Entropy & The 2nd Law of Thermodynamics

Entropy and 2nd Law of Thermodynamics

Overview

What is the most important concept in chapter 19?

- Spontaneous Processes (Reactions)
  - A reaction which occurs on its own without any outside intervention
- What characteristics make reactions spontaneous?
  - They lose energy to the surroundings
    - Ball rolling down hill
    - Hydrocarbons burning
    - Nails rusting
- Exceptions
  - A quick cold pack
- If energy must be lost to the surroundings in order for a reaction to be spontaneous, how do we explain this exception?
  - Our definition of energy is too narrow

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Some Important New Terms

- Reversible Process
  - A process in which it is possible to return a system to its original state with **no net change in either system** or **surroundings**
  - Ice melting and freezing at 0˚C
  - These systems are at equilibrium
- Irreversible Process
  - A process which cannot be undone simply by reversing the events that caused it
  - It can go backwards....but thru a different path
    - Different heat (q) and work (w) values
- Spontaneous Process
  - Process which proceeds on its own without any outside assistance
  - Always occurs only in the spontaneous direction
  - Is irreversible

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A Practical Example

- The Egg Drop
  - What are the two possible processes taking place?
  - Which of them is spontaneous? Which is not?
  - Is the process reversible?
    - What then is the relationship between spontaneity and reversibility?
  - In both egg processes, what is the net energy change?
  - Given the example of the egg, is energy enough to determine spontaneity?
    - What other factors must we consider to determine if a process is spontaneous?
- The take home messages
  - Spontaneous processes have a definite direction
  - Spontaneous processes are irreversible
  - If a process is spontaneous, the reverse process is never spontaneous
  - The enthalpy change of a system is not enough to determine if it will be spontaneous

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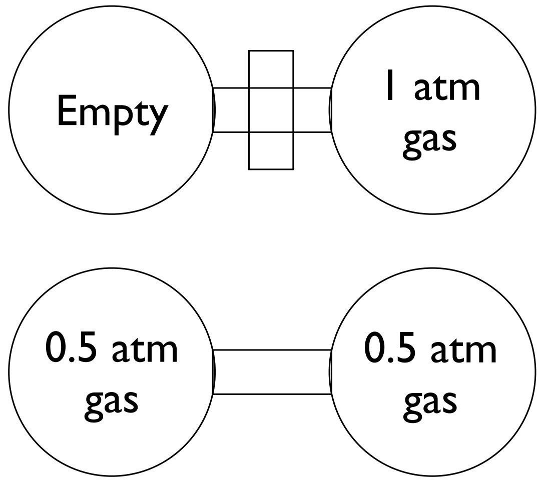
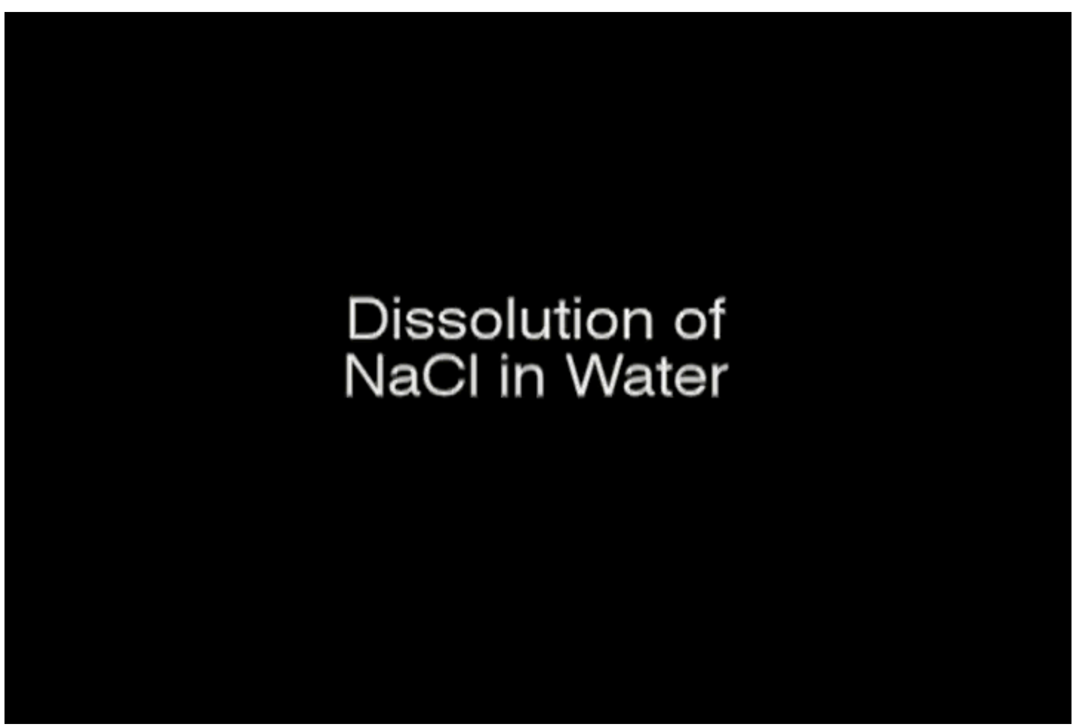
Randomness



- If this is an *isothermal process,* discuss the energy changes involved in the forward process and the reverse process
- Is the process spontaneous in both directions? Why or why not?
  - What would have to happen to reverse the process?
- Processes in which disorder increases tend to occur spontaneously



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Entropy

- The ***dis***order of a system
  - *S*
  - The more disordered or random a system, the larger the entropy
- Consider the following process
  - Dissolving salt in water
    - Salt dissolving in water is an endothermic process.
      - Should it be spontaneous? Why or why not?
    - Is it spontaneous?
      - Thoughts on why?
    - Let's look at disorder...
      - Need to consider all parts of the system
      - Involves both an ordering and a disordering process
      - The disordering process are usually dominant

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Second Law of Thermodynamics

- Unlike enthalpy, when considering entropy changes in processes, we must consider the system and the surroundings
- The total change in entropy for a process is termed the entropy change of the universe (ΔS_{univ})
  - This takes into consideration the entropy change of the system and the surroundings
- $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$
- In any reversible (equilibrium) process
  - $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$
- In any irreversible (spontaneous) process
- $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$
  - The disorder of the universe increases
  - Therefore, a spontaneous chemical reaction that decreases the disorder of the system must increase the disorder of the universe by an equal or greater amount

Gibb's Free Energy

Quantifying Entropy

- Unlike enthalpy changes, there is no easy or direct way to measure entropy changes for reactions.
  - Instead, using experimental data, we can calculate absolute entropy values for substances at given temperatures
- Standard molar entropies
  - S°
- J/mol-K
- Guidelines
  - S° of elements are not zero (unlike enthalpies of formation)
  - S° for gases is greater than liquids or solids
  - S° tends to increase with greater molar mass
  - S° tends to increase with the number of atoms in a formula unit
  - S° tends to increase with elongation
- $\Delta S^\circ = \sum nS^\circ_{(products)} - \sum nS^\circ_{(reactants)}$

Gibb's Free Energy

Sample Problem

- Calculate the ΔS° for the synthesis of ammonia from $N_{2(g)}$ and $H_{2(g)}$.

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- 19.1/19.3a&c/19.4/19.6/19.11/19.15/19.19/19.23a/19.27a&c