Chemistry Lecture #88: Le Chatelier's Principle

Suppose we have a chemical reaction that is in equilibrium. The amount of reactant and product is constant, and the rate at which each is made is also constant. What would happen if we suddenly increased the amount of product or reactant? What would happen if product or reactant is removed?

According to Le Chatelier's principle, if a change is made to a system at equilibrium, the system will react to the change to try to restore the equilibrium. Wikipedia gives a pretty good definition of Le Chatelier's principle:

When any system at equilibrium is subjected to change in concentration, temperature, volume, or pressure, then the system readjusts itself to (partially) counteract the effect of the applied change and a new equilibrium is established.

In other words, whenever a system in equilibrium is disturbed, the system will adjust itself in such a way that the effect of the change will be nullified.

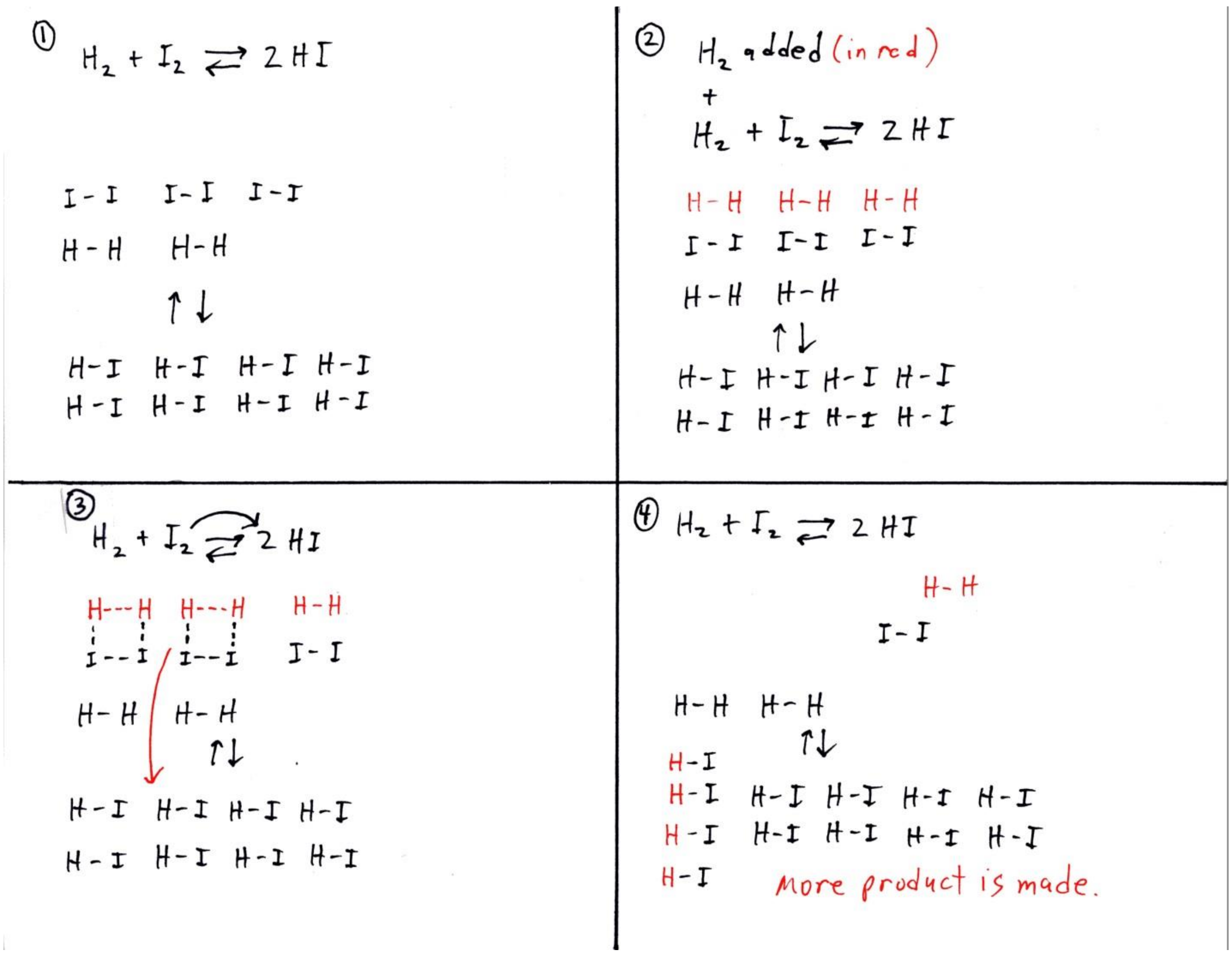
To illustrate, suppose we have the following chemical reaction occurring at equilibrium:

