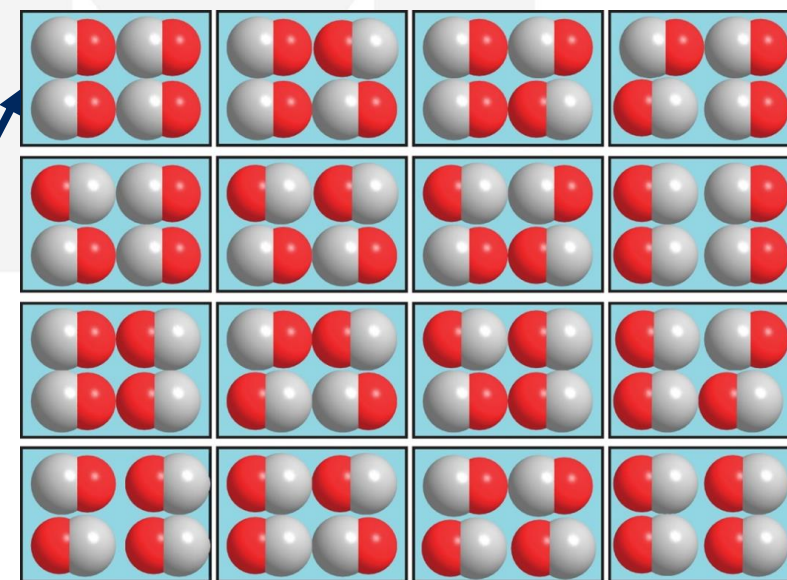
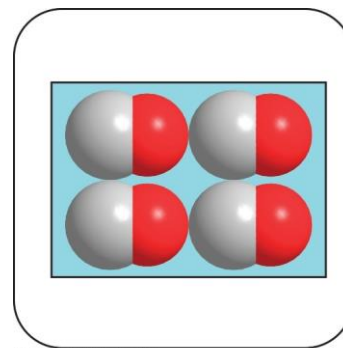


FIGURE 4G.2  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

# Example

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 in which all molecules are aligned with their C atoms on the left (top-left image) and (b) the four molecules lie in random orientations (but parallel).

- a) Here all motion ceases, there is no disorder, the molecules form a perfect crystal and  $W = 1$ . ( $W$  = number of microstates).



Atkins, Chemical Principles: The Quest for Insight, 7e  
W. H. Freeman & Company, © 2014 by P. W. Atkins, L. L. Jones, and L. E. Laverman

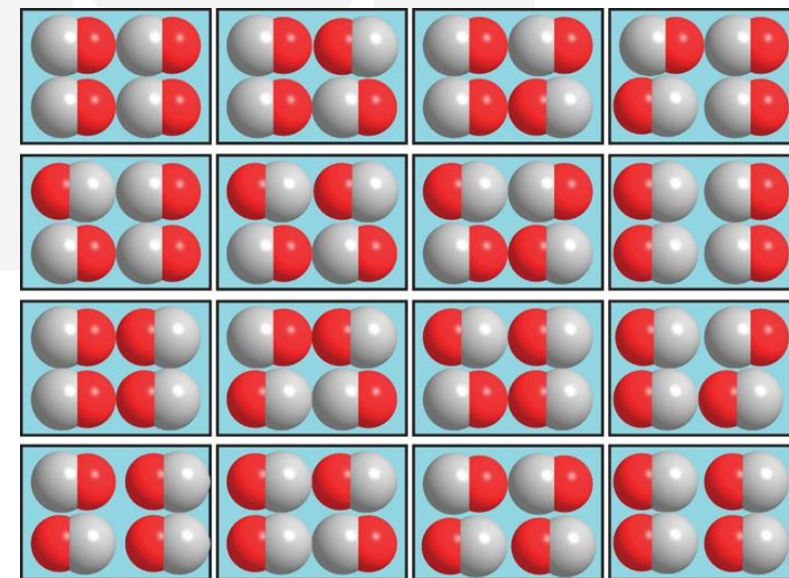


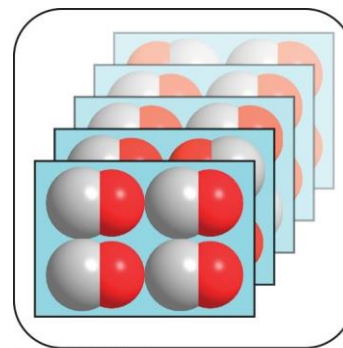
FIGURE 4G.2  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

$$S = k_B \cdot \ln(W) = 1.381 \times 10^{-23} \frac{\text{J}}{\text{K}} \times \ln(1) = 0$$

# Example

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 in which all molecules are aligned with their C atoms on the left (top-left image) and (b) the four molecules lie in random orientations (but parallel).

- b) Because each molecule has 2 different orientations and there are 4 sets of molecules  
 $W = 2 \times 2 \times 2 \times 2 = 2^4 = 16$



Atkins, Chemical Principles: The Quest for Insight, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

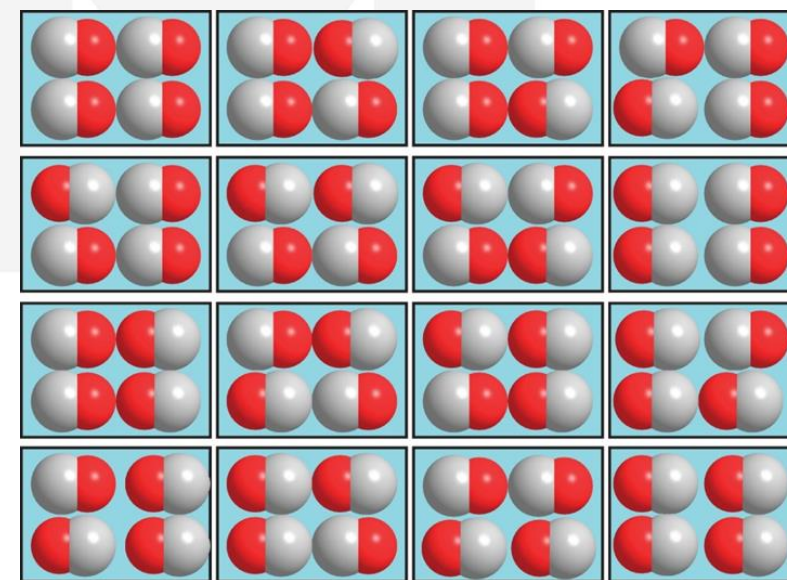


FIGURE 4G.2  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

$$S = k_B \cdot \ln(W) = 1.381 \times 10^{-23} \frac{\text{J}}{\text{K}} \times \ln(16) = 3.828 \times 10^{-23} \frac{\text{J}}{\text{K}}$$

Bulk samples:

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

Boltzmann's formula for statistical behaviour:

$$S = k_B \cdot \ln(W)$$

These are two different expressions for entropy—but are they the same?



# Qualitative Equivalency



Bulk samples:

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

Boltzmann's formula for statistical behaviour:

$$S = k_B \cdot \ln(W)$$

These are identical!

1. Both are state functions:  
 $W$  depends only on the current state of the system (not the past).
2. Both are extensive properties(they depend on the number of atoms, i.e., volume and mass):  
doubling the number of molecules increases the number of microstates from  $W$  to  $W^2$ , or  $k_B \cdot \ln(W)$  to  $k_B \cdot \ln(W^2) = 2 k_B \cdot \ln(W)$ .

# Qualitative Equivalency



Bulk samples:

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

Boltzmann's formula for statistical behaviour:

$$S = k_B \cdot \ln(W)$$

These are identical!

3. Both increase in a spontaneous change: the overall disorder of the system and its surroundings increases, which means that the number of microstates increases.
4. Both increase with temperature: when the temperature of the system increases, more microstates become accessible, and so the statistical entropy increases.

# Standard Molar Entropies



Boltzmann's formula is sometimes very difficult to implement (figuring out the different microstates) and requires a lot of manipulation.

It's easier to combine our idea of the third law of thermodynamics where  $S = 0$  at 0 K and then compare  $S$  at a higher temperature using heat capacities.

# Standard Molar Entropies

- a) The heat capacity determined from close to absolute zero.
- b) The area under the plot of  $\frac{C_p}{T}$  against  $T$  is determined up to the temperature of interest.
- c) This area is the entropy of the substance at that temperature.

