Equilibria,  $\Delta G$ ,  $\Delta H$  and  $\Delta S$ 

In a wide range of situations, we will see that understanding  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  can help us understand where an equilibrium lies and often allow us to control whether the reactants or products are favored.

For some of you, a little algebra might be helpful. (Or just skip to "**What it means**".) The relevant equations are:

 $\Delta G = -RT \ln(K_{eq})$  $\Delta G = \Delta H - T\Delta S$ 

or combining the two equations:

 $\Delta H - T\Delta S = -RT \ln(K_{eq})$ 

Where:

 $\Delta G$  is the change in free energy

 $K_{eq}$  is the equilibrium constant (remember  $K_{eq} = [products]/[reactants]$ 

 $\Delta \dot{H}$  is the change in enthalpy from reactants to products

 $\Delta S$  is the change in entropy (disorder) from reactants to products

R is the gas constant (always positive)

T is the absolute temperature (Kelvin, always positive)

## What it means:

If  $\Delta H$  is negative, this means that the reaction gives off heat from reactants to products. This is favorable.

If  $\Delta S$  is positive, this means that the disorder of the universe is increasing from reactants to products. This is also favorable and it often means making more molecules.

Let's look at this from a qualitative point of view. Consider a reaction that favors products at equilibrium. Doing the math,  $K_{eq} > 1$ ; therefore  $ln(K_{eq}) > 0$  (a positive number), and because R > 0 and T > 0,  $\Delta G < 0$  (a negative number).

Therefore, if  $\Delta G$  is a negative number, the reaction favors products.

What must be true for  $\Delta G$  to be negative and products to be favored?

 $\Delta \mathbf{G} = \Delta \mathbf{H} - \mathbf{T} \Delta \mathbf{S}$ 

- a)  $\Delta H$  is negative and  $\Delta S$  is positive (then both contribute to making  $\Delta G$  negative), for example:  $C_3H_8 + 5 O_2 \rightarrow 3 CO_2 + 4 H_2O$ burning propane gives off heat and makes more molecules.
- b)  $\Delta H$  is negative and  $\Delta S$  is also negative but T is small enough, for example: water<sub>lgas</sub>  $\rightarrow$  water<sub>liquid</sub> Liquid water is more ordered; condensing water releases heat (thunderstorms).
- c) ΔH is positive, but ΔS is positive and T is large enough. for example: CaCO<sub>3</sub> → CaO + CO<sub>2</sub>
  It requires adding heat limestone (heating to high temperatures) to drive off CO<sub>2</sub>, but it makes more molecules.

For reaction type a, the reaction favors products and chemists cannot control it.

For reaction of either type b or c, simply changing the temperature can change the position of the equilibrium. (But from experience, you knew this anyway!)

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Let's look at a familiar example – the equilibrium between liquid water and water vapor.

H <sub>2</sub> O <sub>liquid</sub>	H <sub>2</sub> O gas
more stable	less stable
favored by $\Delta H$	favored by $\Delta S$

Above 100° C, at atmospheric pressure, the equilibrium is entirely to water vapor; that is what the boiling point means. Below the boiling point, both are in equilibrium. Evaporation of water cools things off (think about swamp coolers or sweat). Condensation of water warms things up (not so obvious, but this is where the energy in thunderstorms comes from, or why the temperature doesn't drop as much when there is dew in the morning, or why a glass of ice water warms up faster in a humid climate, when water condensed on it). All of these observations fit into the equilibrium picture.

Now, imagine what happens to your skin, when there is an equilibrium between liquid water and water vapor, but the wind blows. The wind carries away those water molecules in the gas phase, and the system seeks to restore equilibrium (Le Chatlier's principle). To do this, it needs to take molecules from the liquid and turn then into vapor (favored by entropy – more disorder -  $\Delta S > 0$ ). But liquid water is held together by strong hydrogen bonds. To make vapor requires breaking them, taking heat from the environment ( $\Delta H > 0$ ). This means that your skin cools off.



Note that at higher temperature, the equilibrium will be shifted towards the gas (-T $\Delta$ S becomes larger). Above 100° C and at atmospheric pressure, entropy wins and there is no liquid water at equilibrium.

Consider the reverse – water vapor condensing in the clouds. What has to happen here is that as hydrogen bonds form,  $\Delta H < 0$ , heat is given off. This heat is the source of the energy in thunderstorms.