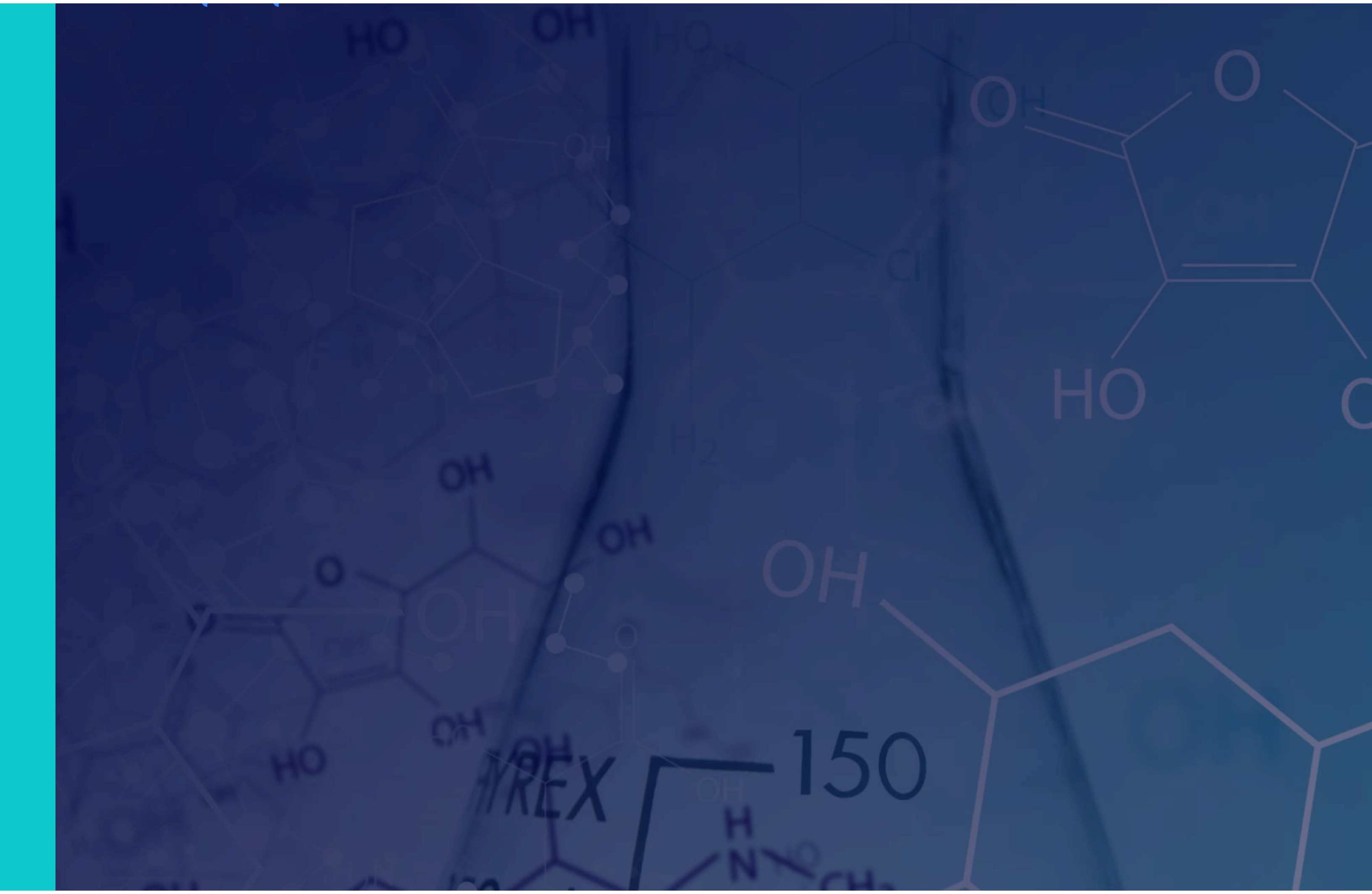

UWO

CHEM 1302

Fall 2024, Chapter 5 Notes

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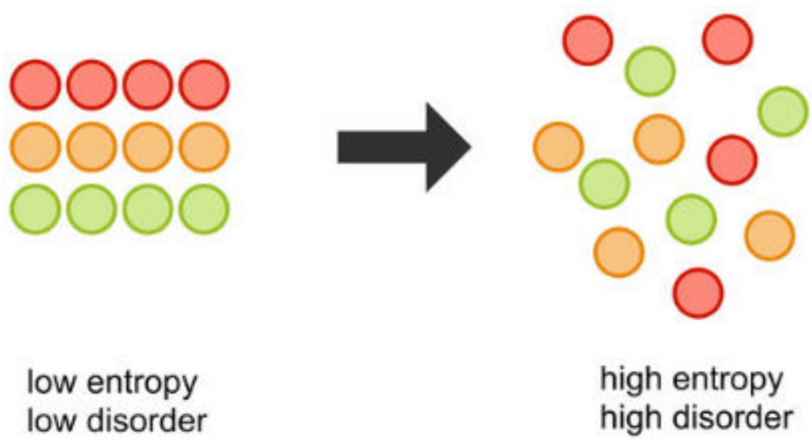
5. Entropy and Spontaneous Change

