

# AP Chemistry Unit 6 Review

## Equilibrium

Honors Lecture Notes: Unit 5

### Definitions

Most reactions are not one way; typically both the forward and the reverse reactions are occurring simultaneously. When the rates of the forward and reverse reaction rates are equal, equilibrium is achieved. This does not mean the reaction stops, but it does mean the concentration of the various species is remaining constant.

### Equilibrium Constant

The equilibrium constant,  $K_{eq}$ , is calculated as follows:

For:  $A(s) + 2 B(aq) \rightleftharpoons C(g) + 3 D(aq)$   $K_{eq} = \frac{[C][D]^3}{[B]^2}$

Note that solids and liquids do not appear in  $K_{eq}$ . If  $K_{eq} > 1$ , the reaction is favored. If  $K_{eq} < 1$ , the reaction is not favored. There are many variants on the equilibrium constant. The two most common are  $K_c$ , which utilized concentrations, and  $K_p$ , which utilizes partial pressures.

### Manipulating $K_{eq}$

When an equation is manipulated, the  $K_{eq}$  values also changes. There are three rules regarding this:

- 1) If you flip the reaction, you take the inverse of  $K_{eq}$
- 2) If you multiply the coefficients on the reaction by any value, you turn that value into an exponent of the  $K_{eq}$
- 3) If you combine two reactions, the  $K_{eq}$  of the new reaction will be the product for the  $K_{eq}$  values of the initial reactions

Given:  $H_2(g) + S(s) \rightleftharpoons H_2S(g)$   $K_{eq} = 9.8 \times 10^5$

$H_2S(g) \rightleftharpoons H_2(g) + S(s)$   $K_{eq} = 1/(9.8 \times 10^5) = 1.0 \times 10^{-6}$

$2 H_2(g) + 2 S(s) \rightleftharpoons 2 H_2S(g)$   $K_{eq} (9.8 \times 10^5)^2 = 9.8 \times 10^{10}$

### Gibbs and $K_{eq}$

The equation which relates Gibbs free energy and  $K_{eq}$  is:

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

$\Delta G$  is in J/mol

$R$  is 8.31 J/mol \* K

$T$  is in Kelvins

$K$  is unitless

As a summary, the three ways favorability (spontaneity) is measured are:

|                  | Favored        | Non-Favored |
|------------------|----------------|-------------|
| $\Delta G$       | Negative       | Positive    |
| $K$              | Greater than 1 | Less than 1 |
| $E^\circ_{cell}$ | Positive       | Negative    |

### Le Chatelier's Principle

When a system at equilibrium is exposed to stress, the system will "shift" in response to that stress in order to re-establish equilibrium. A shift is the increase of either the forward (right shift) or reverse (left shift) reaction rate. There are multiple types of stressors that can cause equilibrium shifts.

- 1) Concentration. If you increase the concentration of a product or reactant, the reaction will shift away from the increase. If you decrease the concentration of a product or reactant, the reaction will shift towards the decrease. Remember, solids and liquids do not appear in equilibrium expressions, so changing the amount of either of these will not change the concentrations or cause shifts.
- 2) Temperature. For exothermic reactions, heat is a product, and for endothermic reactions, heat is a reactant. Increasing temp shifts a reaction away from the side with the heat, and lowering temp shifts a reaction towards the side with the heat.
- 3) Pressure. If the pressure on a reaction is increased (often by decreasing the volume of the container), it shifts to the side with less gas molecules. If the pressure on a reaction is decrease, it shifts to the side with more gas molecules.

The only type of stressor that can actually change the value of the equilibrium constant is a temperature change, and the value would change in accordance with the shift (right shift = increased  $K$  and left shift = decreased  $K$ ). Concentration and pressure stressors do not change the value for  $K$ , and the equilibrium concentrations will eventually be reestablished.

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