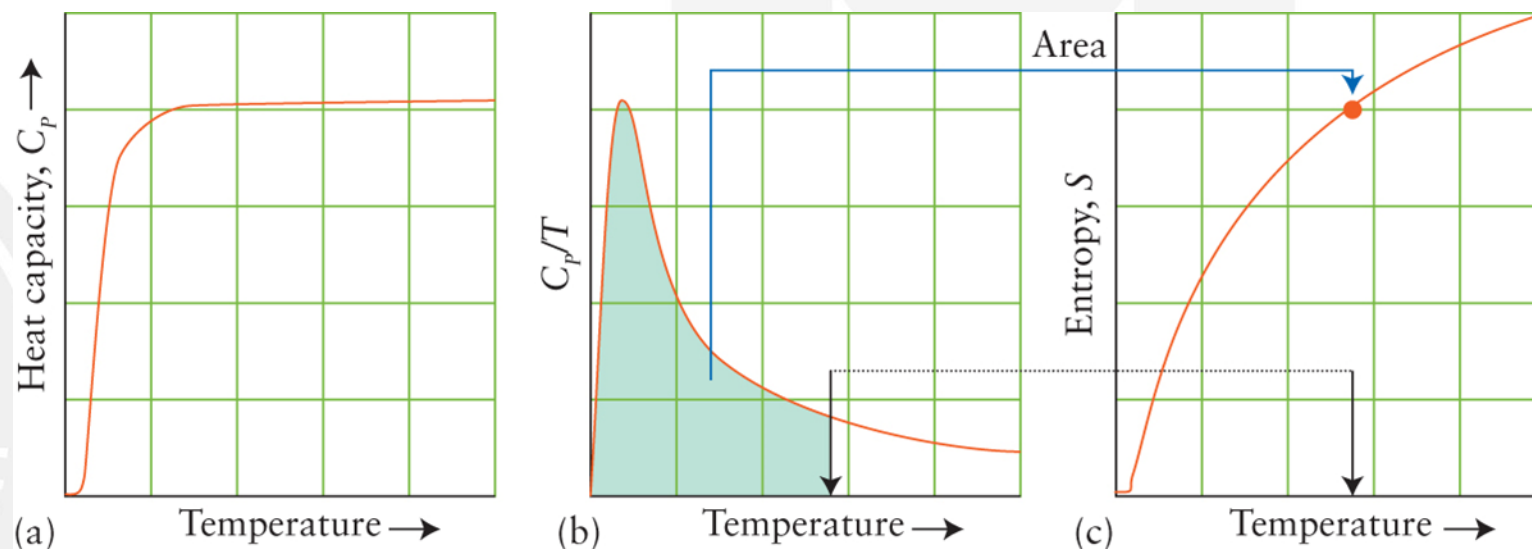


Figure 4H.1

Atkins, *Chemical Principles: The Quest for Insight*, 7e

W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman



# Standard Molar Entropies

$$S^{\circ} = \int_{T_1}^{T_2} \frac{C_{p,m} \cdot dT}{T}$$

Choosing  $T_1 = 0 \text{ K}$  and  $T_2 = 298.15 \text{ K}$  yields the **Standard Molar Entropy**  $S_m^{\circ}$ , making it easy to tabulate them and use them for calculations.

$S_m^{\circ}$  is found in Table 4H.1 or Appendix 2A in the textbook.

For phase changes, where  $\Delta T = 0$ , we use:

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

for either fusion or vaporization

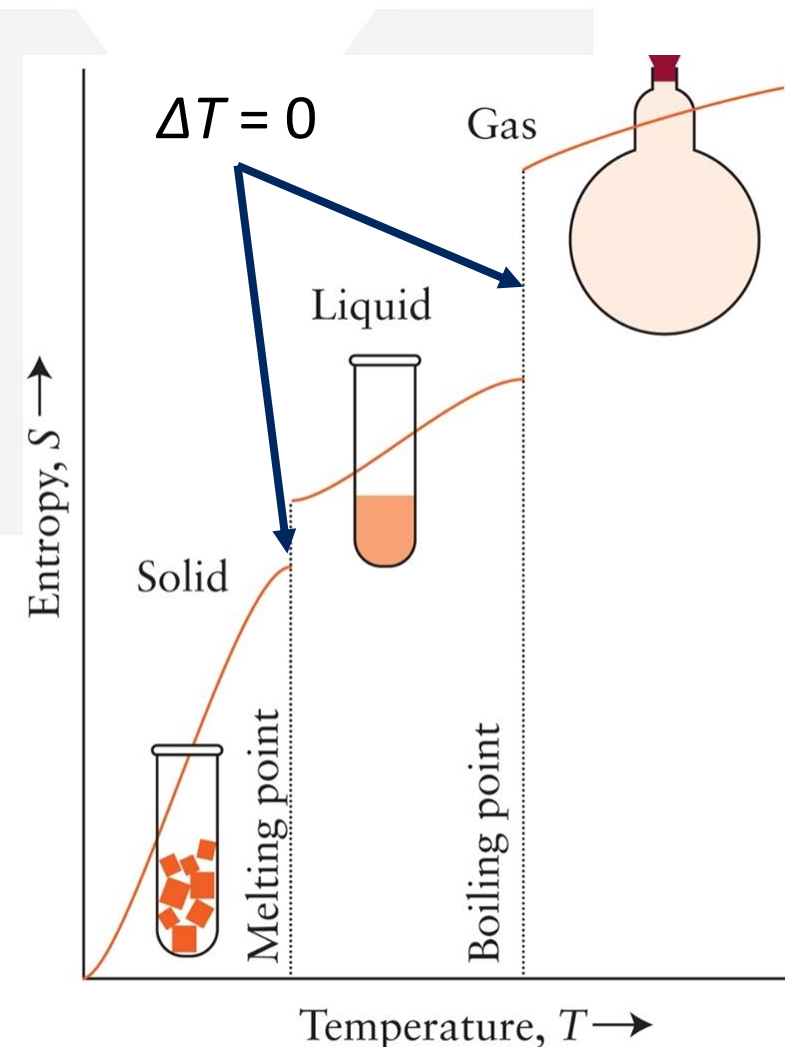


Figure 4H.2  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

# Standard Molar Entropies



**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.



Substance	$S_m^\circ / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	Substance	$S_m^\circ / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
<b>Gases</b>		<b>Solids</b>	
Ammonia, $\text{NH}_3$	192.4	Calcium oxide, $\text{CaO}$	39.8
Carbon dioxide, $\text{CO}_2$	213.7	Calcium carbonate, $\text{CaCO}_3$	92.9
Hydrogen, $\text{H}_2$	130.7	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
<b>Liquids</b>			
Benzene, $\text{C}_6\text{H}_6$	173.3	<b>More complex</b>	
Ethanol, $\text{C}_2\text{H}_5\text{OH}$	160.7		
Water, $\text{H}_2\text{O}$	69.9		

# Standard Molar Entropies



**Diamond's** low entropy is due to its **rigid** bonds: the atoms do not jiggle around as much as the atoms of lead.

**Lead** atoms are **heavier** than carbon atoms, and heavier atoms (more protons, neutrons and electrons) have more vibrational energy levels available than lighter ones.

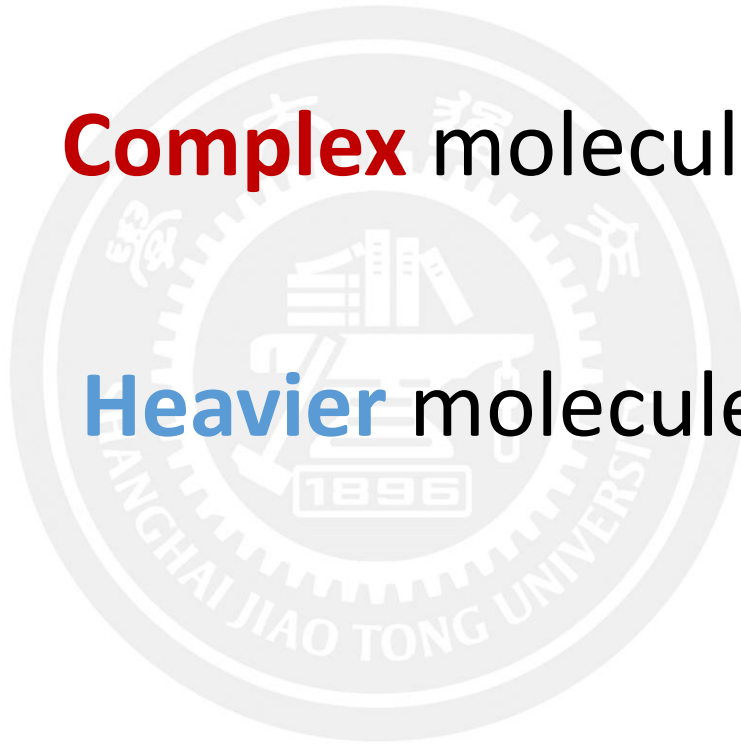
Substance	$S_m^\circ / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	Substance	$S_m^\circ / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
<b>Gases</b>		<b>Solids</b>	
Ammonia, $\text{NH}_3$	192.4	Calcium oxide, $\text{CaO}$	39.8
Carbon dioxide, $\text{CO}_2$	213.7	Calcium carbonate, $\text{CaCO}_3$	92.9
Hydrogen, $\text{H}_2$	130.7	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 
<b>Liquids</b>	<b>Heavier</b>		
Benzene, $\text{C}_6\text{H}_6$	173.3		
Ethanol, $\text{C}_2\text{H}_5\text{OH}$	160.7		
Water, $\text{H}_2\text{O}$	69.9		

# Standard Molar Entropies



**Complex** molecules have greater entropy values.

**Heavier** molecules have greater entropy values.



# Standard Reaction Entropies



Is it possible to predict the sign of the entropy change of the system?

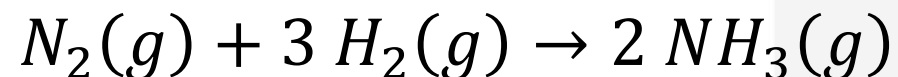
We know a gas has a greater entropy value than either solids or liquids.

A change in the amount of **gas** molecules normally dominates any other entropy change in a reaction.

# Short Quiz



Without doing any calculations, estimate the sign of the entropy change for the reaction and explain your answer.



Answer: negative, because there is a net decrease in the number of moles of gas molecules.

Without doing any calculations, estimate the sign of the entropy change for the reaction and explain your answer.



Answer: positive, an increase in entropy. Producing a gas from a solid increases the entropy of a system.

To calculate the change in entropy in a reaction, we calculate the difference between the entropies of the products and those of the reactants.

$$\Delta S_{sys} = \sum (n \cdot S_{m,products}) - \sum (n \cdot S_{m,reactants})$$

$n$ : stoichiometric coefficients, moles

$S_m$ : molar entropies



# Summary

Entropy can predict the natural direction of a reaction.

So far, we've been calculating the entropy of the **system**, without looking at the effect our *system* atoms and molecules have on the *surrounding* atoms and molecules.

