

Totally Epic AP Chem Review: Thermodynamics!

Entropy: Let the chaos begin!

Entropy can be considered the extent of randomness or disorder in a chemical or physical system. The more positions available (the more space, or more places something can move) the greater the entropy.

The entropy change for a system (Δ) is calculated from the absolute entropies of the products and reactants.

$$\Delta S_{\text{system}}^{\circ} = \sum [S^{\circ}(\text{products})] - \sum [S^{\circ}(\text{reactants})]$$

Units of Entropy: $\frac{\text{J}}{\text{mol}\cdot\text{K}} = \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

*Note: Entropy of element in most stable form is NOT zero!!

→ The entropy of a perfect, pure crystal at 0K is given a value of zero,

→ All absolute entropies for individual substances in the real world, are + → even elements!

Two biggest factors for evaluating ΔS_{rxn}

1) Change in state of matter (gas \gg aqueous $>$ liquid $>$ solid)

2) Change in # of particles (↑ particles = ↑ places for particles to be = ↑ entropy)

In order of lowest to highest entropy:

Solids < Liquids < Aqueous solutions << Gases < More moles of Gas

Thermodynamically Favorable Processes

Neither *entropy* (ΔS) nor *enthalpy* (ΔH) can tell us if a reaction is thermodynamically favored → must use some combination of the two: Gibb's Free Energy!

ΔG (Gibb's free energy) represents the amount of useful work that can be obtained from a process at constant temperature and pressure. "Free" energy refers to the amount of energy available to do work once you have "paid your price" to entropy.

$$\Delta G_{\text{reaction}}^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

T = temperature in Kelvin

ΔH = enthalpy change (usually has units of kJ/mol or kJ mol⁻¹)

ΔS = entropy change (usually has units of J/(mol K) or J mol⁻¹ K⁻¹)

Notice difference in units! You must make both units the same (J or kJ) before you calculate ΔG .

The sign of ΔG tells if any given process is thermodynamically favored:

If ΔG is	The Process Is	Term
Negative (-)	Thermodynamically favored (spontaneous)	Exergonic
Positive (+)	Not thermodynamically favored (reverse reaction is spontaneous)	Endergonic
Zero (0)	At equilibrium	

You can also calculate the standard Gibbs Free Energy Change for a reaction by comparing the standard free energy of formation of reactants and products: this should look very familiar!

$$\Delta G_{\text{reaction}}^{\circ} = \sum [G_f^{\circ}(\text{products})] - \sum [G_f^{\circ}(\text{reactants})]$$

Note: Elements DO have a value of zero for ΔG° , because forming an element from itself results in no change.

Elements ARE zero for: $\Delta H, \Delta G$
 Elements are NOT zero for: ΔS

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

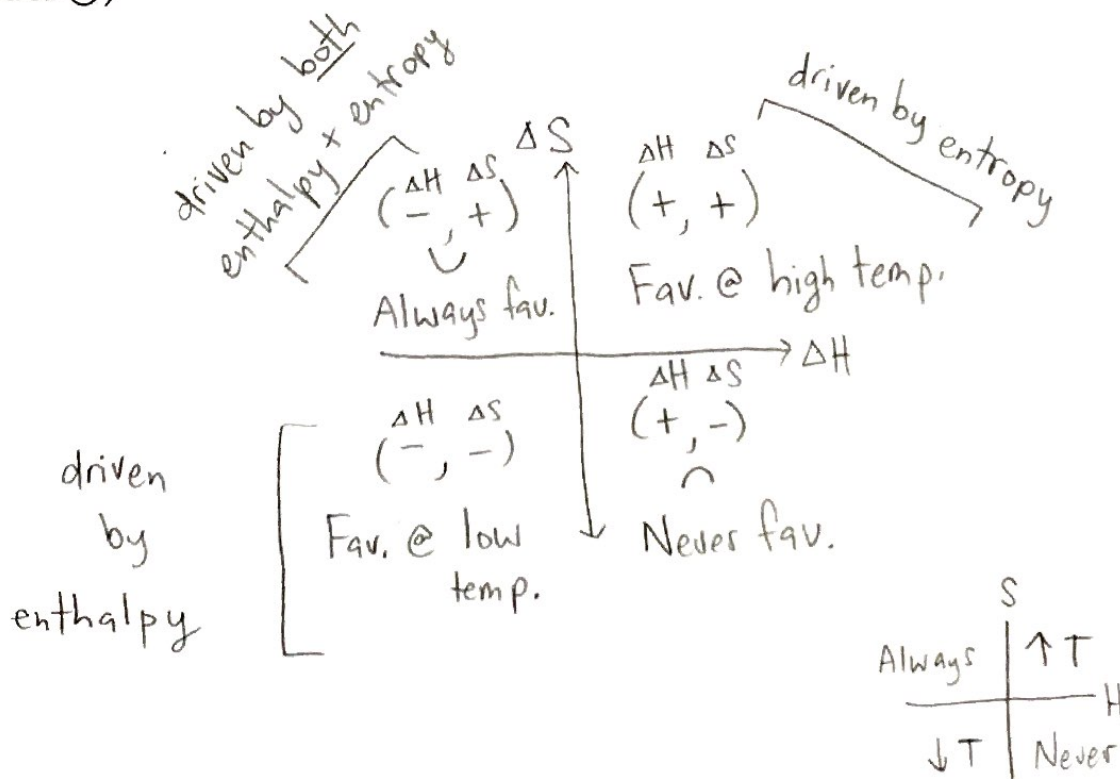
What does it mean when a reaction is "driven" by enthalpy, entropy, or both?

