## Equilibrium

Ron Robertson

## Basic ldeas

A. Extent of Reaction

Many reactions do not go to completion. Those that do not are reversible with a forward reaction and reverse reaction. To be really correct we need to indicate the reversibility with a double arrow when we write the reaction.
B. Equilibrium

When the rates of the forward and reverse reactions are equal, the concentrations do not change. This is the point of equilibrium. Equilibrium is a dynamic condition, not a static one.
C. The Reaction Quotient (Q) and the Equilibrium Constant (K)
We can define a special ratio of reactants and products called the reaction quotient $(\mathbf{Q})$. For the reaction:

$$
\mathbf{j} \mathbf{A}+\mathbf{k B} \leftrightarrow \mathbf{l} \mathbf{C}+\mathbf{m D}
$$

The reaction quotient $Q$ is defined as

$$
Q=\frac{[C]^{l}[D]^{m}}{[A]^{j}[B]^{k}}
$$

The brackets indicate concentrations in molarity units.
When the concentrations stop changing and the reaction is at equilibrium, then the reaction quotient becomes the Equilibrium Constant (K).

There are several types of equilibrium constants that we will explore in coming chapters but in general the following rules apply for the "practical" equilibrium constant talked about in this chapter:

1. Pure solids and liquids are not represented in the reaction quotient or equilibrium constants because their concentrations cannot change.
2. The units of the practical equilibrium constant are not usually given and depend on the reaction.
3. If gases are present we can express the concentrations of the gases in terms of partial pressures. This gives a slightly different equilibrium constant designated as $K_{p}$. Using the ideal gas law equation we see a relationship between pressure and concentration in moles/liter. The relationship between $K$ and $K_{p}$ is:

$$
\mathbf{K}_{\mathbf{p}}=\mathbf{K}(\mathbf{R T})^{\Delta \mathrm{n}}
$$

4. The value of the equilibrium constant does not depend on the concentrations or on the total pressure for gas phase reactions. It does depend on the temperature.

## Applications

The equilibrium constant allows us to predict:

- the tendency of a reaction to occur
- whether or not a set of concentrations represents equilibrium
- the equilibrium concentrations
- in what direction the reaction will occur from a given set of conditions
A. Tendency to occur

If $K>1$, then the forward reaction is favored and there are more products than reactants at equilibrium.
If $K<1$, then the reverse reaction is favored and there are more reactants than products at equilibrium.
B. Is the reaction at equilibrium?

This application is very simple to apply. Calculate the reaction quotient and see if the value equals the equilibrium constant. If the two are not equal, then the reaction is not at equilibrium.
C. What are the equilibrium concentrations?

Two types of problems are possible

- Given the equilibrium constant and all equilibrium concentrations except for one, the missing one can be solved for.
- Given the equilibrium constant and the initial concentrations it is possible to find the concentrations of all reactants and products at equilibrium. These problems can be complex.
D. In what direction is the reaction headed?
- If $\mathbf{Q}<K$ the reaction will shift to the right forming more products to attain equil.
- If $\mathbf{Q}>K$ the reaction will shift to the left forming more reactants to attain equil.
- If $\mathrm{Q}=\mathrm{K}$ then the reaction is at equil.


## Le Chatelier's Principle

If a change (stress) is applied to a system at equilibrium, the position of equilibrium will shift to alleviate the stress.
A. Concentrations (K does not change)

If a reactant or product is added to a system at equil, the system will shift away from the added component. If a reactant or product is removed, the system will shift toward the removed component. The value of $K$ does not change when this happens. The concentrations do change but in a way that restores the value of $K$.
B. Pressure (K does not change)

The increase or decrease of gas pressure due to the addition or removal of a nonreactive (inert) gas from the mixture does not change the point of equilibrium.
When the pressure of a particular reactant or product is increased or decreased the effect is like that for concentration.
C. Volume ( K does not change)

When the volume is decreased the reaction shifts in the direction of less moles of gaseous volume. If the volume is increased the reaction shifts in the direction of more moles of gaseous volume.
D. Temperature ( K does change)

If the temperature increases heat is being added to the system. Write the reaction using heat as a reactant or product (For an exothermic reaction, heat is a product; for an endothermic reaction, heat is a reactant.) Then an increase in temp will cause the reaction to shift away from the production of heat. A decrease in temp will cause the reaction to shift toward the production of heat.