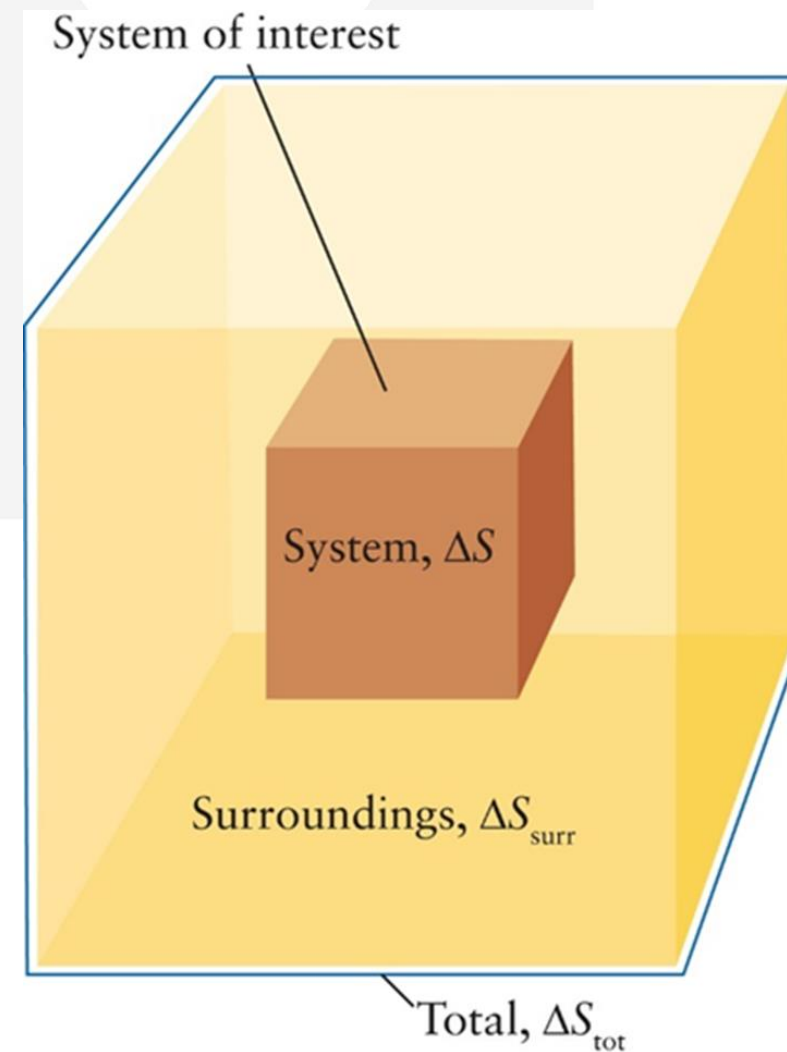


Figure 4L1

Atkins, *Chemical Principles: The Quest for Insight*, 7e

W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

# Total Entropy



Figure 4A.8  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman photo by Ken Karp

**Total entropy** combines both changes to the **system** as reactants form products *and* changes to the **surroundings** as the heat produced or absorbed by the reaction as it enters or leaves them.

The next two sections explore the contribution of the **surroundings** on entropy.

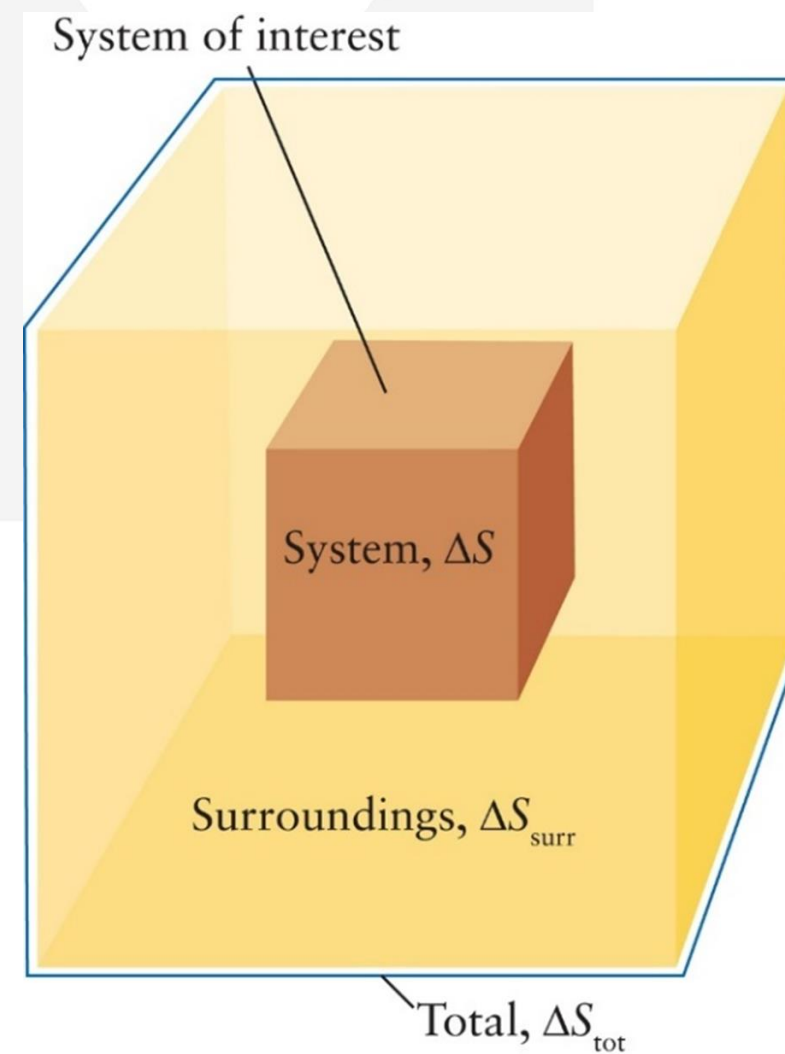


Figure 4L1  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

# Global Changes in Entropy: Total



Some processes seem to defy the second law.

Water freezes to ice naturally at low temperature

The dilemma is resolved when we realize that the second law refers to an **isolated system** that includes the **surroundings** of the **system**.

A process is spontaneous only if the total change in entropy, the **sum** of the changes in the **system** and the **surroundings**, is positive.

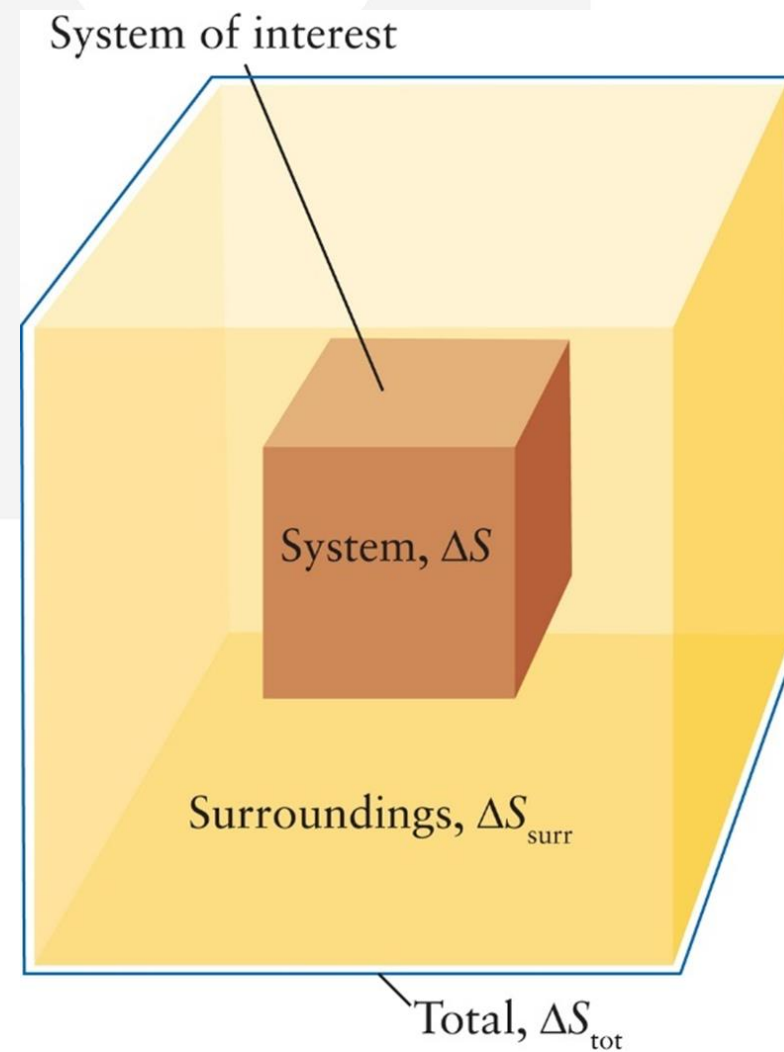


Figure 4I.1  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

# Global Changes in Entropy: Total

The 2 parts to total entropy  $\Delta S_{total}$  are the **system** and the **surroundings**.

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

Missing from our previous discussion was the effect our system had on the surroundings.

