

# UWO **CHEM 1302**

Fall 2024, Chapter 5 Notes



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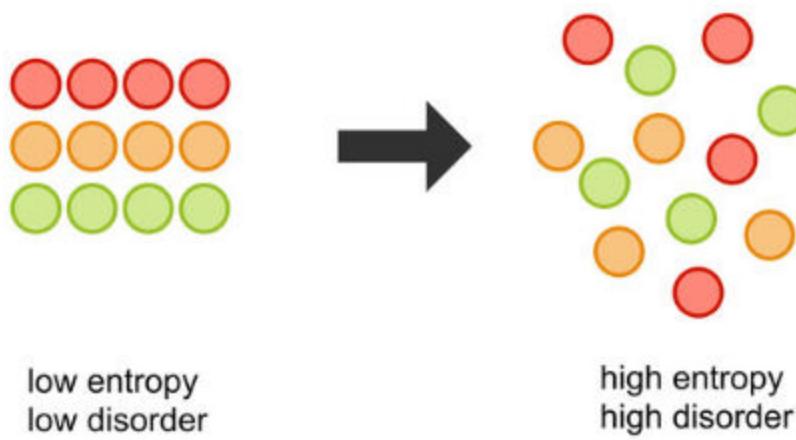
# 5. Entropy and Spontaneous Change

## 5.1 Entropy

5.1.1

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

Entropy (**S**) is a measure of disorder or randomness in a system.



The **2nd Law of Thermodynamics** states that disorder of the universe increases in a spontaneous process.

In other words, things naturally tend to go towards disorder and the universe is constantly getting more and more disordered!

## Entropy Equations

Entropy is defined as:

$$\Delta S_{surr} = \frac{q_{surr}}{T}$$

$\Delta S_{surr}$ =entropy of the surroundings (in J/molK)

$q_{surr}$ =heat in the surroundings (in J)

$T$ =Temperature (in K)

Recall:

$$q_{surr} = -q_{sys}$$

At constant pressure and temperature:

$$\Delta H_{sys} = q_{sys}$$

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

The **2nd law of thermodynamics** states that whenever a spontaneous event takes place in the universe, the total entropy of the universe increases:

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

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## Chemical Reactions

In the same way we can use standard heats of formation to calculate a reaction enthalpy at room temperature and pressure, we can use  $S^o$  (values will be provided to you in a table)

$$\Delta S^o = [(\sum nS^o products) - (\sum nS^o reactants)]$$

## Factoring Affecting Entropy Changes

### Entropy for Different Phases

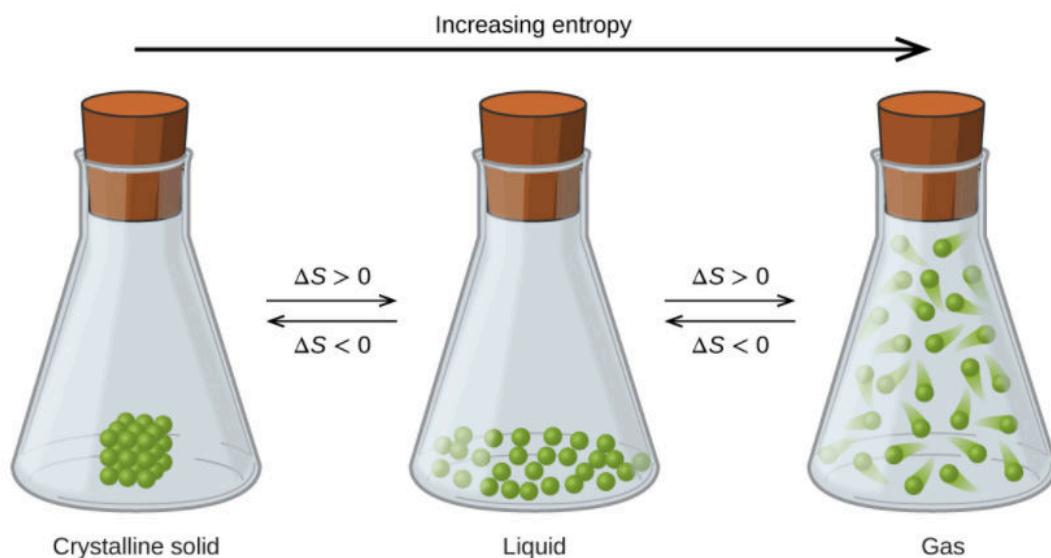
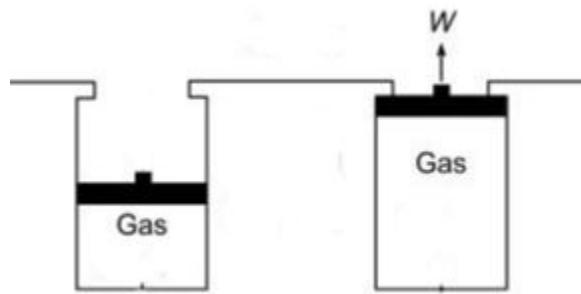


