

# The Second Law

- The entropy change for a system is the change in heat absorbed during a reversible process divided by the temperature of that change.

$$\Delta S = \int \frac{dq_{rev}}{T}$$

- Formally, the second law of thermodynamics states that for any change the total entropy change is greater than or equal to zero:

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} \geq 0, \text{ or } \Delta S_{tot} \geq \int \frac{dq}{T}$$

# The Second Law

- Alternative statements:

$$\Delta S_{sys} \geq \int \frac{dq_{irrev}}{T}$$

“Heat cannot be spontaneously transferred from a cold object to a hot object.”

“Entropy must increase or remain constant in an isolated system.”

“You can’t create a perpetual motion machine.”

# Standard State Entropies

- Same idea as enthalpies: define a standard state and operate relative to that

$$\Delta S^0 = S_{obs} - S_{ref}$$

- Any property of  $\Delta S$  is a property of  $\Delta S^0$  (or  $\Delta \bar{S}^0$ ):

$$\Delta S^0(T_2) - \Delta S^0(T_1) = C_P \ln \left( \frac{T_2}{T_1} \right)$$

- Reference state for entropy is  $S$  at 0 K (more on that later)

# Summary: Entropy Changes

- Temperature (also true for  $C_V$  at const.  $V$ )

$$S(T_2) - S(T_1) = C_P \ln \left( \frac{T_2}{T_1} \right)$$

- Phase Change

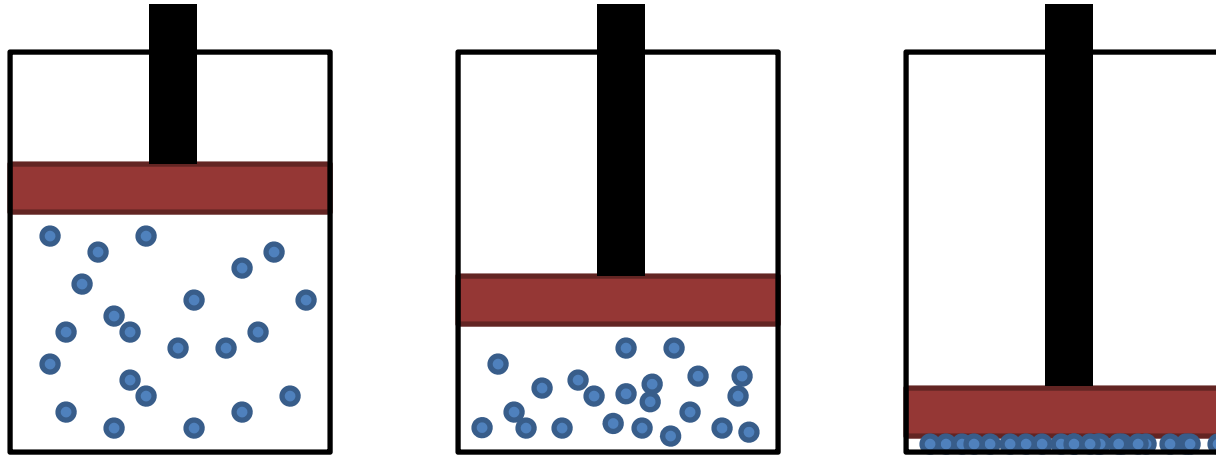
$$\Delta S_{tr}(T_{tr}) = \frac{\Delta H_{tr}(T_{tr})}{T_{tr}}$$

- Pressure Change

- Approximately zero for solids, liquids

- Ideal gasses at constant  $T$ :  $\Delta S = -nR \ln \left( \frac{P_2}{P_1} \right) = nR \ln \left( \frac{V_2}{V_1} \right)$