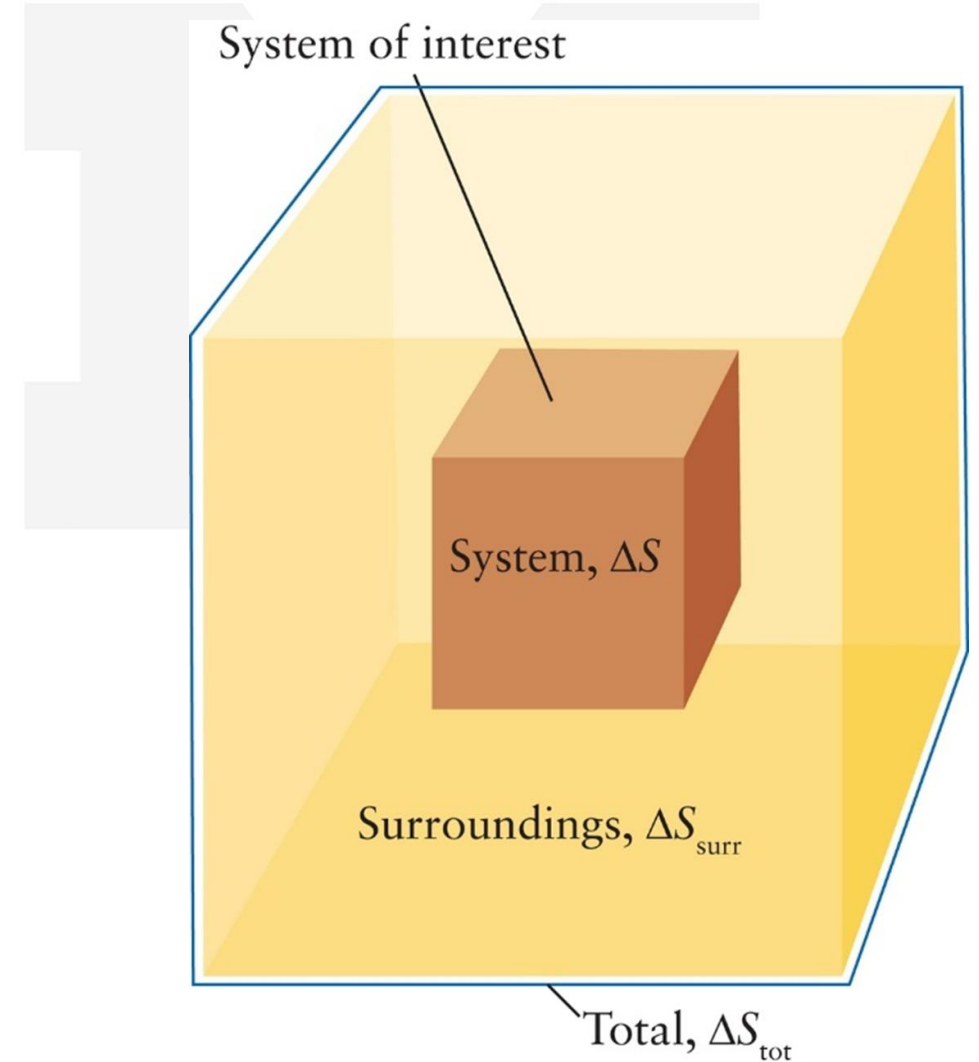


Figure 4I.1

Atkins, *Chemical Principles: The Quest for Insight*, 7e

W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman



# Global Changes in Entropy: Surroundings



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

At **low temperatures**,  $T$ , there is a **greater effect on  $\Delta S$** ; a sneeze in a quiet library will attract attention than sneezing in a noisy street.

In (a) a more chaotic system, adding or removing heat has less of an effect than in (b) a less chaotic system.

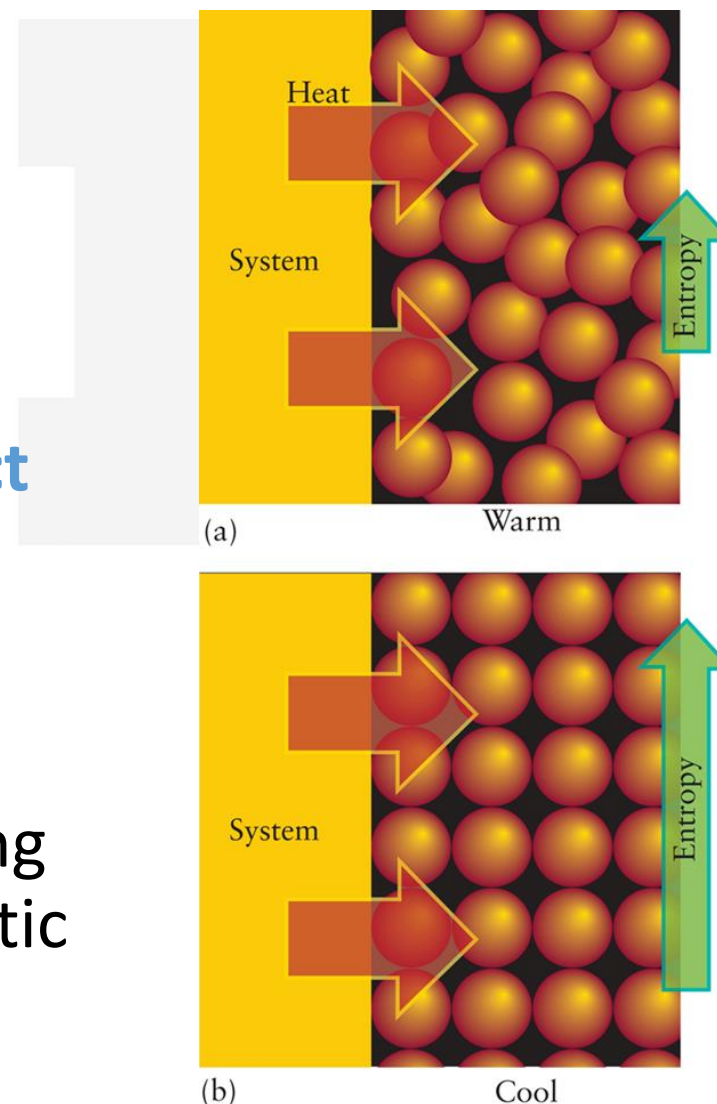


Figure 41.2

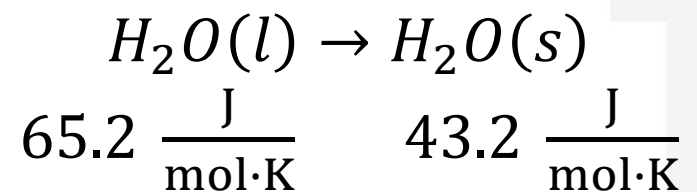
Atkins, *Chemical Principles: The Quest for Insight*, 7e

W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

# Global Changes in Entropy: Surroundings



Freezing liquid water into a solid is not a favourable process.



$$\Delta S_{sys} = \sum (n \cdot S_{m,products}) - \sum (n \cdot S_{m,reactants})$$

$$\Delta S_{sys} = -22.0 \frac{\text{J}}{\text{mol}\cdot\text{K}} \text{ (unfavourable)}$$

This is answered fully when we interpret  $\Delta S_{total}$  to include:

$$\Delta S_{surr} = \frac{Q_{rev}}{T}$$

# Example

Calculate the change in entropy of the *surroundings* when water freezes at  $-10.0\text{ }^{\circ}\text{C}$ .

Use  $\Delta H_{fus,H_2O} = 6.0 \frac{\text{kJ}}{\text{mol}}$  at  $-10.0\text{ }^{\circ}\text{C}$ .

Water will release its heat into the surroundings, so  $6.0 \text{ kJ}\cdot\text{mol}^{-1}$  will be transferred from the water to the surroundings.

$$T = 273.15 + (-10.0\text{ }^{\circ}\text{C}) = 263\text{ K}$$

$$\Delta S_{surr} = -\frac{\Delta H}{T} = -\frac{-6.0 \frac{\text{kJ}}{\text{mol}}}{263\text{ K}} = 23 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

Compare to our previous answer of  $-22 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for the entropy change of the system.

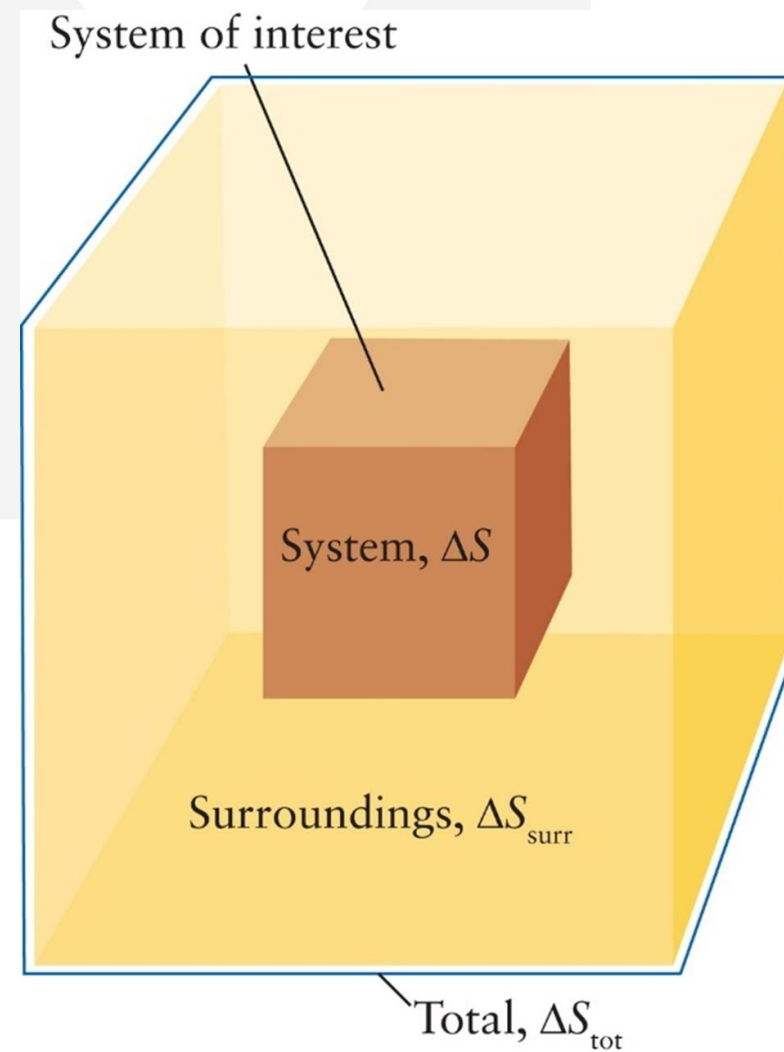


Figure 4L1

Atkins, *Chemical Principles: The Quest for Insight*, 7e

W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman



An isolated system includes both the system and its surroundings:

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

If  $\Delta S_{total} > 0$ , the **process is spontaneous**.