$H_2 + I_2 \rightleftharpoons 2HI$

All three substances, H_2 , I_2 , and HI are in the same container. All three substances collide with each other. Occasionally, H_2 and I_2 will collide to form HI. And occasionally, two HI molecules collide to form H_2 and I_2.

Now suppose we were to increase the amount of one of the reactants, H_2. Basically, we toss more H_2 into the container. How does the system react to this change or stress that has been added?

The following diagrams show what happens. Picture #1 shows the system at equilibrium. Picture #2 shows H_2 (in red) being added to the system. Picture #3 shows that when H_2 is added, it reacts with I_2 to produce HI. The equilibrium is being shifted to produce more HI as a response to the addition of H_2. Picture #4 shows that there is now more HI or product in the system.



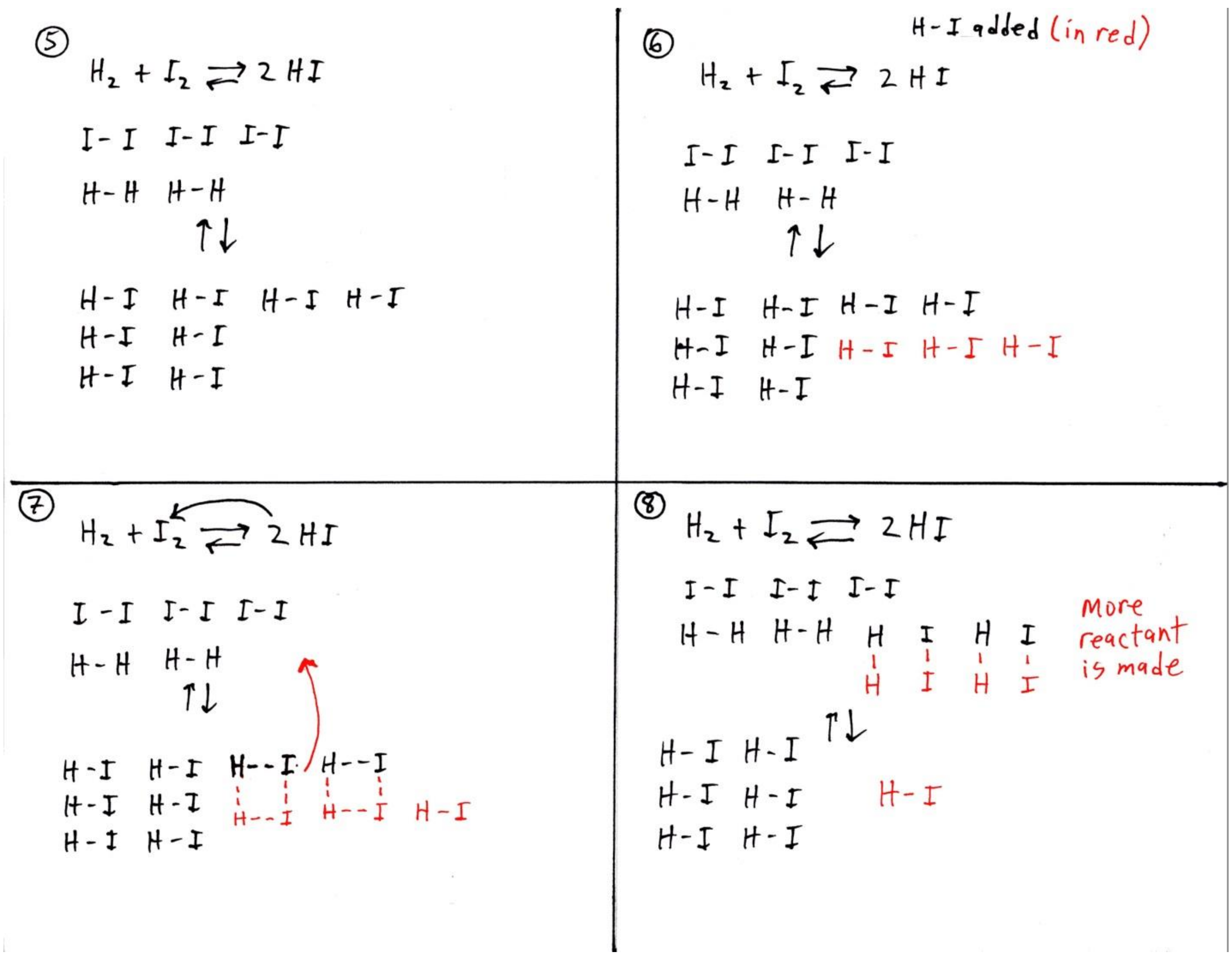
If reactant is added to a system at equilibrium, more product will be made. Or, the reaction will shift to the right.