5.1 Entropy

5.1.1

2nd 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:

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

ΔS_{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:

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

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

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

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

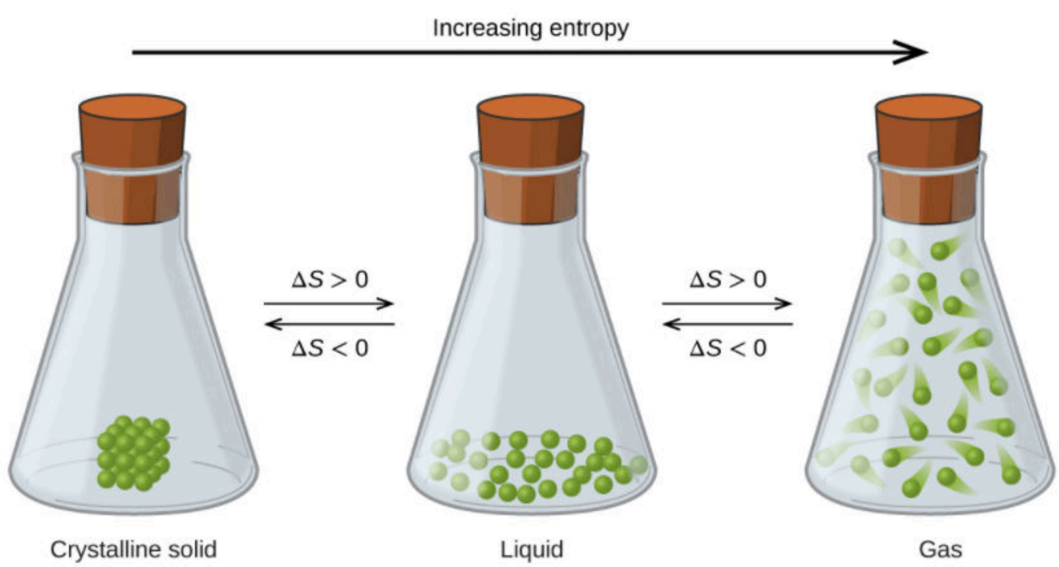
Chemical Reactions

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)

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

Factoring Affecting Entropy Changes

Entropy for Different Phases



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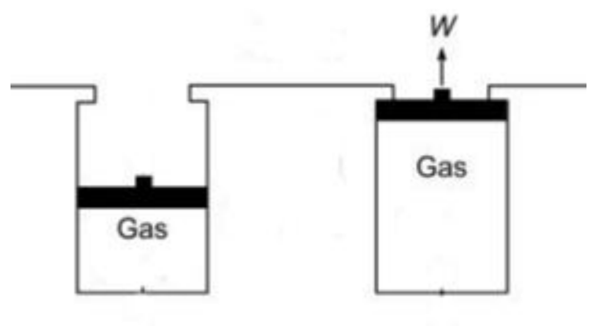
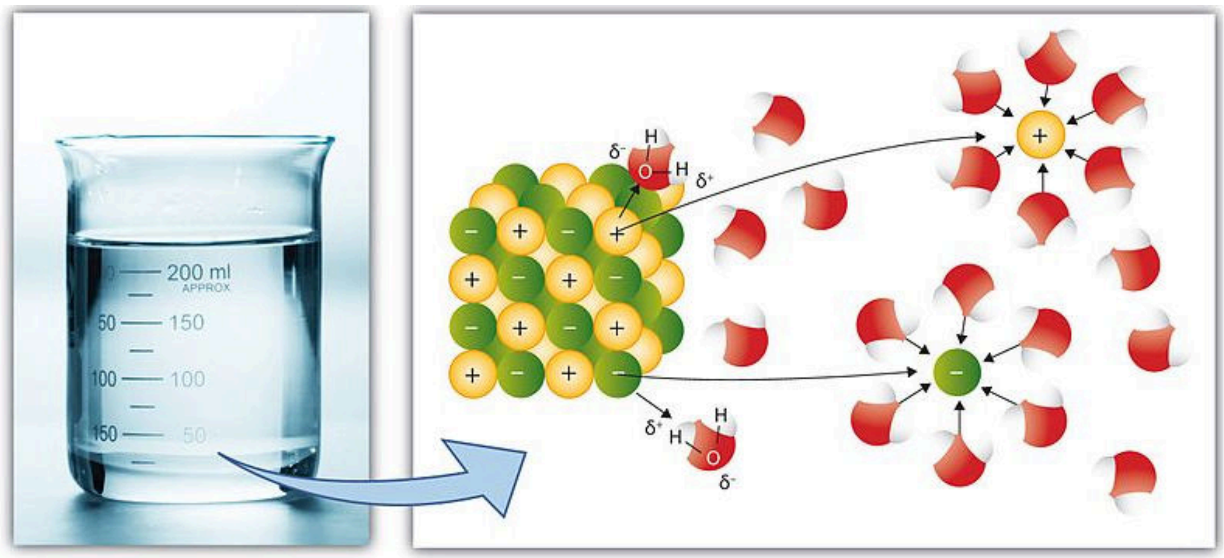
Entropy When a Higher Pressure is Applied to a Gas