Nature favors:

1. $+\Delta S$ (increasing entropy, greater disorder)
2. $-\Delta H$ (exothermic, release of energy)

- **Driven by enthalpy:** a very exothermic reaction ($-\Delta H$) overcomes a decrease in entropy ($-\Delta S$)
- **Driven by entropy:** an endothermic reaction ($+\Delta H$) occurs spontaneously because of a very $+\Delta S$

You can use the signs of ΔS and ΔH (together with the reaction $\Delta G = \Delta H - T\Delta S$) to predict qualitatively the spontaneity of a given reaction. You can show this graphically, which leads to the best graph of all time (but SHHHH! It's a secret. 😊)



Connections to Electrochem and Equilibrium

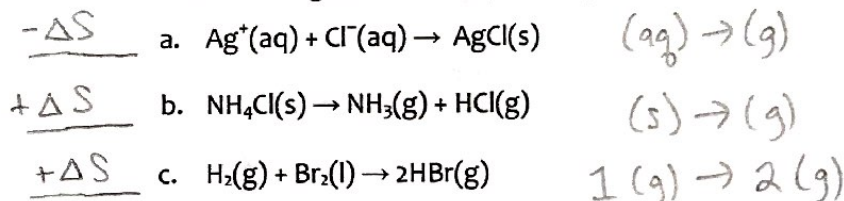
$$\Delta G^\circ = -n \mathcal{F} E^\circ$$

$$\Delta G^\circ = -RT \ln K$$

ΔG°	K	E°
0	at equilibrium	0
negative	>1, products favored	+
positive	<1, reactants favored	-

Let's Practice!

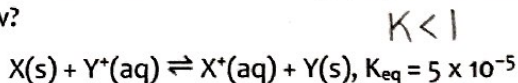
1. Predict the sign of the entropy change for each of the following reactions:



2. Which of the following is true concerning the reaction where two chlorine atoms form one chlorine molecule, as shown in the following equation: $2 \text{Cl}(\text{g}) \rightarrow \text{Cl}_2(\text{g})$?

- a. This reaction is driven by enthalpy: the large negative ΔH overcomes a positive ΔS .
- b. This reaction is driven by enthalpy: the large negative ΔH overcomes a negative ΔS .
- c. This reaction is driven by entropy: the large positive ΔS overcomes a positive ΔH .
- d. This reaction is driven by entropy: the large positive ΔS overcomes a negative ΔH .

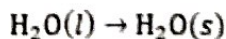
3. Which of the following correctly describes the standard voltage, E° , and the standard free energy change, ΔG° , for the reaction represented below?



- a. E° and ΔG° are both positive.
- b. E° and ΔG° are both negative.
- c. E° is positive and ΔG° is negative.
- d. E° is negative and ΔG° is positive.
- e. E° and ΔG° are both zero.

4. A given reaction, $\text{X}_2(\text{g}) + \text{Y}_2(\text{g}) \rightarrow 2 \text{XY}(\text{g})$, is not thermodynamically favorable at 298 K. However, at higher temperatures the reaction becomes spontaneous. Which of the following is true at 298 K?

	ΔH	ΔS	ΔG
<input checked="" type="radio"/> a.	+	+	+
b.	-	-	-
c.	+	-	+
d.	+	+	-



5. Which of the following is true for the above reaction? $\times @ 25^\circ\text{C}?$

- a. The value of ΔS is positive.
- b. The value of ΔG is positive.
- c. The value of ΔH is positive.
- d. The reaction is favored at 1.0 atm and 298 K.