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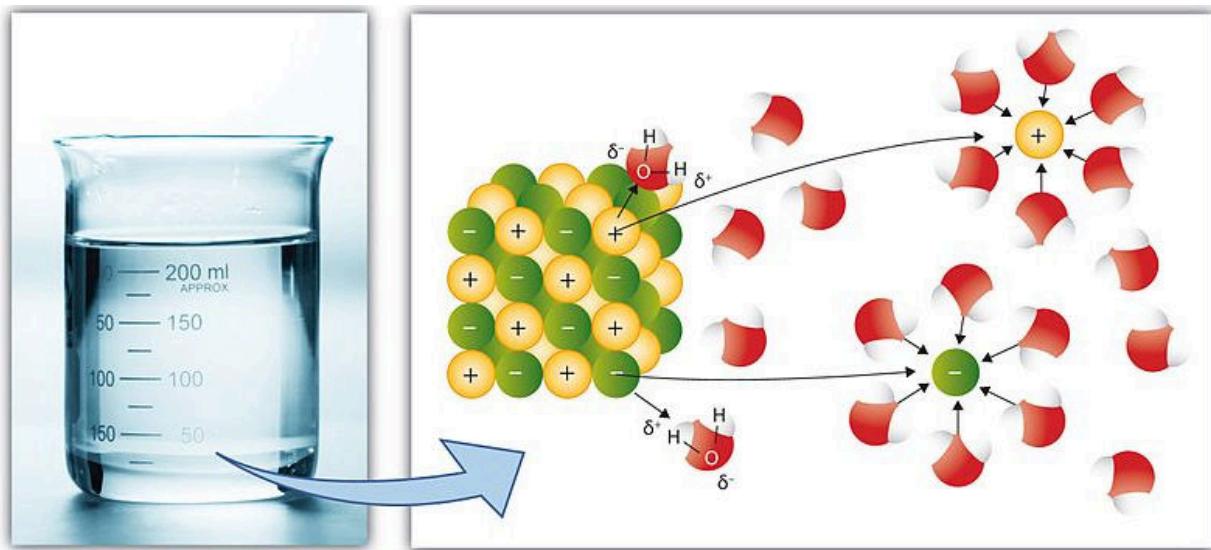
## Entropy When a Higher Pressure is Applied to a Gas

If we have **two gases, and apply a higher pressure to one of them**, will the gas with the higher pressure applied have more or less entropy?



The gas with the higher pressure applied to it will have (more/less) more organized molecules and therefore there is (more/less) less disorder, meaning there is (more/less) less entropy!

## Entropy of a Solid Alone vs Dissolved in a Liquid



*Example:*

KCl(s) vs KCl(aq)

There is (more/less) more entropy when the solid is dissolved in a solvent.