A

+

$A + B \rightleftarrows C + D$

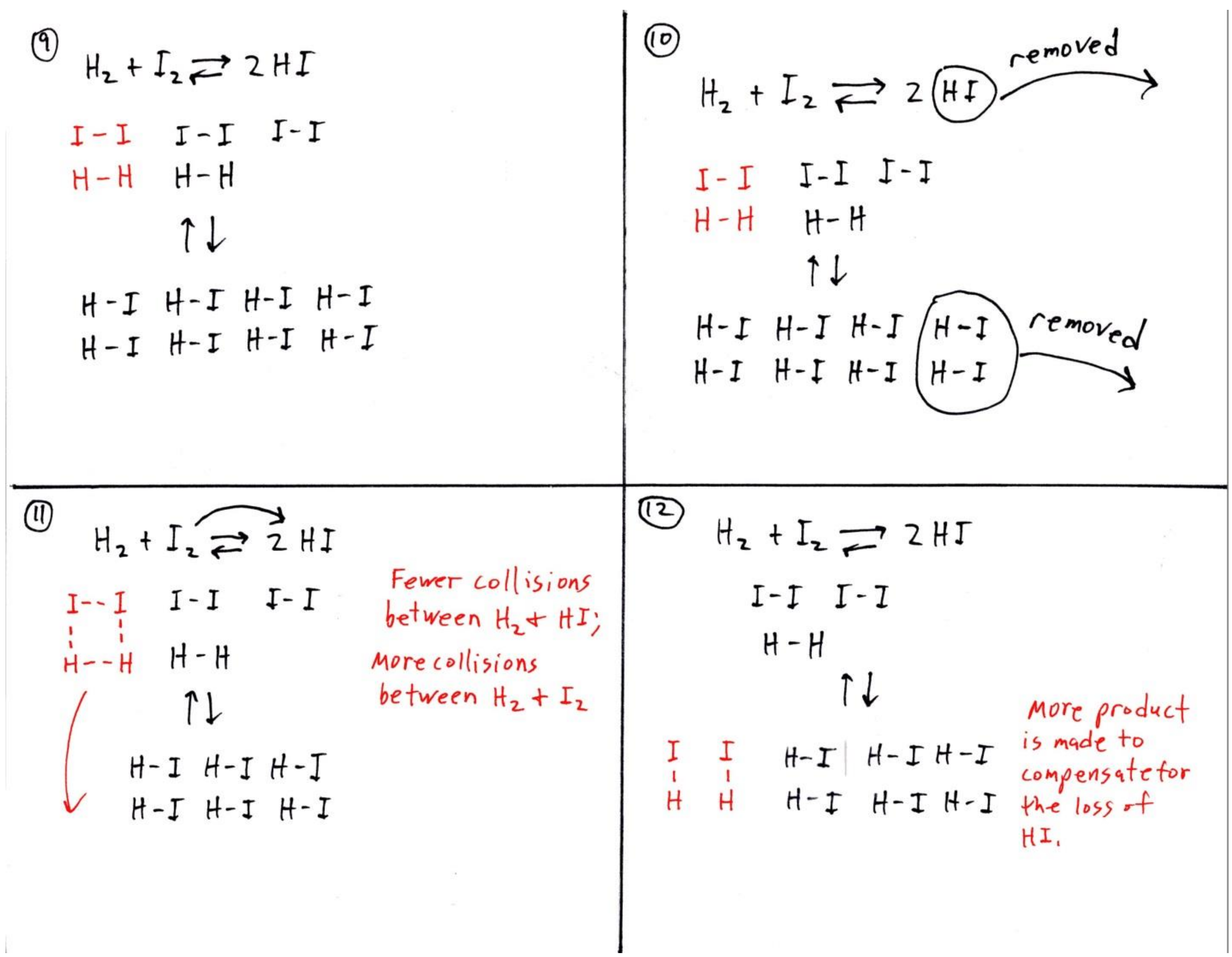
What would happen if we added HI or product to the system? Picture #5 shows the reaction at equilibrium. Picture #6 shows HI (in red) being added. Picture #7 shows that the addition of HI molecules causes them to react with each other and produce H_2 and I_2. The equilibrium is being shifted to the left to produce more H_2 and I_2 as a response to the addition of HI. Picture #8 shows that there are more reactants (H_2 and I_2) in the system.