So even if  $\Delta S_{sys}$  is negative, a larger, more positive  $\Delta S_{surr}$  can overcome a small negative  $\Delta S_{sys}$ .

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

small “-”      large “+”

# System and Surroundings



The two parts to total entropy are the system and surroundings.

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

$$\Delta S_{sys} = \sum (n \cdot S_{m,products}) - \sum (n \cdot S_{m,reactants})$$

$$\Delta S_{surr} = -\frac{\Delta H}{T}$$

# Overall Change in Entropy



$\Delta S_{total}$  is a combination of both the system and surroundings:

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

- If  $\Delta S_{total}$  is **positive** (an increase), the process is spontaneous.
- If  $\Delta S_{total}$  is **negative** (a decrease), the reverse process is spontaneous.
- If  $\Delta S_{total} = 0$ , the process has no tendency to proceed in either direction (phase changes are the most common examples of when  $\Delta S_{total} = 0$ ).

# Example



Assess whether the combustion of magnesium is spontaneous at 25 °C under standard conditions, given:



$$\Delta S_{\text{sys}}^{\circ} = -217 \frac{\text{J}}{\text{K}}, \Delta H^{\circ} = -1,202 \text{ kJ (exothermic)}$$

$$\Delta S_{\text{total}}^{\circ} = \Delta S_{\text{sys}}^{\circ} + \Delta S_{\text{surr}}^{\circ} = \Delta S_{\text{sys}}^{\circ} - \frac{\Delta H^{\circ}}{T}$$

$$\Delta S_{\text{total}}^{\circ} = -0.217 \frac{\text{kJ}}{\text{K}} - \frac{-1,202 \text{ kJ}}{(273.15 + 25) \text{ K}} = +3.82 \frac{\text{kJ}}{\text{K}}$$

Because  $\Delta S_{\text{total}}^{\circ}$  is positive, the reaction is spontaneous under standard conditions, even though the entropy of the system decreases. The large amount of heat produced drives the reaction.

# Example



Is the formation of iodine chloride from its elements in their most stable forms spontaneous under standard conditions at 25 °C?



$$\Delta S_{\text{sys}}^{\circ} = +155.9 \frac{\text{J}}{\text{K}}, \Delta H^{\circ} = +35.0 \text{ kJ (endothermic)}$$

$$\Delta S_{\text{total}}^{\circ} = \Delta S_{\text{sys}}^{\circ} + \Delta S_{\text{surr}}^{\circ} = \Delta S_{\text{sys}}^{\circ} - \frac{\Delta H^{\circ}}{T}$$

$$\Delta S_{\text{total}}^{\circ} = +0.1559 \frac{\text{kJ}}{\text{K}} - \frac{+35.0 \text{ kJ}}{(25 + 273.15) \text{ K}} = +38.45 \frac{\text{J}}{\text{K}}$$

Yes, this reaction is spontaneous, even though it is **endothermic**. The reason: entropy is driving the reaction.

# Summary



*Spontaneous endothermic reactions were a puzzle for nineteenth-century chemists, who believed reactions ran only if the energy of the system decreased; that is, if reactions were driven by heat leaving the system.*

- 1) As just seen, endothermic reactions are sometimes driven by the dominating increase in disorder of the system.

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

$$\Delta S_{surr} = -\frac{\Delta H}{T}$$

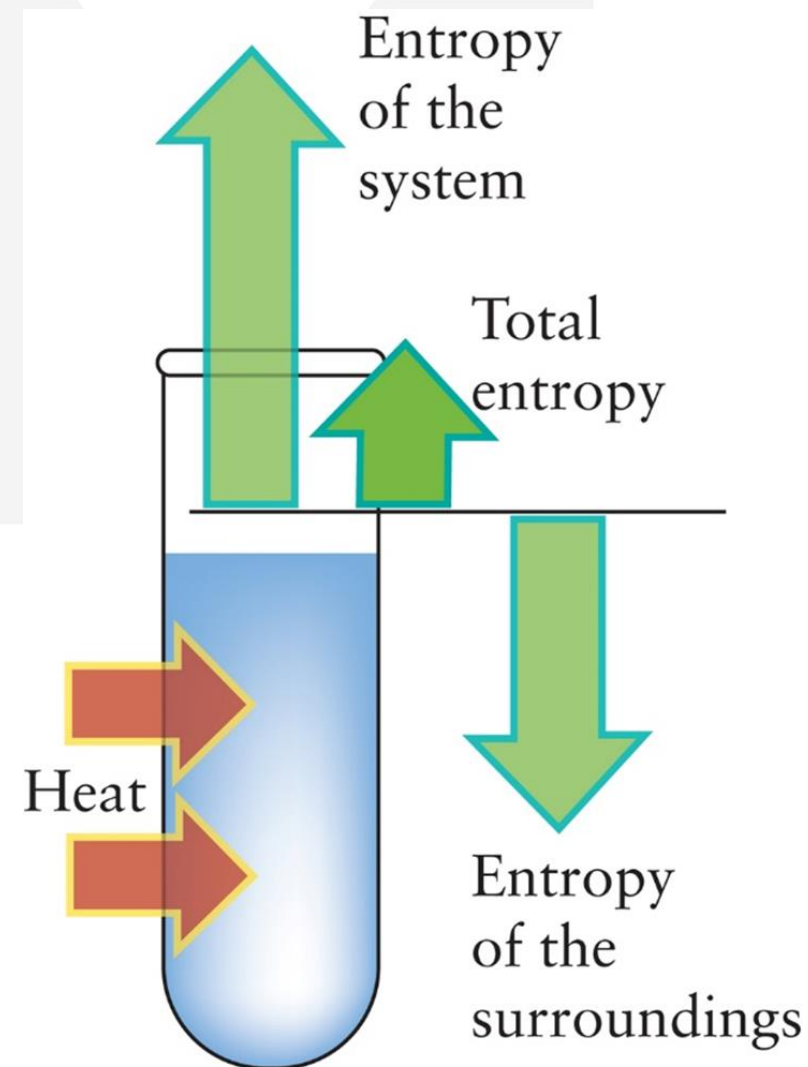


Figure 41.4

Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

2) Maximum work is achieved if expansion takes place reversibly.

Work is related to heat by  $\Delta U = Q + W$  (state functions) and we have shown  $W_{rev} > W_{irrev}$  ( $W$  more negative). It follows that  $Q_{rev} > Q_{irrev}$  ( $Q$  more positive), which means  $\Delta S \geq \frac{Q}{T}$ .

In an isolated system  $Q = 0$ , so  $\Delta S \geq 0$ , meaning the entropy *cannot decrease* in an isolated system, or in other words, the entropy of the universe is steadily increasing (Clausius inequality).



3) A reversible and irreversible path between two given states of the system leaves the surroundings in different states.

$\Delta S_{sys}$  is a state function, so it only depends on the difference between the final and initial states.

$\Delta S_{surr}$  is *not a state function*. That's because work can be calculated either as  $W_{rev}$  or  $W_{irrev}$ , so  $\Delta S \geq \frac{Q}{T}$  is different for different processes.

# Equilibrium: A Quick Overview



A system at **equilibrium** has *no tendency to change* in either direction (forward or reverse).

The idea of change applies to gaining or losing heat and gaining or losing pressure.

It even applies in the broader sense to changes in populations of people in a country or molecules in a chemical reaction.

# Equilibrium: A Quick Overview



The equilibrium state is a dynamic equilibrium, where the forward and reverse processes are continually at matching rates.

A block of metal at the same temperature as its surroundings is in thermal equilibrium.

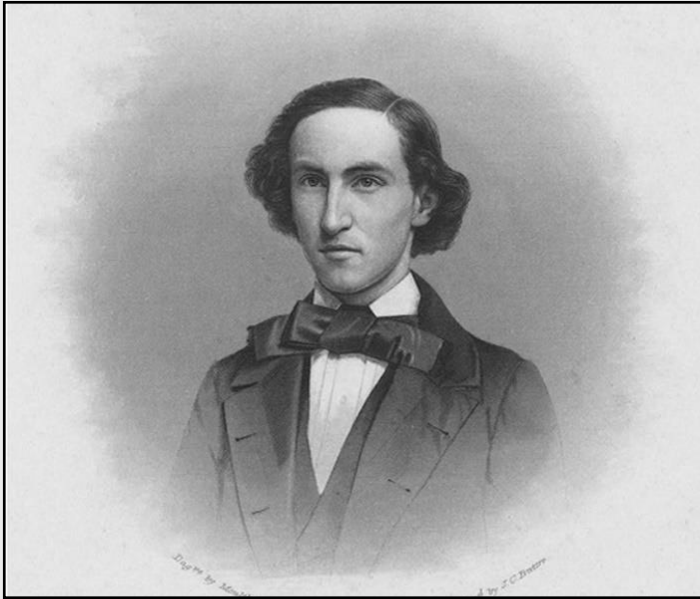
Energy has no net tendency to flow into or out of the block as heat. Energy continues to flow in both directions, but there is no net flow.

This chapter started by stating that spontaneity is:

The **natural progression** of a system and its surroundings **from order to disorder**, **from lower to higher entropy**; this is one version of the second law of thermodynamics.

Now we look at Gibbs free energy.

Gibbs free energy accomplishes the same task more simply, and it also tells us how much *non-expansion work* (work under *free* expansion when usually  $W = 0$ ) we can get from the system.