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) ________ organized molecules and therefore there is (more/less) ________ disorder, meaning there is (more/less) ________ entropy!

Entropy of a Solid Alone vs Dissolved in a Liquid



Example:

KCl(s) vs KCl(aq)

There is (more/less) ________ 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 CO_2(g) vs CO_2(aq)

The gas would have (more/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) ___________

Example:

H_2(g) (MM=2g/mol)   vs   Ar(g) (MM=40g/mol)   vs CO_2(g) (MM=44g/mol)

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

Entropy would (increase/decrease) ___________

Example:

CH_4(g) vs C_2H_6(g) vs $C_{10}H_{22}$(g)

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

Cyclopentane vs C_5H_{12}

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

Entropy in a Chemical Equation

Example:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

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

Therefore, entropy ______________ We could also say that ΔS is _____ 0

Example: Qualitatively Estimating Entropy Changes

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

$$(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_3(s) + 4H_2O(l) + N_2(g)$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

$$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$$

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)

$$2\ Al_{(s)} + 3\ ZnO_{(s)} \rightarrow Al_2O_{3(s)} + 3Zn_{(s)}$$

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

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

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

$$S^o(Al_2O_{3(s)}) = 51.0\ J\ mol^{-1}K^{-1}$$

Answer

5.1.5

Using the ΔH^0 of fusion for water 6.03 kJ/mol and the ΔS^0 of fusion for water 22.1 J K^{-1} mol^{-1}, calculate the ΔS_{univ} for ice melting at -10°C, 0°C and 10°C. Remember: the universe transfers heat in a reversible way.

A ΔSuniv at -10C

B ΔSuniv at 0C

C ΔSuniv at 10C

5.2 3rd Law of Thermodynamics

5.2.1

3 rd 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.

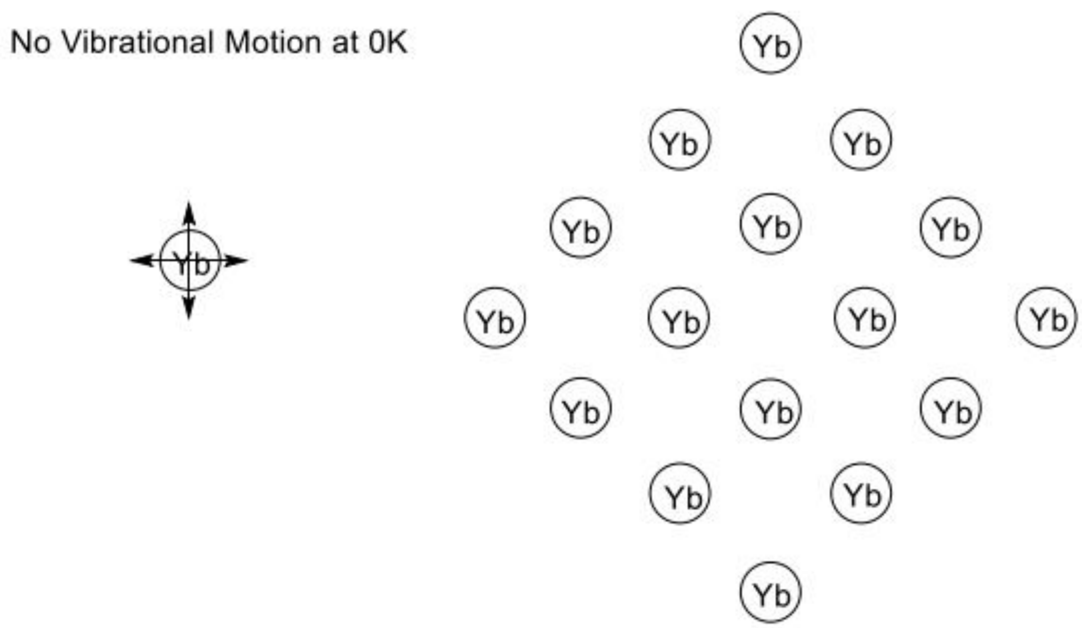


Figure 2.2.4

5.2.2

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.

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

$$\Delta U = q + w ... where\ w = -P\Delta V$$

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

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

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

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!