## Entropy of a Gas Alone vs Dissolved in a Solvent



*Example:* Think of shaking a bottle of pop  $\text{CO}_2(\text{g})$  vs  $\text{CO}_2(\text{aq})$

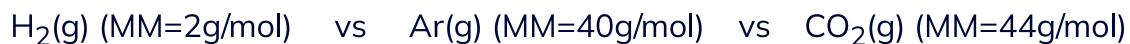
The gas would have (more/less) less more entropy when dissolved in the solvent.

## Entropy of Similar Substances in the Same Physical State

How would entropy change with increasing mass?

Entropy would (increase/decrease) increase

Example:



How would entropy change as we increase the number of atoms in the molecule?

Entropy would (increase/decrease) increase

Example:



How would entropy be different if we compared the following two molecules?



Would entropy increase or decrease with increasing molecular freedom or flexibility? increase

## Entropy in a Chemical Equation

Example:



If we were asked if entropy increases or decreases in this equation, what would you consider?

Therefore, entropy increase We could also say that  $\Delta S$  is < 0

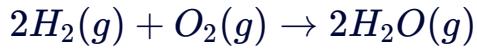
- Look at the phase of equation on the reactant side and product side of the equation
- If the phase are all the same, you can also look at the number of moles on each side
- Here are two gases on the left, and one gas and one liquid on the right
- Since there is a liquid on the right, that is less disordered so overall from reactants to product the reaction got less disordered.

## Example: Qualitatively Estimating Entropy Changes

Determine if the entropy change will be positive or negative for the following reactions:



- solid phase on left side only, but left side with solid, liquid and gas phase.
  - there is more molecular on right than left.
- $\therefore$  Entropy is increase and positive.



Entropy is negative

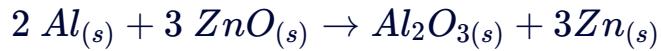


Entropy is positive

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#### 5.1.4

Using the following data, calculate the standard entropy of the reaction shown below. Enter your answer in units of J / (mol\*K)



$$S^\circ(Al_{(s)}) = 28.3 \text{ J mol}^{-1}\text{K}^{-1}$$

$$S^\circ(Zn_{(s)}) = 41.6 \text{ J mol}^{-1}\text{K}^{-1}$$

$$S^\circ(ZnO_{(s)}) = 43.9 \text{ J mol}^{-1}\text{K}^{-1}$$

$$S^\circ(Al_2O_3(s)) = 51.0 \text{ J mol}^{-1}\text{K}^{-1}$$

$$\begin{aligned} S^\circ_{\text{product}} &= 1 \times 51 + 3 \times 41.6 \\ &= 175.8 \text{ J/mol}\cdot\text{K} \end{aligned}$$

$$\begin{aligned} S^\circ_{\text{reactant}} &= 2 \times 28.3 + 3 \times 43.9 \\ &= 188.3 \text{ J/mol}\cdot\text{K} \end{aligned}$$

$$\Delta S^\circ_{\text{rxn}} = 175.8 - 188.3 = -12.5 \text{ J/mol}\cdot\text{K}$$

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Answer

### 5.1.5

Using the  $\Delta H^0$  of fusion for water 6.03 kJ/mol and the  $\Delta S^0$  of fusion for water 22.1 J K<sup>-1</sup> mol<sup>-1</sup>, calculate the  $\Delta S_{\text{univ}}$  for ice melting at -10°C, 0°C and 10°C. Remember: the universe transfers heat in a reversible way.

$$\Delta H_f^0 = 6.03 \text{ kJ/mol}$$

$$\Delta S_f^0 = 22.1 \text{ J/mol}\cdot\text{K} \quad \text{at } 0^\circ\text{C}$$

$$\Delta S_{\text{surv}} = \frac{-\Delta H_f^0}{T}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = \Delta S_f^0 + \frac{-\Delta H_f^0}{T}$$

A  $\Delta S_{\text{univ}}$  at -10°C

$$\Delta S_{\text{surv}} = \frac{-6030}{263.15} = -22.9 \text{ J/mol}\cdot\text{K} \quad \Delta S_{\text{uni}} = 22.1 + (-22.9) = -0.8 \text{ J/mol}\cdot\text{K}$$