Josiah Willard  
Gibbs

It would be more convenient to use only a single table of variables instead of using  $\Delta S_{sys}$  tables and  $\Delta H$  tables to calculate  $\Delta S_{tot} = \Delta S_{sys} - \frac{\Delta H}{T}$ :

$$-T \cdot \Delta S_{tot} = -T \cdot \Delta S_{sys} + \Delta H$$

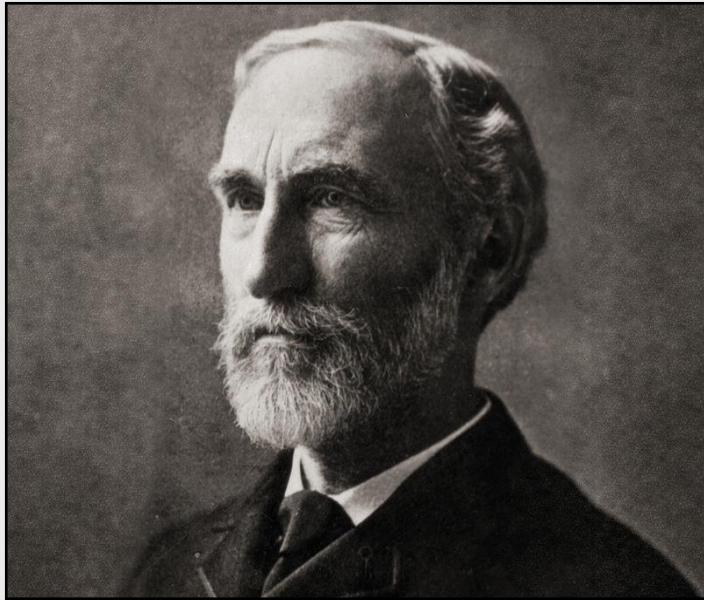
$$\Delta G = \Delta H - T \cdot \Delta S$$

The absolute Gibbs free energy can be calculated as:

$$G = H - TS$$

Where  $G$ , for Gibbs, is a state function.

# Josiah Willard Gibbs



Josiah Willard  
Gibbs

1839 -1903

Yale, first Ph.D. in engineering in US

Instrumental contribution to Physical Chemistry

Copley Medal

*“the greatest mind in American history.”*

– Albert Einstein

*“[In pure science, Gibbs] did for statistical mechanics and for thermodynamics what Laplace did for celestial mechanics and Maxwell did for electrodynamics.”*

– Robert Millikan



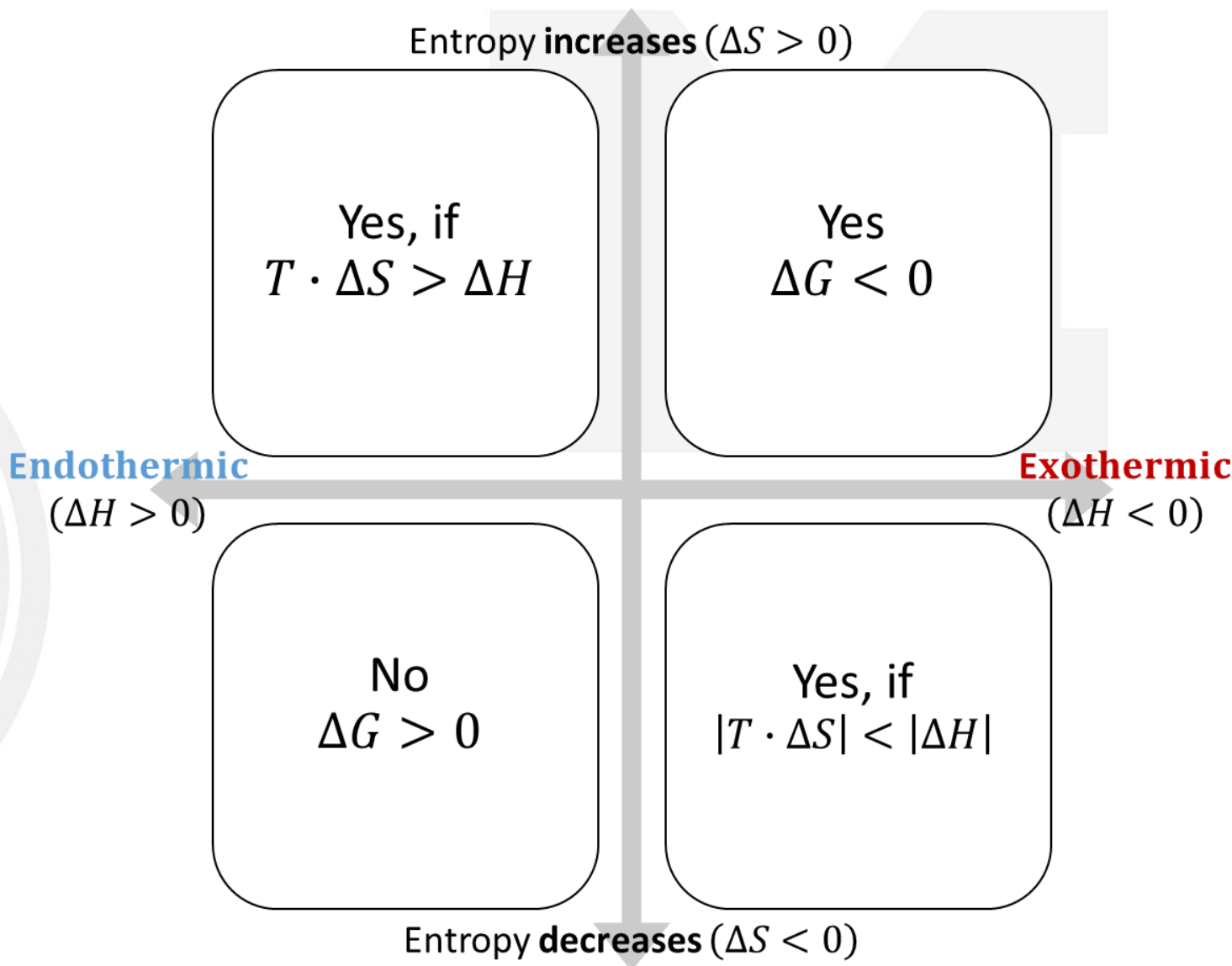
# Gibbs Free Energy



Using Gibbs free energy formula to find spontaneity, we use the following criteria.

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

Note when  $\Delta G < 0$  the process is **spontaneous**.



# Example



Calculate the change in molar Gibbs free energy,  $\Delta G_m$ , for the process  $H_2O(s) \rightarrow H_2O(l)$  at 1 atm and (a) 10 °C; (b) 0.0 °C. Decide for each temperature whether melting is spontaneous or not. Treat  $\Delta H_{fus} = 6.01 \frac{\text{kJ}}{\text{mol}}$  and  $\Delta S_{fus} = 22.0 \frac{\text{J}}{\text{mol}\cdot\text{K}}$  as independent of temperature.

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

a) 10 °C

$$\Delta G = \Delta H - T \cdot \Delta S = 6.01 \frac{\text{kJ}}{\text{mol}} - (10 + 273.15)\text{K} \times 0.0220 \frac{\text{kJ}}{\text{mol} \cdot \text{K}} = -0.22 \frac{\text{kJ}}{\text{mol}}$$

b) 0.0 °C

$$\Delta G = \Delta H - T \cdot \Delta S = 6.01 \frac{\text{kJ}}{\text{mol}} - (0.0 + 273.15)\text{K} \times 0.0220 \frac{\text{kJ}}{\text{mol} \cdot \text{K}} = 0.0 \frac{\text{kJ}}{\text{mol}}$$

In a)  $\Delta G$  is negative, so ice melting above freezing is spontaneous, in b) at 0.0 °C it's at equilibrium. This makes sense since it's in a phase change where we've already calculated for fusion that  $\Delta S_{tot} = 0$ .

# Gibbs Free Energy

$$G = H - TS$$

For  $\Delta H > 0$  and  $\Delta S > 0$ , the molar Gibbs free energy decreases as the temperature is raised.

As  $T$  increases,  $TS$  increases and a larger quantity is subtracted from  $H$ , favourably making  $G$  negative.

Gibbs free energy decreases more sharply with temperature for gases than for liquids.

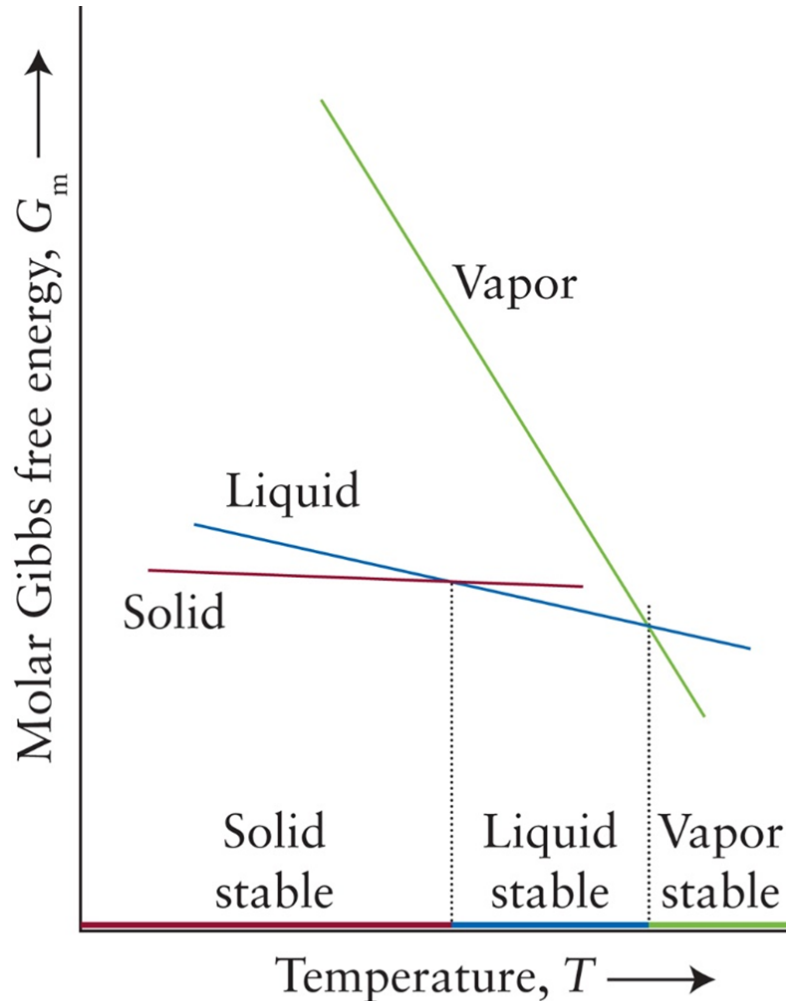


Figure 4J.3  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

$$S_{m,gas}^{\circ} > S_{m,liquid}^{\circ} > S_{m,solid}^{\circ}$$

# Gibbs Free Energy of Reaction



Our principal interest in chemistry is to calculate  $\Delta G$  for a reaction.