# Molecular Interpretation of Entropy



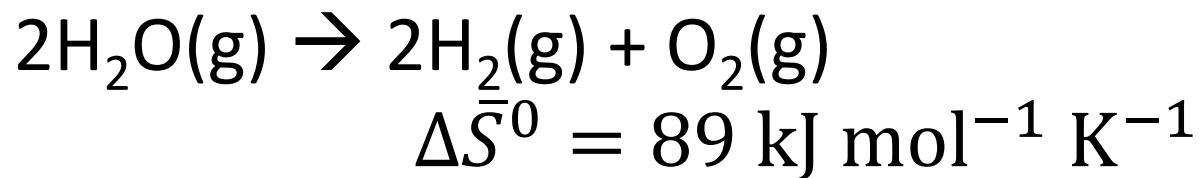
Many configurations for gas molecules

Fewer configurations for gas molecules

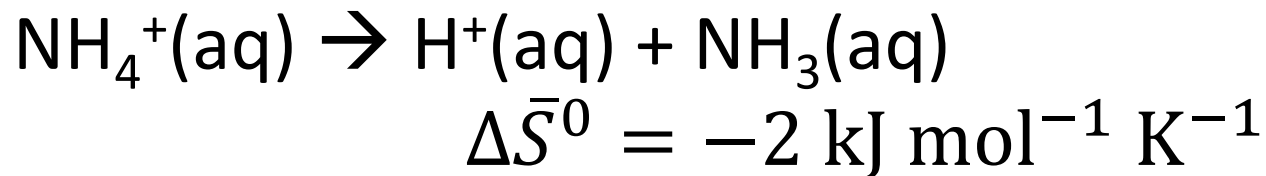
- *Entropy is a measure of the number of microscopic configurations a system can have while maintaining the same macroscopic properties (volume, temp., density, etc.)*

# Predicting Entropic Changes

- Using concept of disorder, we can often predict sign of entropy

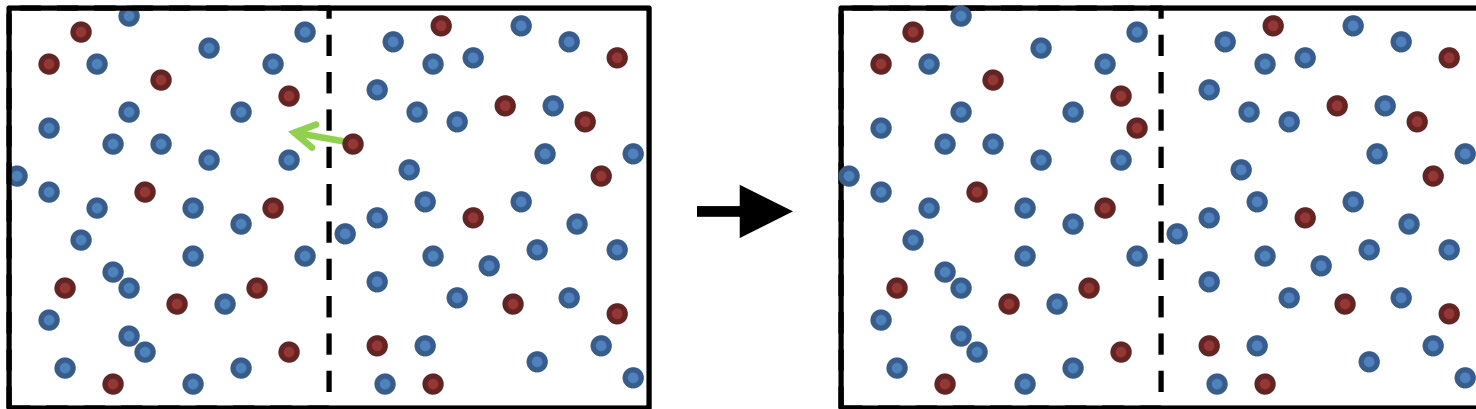


- Hard to predict total changes in aqueous solution (system + surroundings) because water can become ordered or disordered



# Is the Second Law Always True?

- Consider a microscopic fluctuation, caused by random (Brownian) motion:



- The red molecules are no longer evenly distributed

# Introduction: Gibbs Energy

- **Recall:** Any combination of state variables is also a state variable

$$G \equiv H - TS = E + PV - TS$$

- Any change in G can be represented as before:

$$\Delta G = \Delta H - \Delta(TS)$$

- Additionally, let's no longer assume only P, V work:

$$dw = -P_{ex}\Delta V + dw_{rev}^*$$

# Implications: $\Delta G$ at const. T, P

- In a chemical reaction, some work is required to change volume a small amount
  - This is not *useful* work to a chemist
- $\Delta G$  is the (useful) work done *by* the system for a given process
  - The inverse,  $-\Delta G$  is the maximum amount of useful work the system can do on the surroundings
  - Irreversible work is not as efficient

# Implications: $\Delta G$ at const. T, P

- If  $\Delta G = 0$  for a process:
  - System can do no (non-PV) work on surroundings
  - Equilibrium state
- If  $\Delta G > 0$  for a process:
  - Work done by surroundings is negative; work is required to complete process
  - Process is not spontaneous (it needs work)
- If  $\Delta G < 0$  for a process:
  - Work done on surroundings is positive  
( $-dw_{rev}^* > 0$ )
  - Process occurs spontaneously (no work needed)

# Implications: $\Delta G$ at const. T, P

- If we know  $\Delta H$  and  $\Delta S$  for any process at constant T, P (or  $\Delta H^0$  and  $\Delta S^0$ )

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

and

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

- Follows directly from the definition of G