B  $\Delta S_{\text{univ}}$  at 0°C

$$\Delta S_{\text{surv}} = \frac{-6030}{273.15} = -22.1 \text{ J/mol}\cdot\text{K} \quad \Delta S_{\text{uni}} = 22.1 + (-22.1) = 0$$

C  $\Delta S_{\text{univ}}$  at 10°C

$$\Delta S_{\text{surv}} = \frac{-6030}{283.15} = -21.3 \text{ J/mol}\cdot\text{K} \quad \Delta S_{\text{uni}} = 22.1 + (-21.3) = 0.8 \text{ J/mol}\cdot\text{K}$$

## 5.2

# 3rd Law of Thermodynamics

5.2.1

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

- The Third Law states: All perfect crystals in equilibrium at 0K have the same entropy, defined as 0
- Conceptually this makes sense given our understanding of order and disorder. The system described in the third law would be the most ordered system imaginable.

No Vibrational Motion at 0K

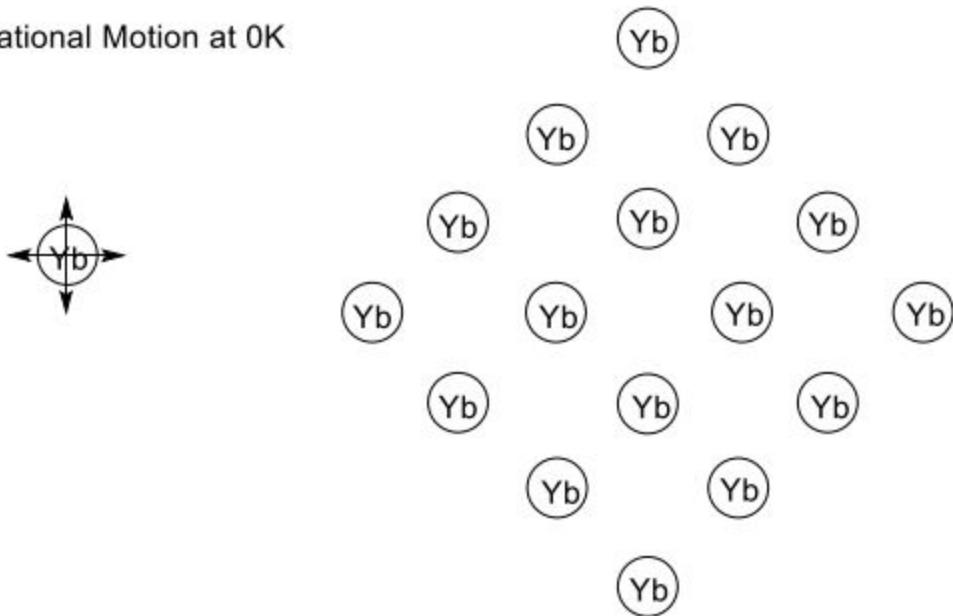


Figure 2.2.4

## Summary of the Laws of Thermodynamics

 **WIZE CONCEPT**

**It is more important to understand each law and the related equations than to memorize what each law is!**

**0th Law:** 2 bodies that are in thermal equilibrium with a 3rd body are in thermal equilibrium with each other as well! All 3 bodies would be at the same temperature.

**1st Law:** Energy is conserved and cannot be created and destroyed. Energy can only be transformed into different forms like heat.

$$\Delta U_{surr} = -\Delta U_{sys}$$

$$\Delta U = q + w \dots \text{where } w = -P\Delta V$$

**2nd Law:** Entropy (disorder) in the universe will spontaneously increase. Energy like to be more spread out!

$$\Delta S^o_{rxn} = \left[ \left( \sum n \Delta S^o_{products} \right) - \left( \sum n \Delta S^o_{reactants} \right) \right]$$

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

**3rd Law:** A perfect crystal has 0 entropy at a temperature of 0K (hypothetical temperature that is the absolute lowest temperature). Any temperature higher than this would have entropy and there is more entropy as temperature increases!