If product is added to a system at equilibrium, more reactant will be made. Or, the reaction will shift to the left.

$$A + B \rightleftharpoons C + D \quad (+\, D)$$

What if we removed product or reactant from the system? Pictures #9-12 show what happens if we remove HI from the system. Picture #9 shows the system at equilibrium. Picture #10 shows the product, HI, being removed from the system. Picture #11 shows H_2 and I_2 reacting to form more HI to compensate for the loss of HI. The system is shifting to the right. Picture #12 shows that the HI has been replaced but there is less H_2 and I_2.



If product is removed from the system, the reactants will react to form more product. Or, the reaction shifts to the right.

$$A + B \rightleftharpoons C + D \xrightarrow{\text{removed}}$$

Why would the reaction shift to the right if product is removed? Remember that all the reactants and products are in one container and all of them are colliding with each other. If some HI is removed, there will be fewer collisions between HI and H_2. H_2 thus more likely to collide with other molecules, such as I_2. More collisions between H_2 and I_2 result in more product, HI, being made.

If reactant is removed from the system, the products will react to form more reactant. Or, the reaction shifts to the left.

removed

$$A + B \rightleftharpoons C + D$$

An endothermic reaction at equilibrium can be represented as

$$A + B + \text{energy} \rightleftharpoons C + D$$

Remember that an endothermic reaction absorbs energy; energy is added to the reactants. If we add energy to an endothermic reaction, the equilibrium will shift to the right.

energy

+

$$A + B + \text{energy} \rightleftharpoons C + D$$

If energy is removed from an endothermic reaction, the equilibrium will shift to the left.

remove

$$A + B + \text{energy} \rightleftharpoons C + D$$

An exothermic reaction at equilibrium can be represented as

$$A + B \rightleftharpoons C + D + \text{energy}$$

Remember that energy is produced in an exothermic reaction; energy can be considered as a product of the reaction.

If energy is added to an exothermic reaction, the equilibrium will shift to the left.

$$A + B \rightleftharpoons C + D + \overset{\substack{\text{energy}\\+}}{\text{energy}}$$

If energy is removed from an exothermic reaction, the equilibrium will shift to the right.