The Gibbs free energy of reaction,  $\Delta G$ , is commonly referred to as the “reaction free energy.”

$$\Delta G = \sum (n \cdot G_{m,products}) - \sum (n \cdot G_{m,reactants})$$

$n$ : stoichiometric coefficients, moles

$G_m$ : molar Gibbs free energy

# Gibbs Free Energy of Reaction



For a chemical reaction under standard conditions:

$$\Delta G^\circ = \sum (n \cdot G_{m,products}^\circ) - \sum (n \cdot G_{m,reactants}^\circ)$$

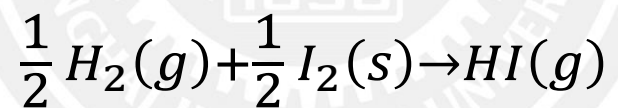
$\Delta G_f$ , meaning formed from its elements under variable condition.

$\Delta G_f^\circ$ , meaning formed at 1 bar and 298.15 K per mol.

# Gibbs Free Energy: Constants



The standard Gibbs free energy of formation of hydrogen iodide gas at 25 °C is  $\Delta G_{f, HI(g)}^{\circ} = 1.70 \frac{\text{kJ}}{\text{mol}}$ . It is the standard Gibbs free energy of reaction for:



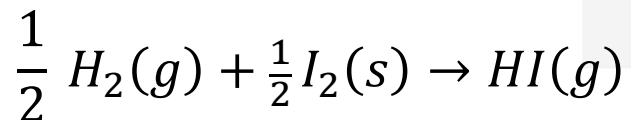
Substance	$\Delta G_f^{\circ} / \text{kJ}\cdot\text{mol}^{-1}$
<b>Gases</b>	
Ammonia, $\text{NH}_3$	-16.45
Carbon dioxide, $\text{CO}_2$	-394.4
Nitrogen dioxide, $\text{NO}_2$	+51.3
Water, $\text{H}_2\text{O}$	-228.6
<b>Liquids</b>	
Benzene, $\text{C}_6\text{H}_6$	+124.3
Ethanol, $\text{C}_2\text{H}_5\text{OH}$	-174.8
Water, $\text{H}_2\text{O}$	-237.1
<b>Solids</b>	
Calcium carbonate, $\text{CaCO}_3$ (Calcite)	-1128.8
Silver chloride, $\text{AgCl}$	-109.8



# Example



Calculate the standard Gibbs free energy of formation of  $\text{HI}(g)$  at  $25^\circ\text{C}$  from its standard molar entropy and standard enthalpy of formation.



$$\Delta H_{f,\text{HI}(g)}^\circ = +26.48 \text{ kJ (From table 8.3)}$$

$$\Delta S^\circ = \sum (n \cdot S_{m,\text{products}}^\circ) - \sum (n \cdot S_{m,\text{reactants}}^\circ) = n \cdot S_{m,\text{HI}(g)}^\circ - (n \cdot S_{m,\text{H}_2(g)}^\circ + n \cdot S_{m,\text{I}_2(s)}^\circ)$$

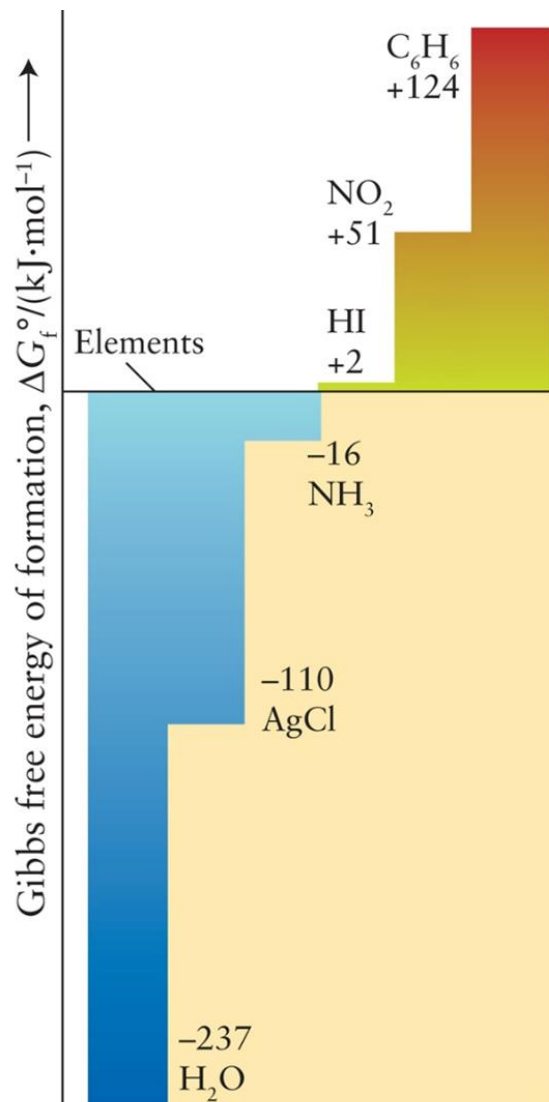
$$\Delta S^\circ = 1 \text{ mol} \times 206.6 \frac{\text{J}}{\text{mol} \cdot \text{K}} - \left( \frac{1}{2} \text{ mol} \times 130.7 \frac{\text{J}}{\text{mol} \cdot \text{K}} + \frac{1}{2} \text{ mol} \times 116.1 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) = +83.2 \frac{\text{J}}{\text{K}}$$

$$\Delta G_f^\circ = \Delta H_f^\circ - T \cdot \Delta S^\circ = +26.48 \text{ kJ} - \left( 298 \text{ K} \times 0.0832 \frac{\text{kJ}}{\text{K}} \right) = +1.69 \text{ kJ}$$

This is very close to the reported standard Gibbs free energy of formation of hydrogen iodide gas at  $25^\circ\text{C}$ :

$$\Delta G_{f,\text{HI}(g)}^\circ = 1.70 \frac{\text{kJ}}{\text{mol}}$$

# Labile versus Inert



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

If  $\Delta G_f^\circ < 0$ , then elements are poised to change spontaneously into the compound.

If  $\Delta G_f^\circ > 0$ , then the reverse is true; the compound is poised to change spontaneously into the pure elements.

$\Delta G_f^\circ = 124 \frac{\text{kJ}}{\text{mol}}$  for benzene at 25 °C, so benzene is unstable and is **poised to decompose spontaneously** into its elements.

Figure 4J.5  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

# Labile versus Inert

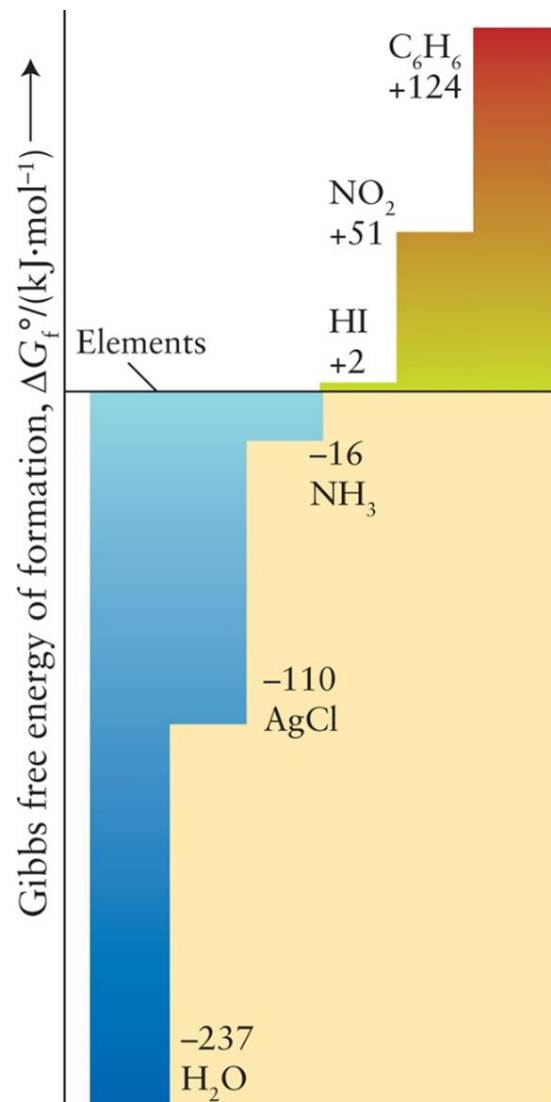


Figure 4J.5  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

That tendency may not be realized 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 **nonlabile** or even **inert**. So, benzene is thermodynamically unstable but nonlabile.

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

We are now ready to see why the Gibbs free energy is called *free energy*.

