13.1 - Le Chatelier's Principle

Altering Reaction Parameters

So far we have dealt with reactions at equilibrium, and have made predictions of directional shifts by comparing the reaction quotient *Q* to the equilibrium coefficient *K*.
Industrial chemists tinker with other parameters to maximize their reaction outputs: the goal is to make as much of the chemical with the least amount of wasted material.
To do this, they alter reactant amounts, pressures, and temperatures and use Le Chatelier's Principle, which states: "If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change."

Changing Concentration

Any time a reactant or product is added to a system at equilibrium, the equilibrium position will shift in the direction that lowers the concentration of that component.
Thinking about it from a reaction rates perspective: increasing a reactant amount results in more collisions between that component and the other reactant, thus increasing the probability of product formation, and pushing the direction to the right.

Conversely, adding more product increases the probability of pushing the reaction left.

1. Concentration Example

Arsenic can be extracted from its ores by first reacting the ore wiht oxygen to form solid As4O6, which is then reduced by carbon:

$$As_4O_{6(s)} + 6C_{(s)} \rightleftharpoons As_{4(g)} + 6CO_{(g)}$$

Predict the direction of the shift in equilibrium for each of the following alterations of condition:

A. Addition of CO.

B. Addition of carbon.

C. Removal of gaseous arsenic.

1. Concentration Answer

$$As_4O_{6(s)} + 6C_{(s)} \rightleftharpoons As_{4(g)} + 6CO_{(g)}$$

A. Addition of CO will drive the reaction to the left - back toward reactants.

B. Addition of carbon will have no effect: the amount of a pure solid or liquid has no effect on the equilibrium position.

C. Removal of gaseous arsenic will drive the reaction to the right - more product will form as a response to its removal.

Changing Pressure

There are three ways to alter the pressure of a reaction:

A. Add or remove a gaseous reactant or product.

B. Add an inert gas (one not involved in the reaction).

C. Change the volume of the container.

We've already discussed changing reactant or product amounts, and the addition of an inert gas will not contribute to an equilibrium shift.

When the container volume is changed, however, things begin to happen. Firstly, the concentrations of the substances change, so a value of *Q* could be found, and compared to *K*.

Changing Pressure Continued

There's an easier way, however: focus on volume.

When a system's volume is reduced (and pressure increases), the reaction position will shift such that the total number of gaseous molecules decreases.

The converse is true - reducing pressure will generate more gas molecules.

2. Pressure Example

Predict the shift in equilibrium the following three reaction systems will undergo when volume is reduced:

A. $P_{4(s)} + 6\ Cl_{2(g)} \longleftrightarrow 4\ PCl_{3(l)}$

B. $PCl_{3(g)} + Cl_{2(g)} \longleftrightarrow PCl5_{(g)}$

C. $PCl_{3(g)} + 3\ NH_{3(g)} \longleftrightarrow P(NH_2)_{3(g)} + 3\ HCl_{(g)}$

2. Pressure Answer

A. $P_{4(s)} + 6\ Cl_{2(g)} \longleftrightarrow 4\ PCl_{3(l)}$
Since only chlorine is a gas, when the volume is decreased the reaction shifts right to minimize the amount of that gas.

B. $PCl_{3(g)} + Cl_{2(g)} \longleftrightarrow PCl5_{(g)}$
Here, there are two parts gas on the left, vs. one on the right. As volume is decreased, the reaction again shifts right to minimize pressure.

C. $PCl_{3(g)} + 3\ NH_{3(g)} \longleftrightarrow P(NH_2)_{3(g)} + 3\ HCl_{(g)}$
In this reaction, both sides of the equation have four parts gas. A change in pressure will not have an effect upon equilibrium.

Changing Temperature

So far we have dealt with changes that alter position, but changing temperature alters the equilibrium constant *K* itself.
Altering temperature works such that an exothermic reaction will shift left if heated (in the direction of energy consumption), but will shift right if cooled. Endothermic reactions are the opposite - producing more products if heated, and more reactants if cooled.

3. Temperature Example

For each of the reactions, predict how the value of *K* changes as temperature is increased.
A. $N_{2(g)} + O_{2(g)} \longleftrightarrow 2\ NO_{(g)}$ $\Delta H^o = 181$ kJ
B. $2\ SO_{2(g)} + O_{2(g)} \longleftrightarrow 2\ SO_{3(g)}$ $\Delta H^o = -198$ kJ

3. Temperature Answer

A. $N_{2(g)} + O_{2(g)} \longleftrightarrow 2\ NO_{(g)}$ $\Delta H^o = 181$ kJ
This is endothermic, as the positive enthalpy change shows. Energy can be viewed as a reactant, and *K* increases as the temperature increases - the reaction shifts right.

B. $2\ SO_{2(g)} + O_{2(g)} \longleftrightarrow 2\ SO_{3(g)}$ $\Delta H^o = -198$ kJ
This reaction is exothermic (energy can be regarded as a product), so heating it will drive the reaction left as *K* decreases.

Summary Example

Consider the following reaction, and choose whether the various changes shift it right, left or none:

$N_2O_{4(g)} \longleftrightarrow 2\ NO_{2(g)}$ $\Delta H^o = 58$ kJ

4.A. Addition of $N_2O_{4(g)}$.	Right
4.B. Addition of $NO_{2(g)}$.	Left
4.C. Removal of $N_2O_{4(g)}$.	Left
5.A. Removal of $NO_{2(g)}$.	Right
5.B. Addition of $He_{(g)}$.	None
5.C. Decrease in volume.	Left
6.A. Increase in volume.	Right
6.B. Increase temperature.	Right
6.C. Decrease temperature.	Left

Homework

13.7 Problems in your Booklet
Due: Next Class

Finish Unit 4.B Review Scan (Due: 12/13)
and Challenge Problems