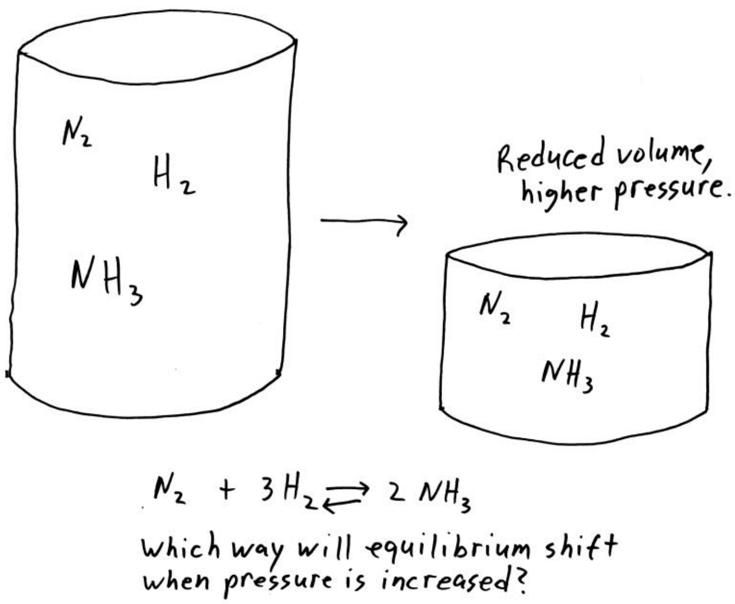
$$A + B \rightleftharpoons C + D + \text{energy} \xrightarrow{\text{removed}}$$

Pressure affects the equilibrium if the reactants and products are in the gaseous state. When pressure is increased, the reaction will shift in the direction of the fewest molecules.

For example, nitrogen gas (N_2) and hydrogen gas (H_2) can produce gaseous ammonia (NH_3).

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Suppose we have N_2, H_2, and NH_3 molecules in a container, and the above reaction is occurring at equilibrium. We then increase the pressure on these substances by reducing the volume of the container. Which way will the equilibrium shift?



On the left side of the arrows, there is one N_2 molecules and three H_2 molecules, giving us a total of 1 + 3 = 4 molecules on the left. On the right side of the arrows, there are two NH_3 molecules. At higher pressure, the equilibrium shifts to the fewest number of molecules, so the equilibrium will shift to the right.

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ at higher pressure.

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ + heat

NH_3 is an important substance since it is used to make nitrogen fertilizer. The Haber process is a method of increasing the yield of NH_3 in the above equilibrium reaction. In 1909, Fritz Haber increased the yield of NH_3 by increasing the pressure on the equilibrium reaction. He also removed some of the heat as it was generated in the reaction. Finally, he added a catalyst to the reaction to loosen the strong triple bond between the nitrogen atoms in N_2. Nitrogen gas is very unreactive, but adding a catalyst allowed the reaction to reach equilibrium more quickly.

Red cabbage juice can be used to demonstrate shifts in equilibrium. Red cabbage contains a pigment called anthocyanin that changes color in the presence of H^+ or OH^-. Below is a very simplified chemical equation showing how the color of anthocyanin (which we'll represent with the letter "R") changes as it combines with H^+ and OH^-.

$RH + OH^- \rightleftharpoons ROH + H^+$
Red/purple blue/green

If OH^- is added to the system, the equilibrium will shift right and the solution will turn from red/purple to blue/green. One way to increase the amount of OH^- is to add ammonia to the system.

If H^+ is added to the system, the equilibrium will shift to the left, and the solution will turn from blue/green to red/purple. One way to increase the amount of H^+ is to add vinegar to the system.

$RH + OH^- \rightleftharpoons ROH + H^+$

Red/purple blue/green

Below is a picture of some freshly squeezed red cabbage juice. The blue color indicates that there is probably more ROH (product) than reactant (RH).

The next picture shows what happens after vinegar, or H^+ is added. The pink color indicates that the equilibrium has shifted to the left.

The color can be changed back to the original blue shade if you increase the amount of OH^-. This can be done by adding ammonia to the mixture. The addition of ammonia shifts the equilibrium back to the right.