April 8, 2019 : Thermodynamics Pt. 2 Chp. 19

2nd Law of Thermodynamics: Entropy/disorder of system + surrounding / the universe increases in a spontaneous process : $\Delta S_{universe} > 0$

- Entropy(S): measure of randomness/multiplicity (ways to arrange system)
- State function: Path independent : $\Delta S = S_{final} - S_{initial}$

3rd law of thermodynamics: entropy of a pure crystalline substance at absolute zero is 0 (1 way to arrange means its at abs. 0)

- All motion stops at absolute zero
- only one way to arrange a perfect crystal

$S = k \ln W$

- $T > 0$ is always true in the real world : 3rd law is mostly theoretical

Standard Molar Entropy — related to molecular size

- Standard molar entropy values for elements are all positive at 298k ← more molecular motion
- SME for gases is generally greater than for liquids & solids
- SME increase with molar mass & # of atoms in a formula
- Entropy changes for a chemical reaction can be calculated:

$\Delta S°_{system} = \Sigma n \Delta S°(products) - \Sigma m \Delta S°(reactants)$

n and m: coefficients in the balanced chemical equation

Predicting Entropy — more uncertainty $S°(g) > S°(l) > S°(s)$

- Entropy increases with freedom of motion of molecules
- Effect of volume on the entropy of a gas
  - Increase in volume → more positions possible for molecules
    - ↳ more microstates + (by extension) increased entropy
- Effect of temperature on the entropy of a gas
  - Increase temperature → average kinetic energy increases
    - ↳ more microstates & increased entropy
- Entropy increases with size and complexity: more uncertainty
- Entropy increases for processes involving:
  - Increasing # of molecules during a chemical reaction
  - Formation of gases from either solids or liquids
  - Formation of liquids or solutions from solids

Calculating ΔS_{system} — heat comes from surroundings

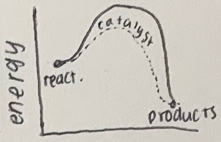
- Entropy can be calculated from SMEs of products − reactants
- " as heat transferred reversibly to the system at temperature T: $\Delta S = \frac{q_{rev}}{T} = \frac{\text{reverse process}}{\text{temperature}}$

When you go from a solid to liquid, you are breaking intermolecular forces
higher temp = more ~~entropy~~ energy = breaking of H+ bonds

Zeroth Law of Thermodynamics: 2 bodies in contact reach thermal equilibrium, w/ heat flowing from warm → cool object

Reversible Heat Flow

- If system + surroundings have small temp. differential, then heat will flow from warm → cool w/ NO ENERGY LOSS
- only theoretical bc it would have to occur infinitely slowly



chemical rxn of chemical change

Standard Molar Entropy

- Increases with molecular complexity
  - More atoms = more bonds = higher entropy

$\Delta S°_{system} = \Sigma n \Delta S°(products) - \Sigma m \Delta S°(reactants)$

- only at 298 K

predicts the $\Delta S°$ for the following reaction at 298k

$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$ - pretty sure SME for all is $\neq 0$

$\Delta S° < 0$, entropically unfavorable

If positive entropy change = more disorder/multiplicity
" negative entropy change = more orderly, less uncertainty

- we have g → ℓ, which is ~~less~~ orderly (more so)
- also have 3 moles (2+1) → 2 moles, also more orderly

$(2\,mol\,H_2O_{(\ell)} \times 70\,J/K\,mol) - (2\,mol\,H_{2(g)} \times 131\,J/K\,mol) - (1\,mol\,O_{2(g)} \times 205\,J/K\,mol)$

$-327\,J/K$ ← negative: more orderly system

Ex. $2NO_2(g) \rightarrow 2NO_{(g)} + O_2(g)$: expect positive $\Delta S°$ bc more molecules in products than reactants

$(2\,mol\,NO_{(g)} \times 211\,J/K\,mol) + (1\,mol\,O_{2(g)} \times 205\,J/K\,mol) - (2\,mol\,NO_{2(g)} \times 240\,J/K\,mol)$

$422 + 205 - 480 = +147\,J/K$ - assumption was correct!

Entropy increases with size + complexity

Neeeeee 0 vs

No

Predict the $\Delta S°$ for the rxn $6H_2O_{(g)} + 6CO_{2(g)} \rightarrow 6O_{2(g)} + C_6H_{12}O_{6(s)}$ (photosynthesis)

$\Delta S° < 0$: entropically unfavorable, but energy from sun

What is ΔS for an ice cube melting at 0°C? (heat comes from surrounding)

$\Delta H_{fusion} = +6.01\,KJ/mol$, 28 g of ice (1.56 mol)

$\Delta S = \frac{q_{rev}}{T} = \frac{\Delta H_{fusion}}{T} = \frac{6.01\,KJ/mol \times 1.56\,mol}{273} = 34.3\,J/K$

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} = 34.3\,J/K + (-34.3\,J/K) = 0$, reversible

If spontaneous, $\Delta S > 0$