Gibbs free energy is a measure of the **energy free to do nonexpansion work**.

**Nonexpansion work**, is any kind of work other than expansion against an opposing pressure.

**Nonexpansion** work includes ***electrical work*** and mechanical work (like stretching a spring or carrying a weight up a slope ).

Electrical work—the work of **pushing electrons** through an electrical circuit—is the basis of generating chemical electrical power.

Nonexpansion work also includes the work of **muscular activity**, the work of **linking amino acids** together to form protein molecules, and the work of **sending nerve signals** through neurons, key ideas in bioenergetics.

Maximum nonexpansion work for an infinitesimal change (denoted “d”) in  $G$  at constant temperature:

$$dG = dH - T \cdot dS \text{ at } T = \text{const.}$$

We substitute  $dH = dU + p \cdot dV$  and  $dU = W + Q$ , both for an infinitesimal change in energy:

$$dG = W + Q + p \cdot dV - T \cdot dS \text{ at } T, p = \text{const.}$$

As we have seen before, the maximum work is done in reversible processes.

$$dG = W_{rev} + Q_{rev} + p \cdot dV - T \cdot dS \text{ at } T, p = \text{const.}$$

We can substitute  $dS = \frac{Q_{rev}}{T} \rightarrow Q_{rev} = T \cdot dS$ :

$$dG = W_{rev} + T \cdot dS + p \cdot dV - T \cdot dS \text{ at } T, p = \text{const.}$$

$$dG = W_{rev} + p \cdot dV \text{ at } T, p = \text{const.}$$



$$dG = W_{rev} + p \cdot dV \text{ at } T, p = \text{const.}$$

At this point, we recognize that the system may do both expansion work and nonexpansion work:

$$W_{rev} = W_{rev,nonexpansion} + W_{rev,expansion}$$

Reversible expansion work (matching the external to the internal pressure):

$$W_{rev} = W_{rev,nonexpansion} + W_{rev,expansion} = W_{rev,nonexpansion} - p \cdot dV$$

$$dG = W_{rev,nonexpansion} - p \cdot dV + p \cdot dV \text{ at } T, p = \text{const.}$$

$$dG = W_{rev,nonexpansion} \text{ at } T, p = \text{const}$$

Because  $W_{rev,nonexpansion}$  is the maximum **nonexpansion work** that the system can do (because it is achieved reversibly), we obtain:

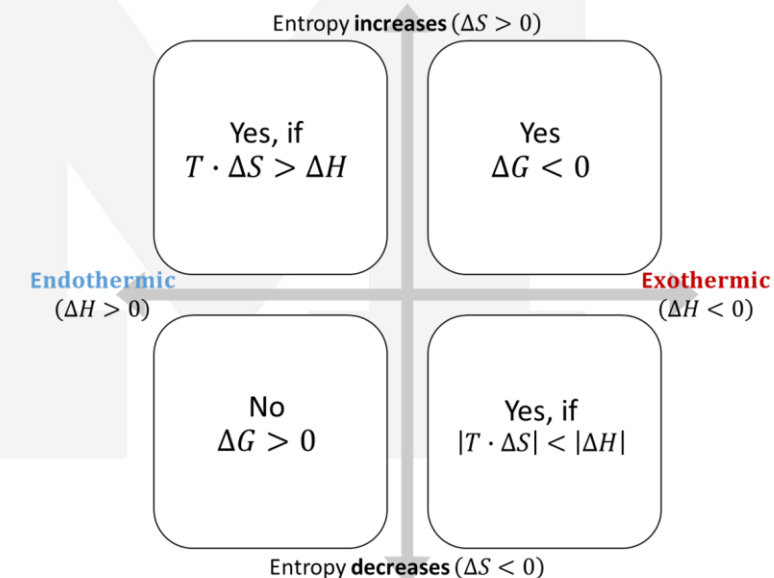
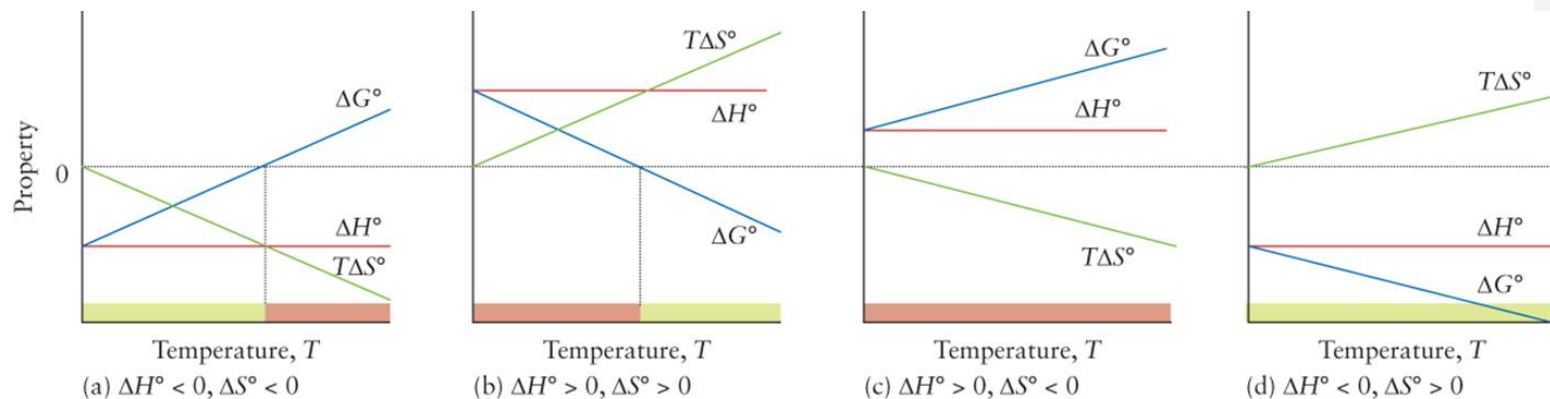
$$dG = W_{nonexpansion,max} \text{ or } \Delta G = W_{nonexpansion,max} \text{ at } T, p = \text{const.}$$

for any  $G$  we calculate!

# The Effect of Temperature



$\Delta G$  depends on temperature:  $\Delta G = \Delta H - T \cdot \Delta S$

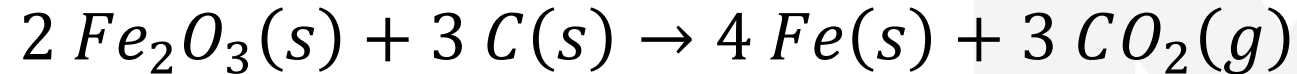


Case	Enthalpy Change	Entropy Change	Spontaneous?
a)	Exothermic ( $\Delta H < 0$ )	Decreasing ( $\Delta S < 0$ )	When $T$ is low
b)	Endothermic ( $\Delta H > 0$ )	Increasing ( $\Delta S > 0$ )	When $T$ is high
c)	Endothermic ( $\Delta H > 0$ )	Decreasing ( $\Delta S < 0$ )	Never
d)	Exothermic ( $\Delta H < 0$ )	Increasing ( $\Delta S > 0$ )	Always

# Example



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



$S_m^\circ / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	87.4	5.7	27.3	213.7
$\Delta H_f^\circ / \text{kJ}\cdot\text{mol}^{-1}$	-824.2	0	0	-393.5

For an endothermic reaction when  $\Delta H > 0$  and if  $\Delta S > 0$ , the reaction could be spontaneous if  $T$  is high enough to make  $\Delta G < 0$  (favourable).

The crossover point is where  $\Delta G = 0$  (going from positive to negative):

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

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

# Example



$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{\sum(n \cdot \Delta H_{f,products}^\circ) - \sum(n \cdot \Delta H_{f,reactants}^\circ)}{\sum(n \cdot S_{m,products}^\circ) - \sum(n \cdot S_{m,reactants}^\circ)}$$

$$T = \frac{(n \cdot \Delta H_{f,Fe(s)}^\circ + n \cdot \Delta H_{f,CO_2(g)}^\circ) - (n \cdot \Delta H_{f,Fe_2O_3(s)}^\circ + n \cdot \Delta H_{f,C(s)}^\circ)}{(n \cdot S_{m,Fe(s)}^\circ + n \cdot S_{m,CO_2(g)}^\circ) - (n \cdot S_{m,Fe_2O_3(s)}^\circ + n \cdot S_{m,C(s)}^\circ)}$$

$$T = \frac{\left(4 \text{ mol} \times 0 \frac{\text{kJ}}{\text{mol}} + 3 \text{ mol} \times \left(-393.5 \frac{\text{kJ}}{\text{mol}}\right)\right) - \left(2 \text{ mol} \times \left(-824.2 \frac{\text{kJ}}{\text{mol}}\right) + 3 \text{ mol} \times 0 \frac{\text{kJ}}{\text{mol}}\right)}{\left(4 \text{ mol} \times 27.3 \frac{\text{J}}{\text{mol} \cdot \text{K}} + 3 \text{ mol} \times 213.7 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right) - \left(2 \text{ mol} \times 87.4 \frac{\text{J}}{\text{mol} \cdot \text{K}} + 3 \text{ mol} \times 5.7 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)}$$

$$T = \frac{+467.9 \text{ kJ}}{+0.05584 \frac{\text{kJ}}{\text{K}}} = 838 \text{ K}$$

Therefore, carbon can thermodynamically reduce iron above temperatures of 565 °C.

# The Three Laws of Thermodynamics



## 0<sup>th</sup> Law

“If two systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.”

## 1<sup>st</sup> Law

“The internal energy of an isolated system is constant.”

## 2<sup>nd</sup> Law

“The entropy of an isolated system increases during any spontaneous reaction.”

## 3<sup>rd</sup> Law

“The entropies of all perfect crystals approach zero as the absolute temperature approaches zero.”