II) LeChatelier's Principle

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https://www.youtube.com/watch?v=7zuUV455zFs

What will happen if an equilibrium system is disturbed?
Possible disturbances include a change in concentration of one of the substances, a change of temperature, or a change in the pressure (essentially the concentration) of a gas, or the addition of a catalyst.
The French chemist LeChatelier developed a principle to help chemists predict the effect of a disturbance.
What is **LeChatelier's Principle**?
If an equilibrium system is subjected to a stress (change), processes will occur to shift the equilibrium to alleviate the stress, until a *new* equilibrium is established.
shift = direction FWD/RVS that will counteract the change.

Concentration Change: shift

Consider the following system at equilibrium:

↑ $2HI_{(g)} \Leftrightarrow H_{2(g)} + I_{2(g)}$

Now, let's subject the equilibrium to a change: the addition of more $HI_{(g)}$ to the system.
What substance initially increases in concentration? ↑[$HI_{(g)}$]
What does this affect the amount of collisions?
↑HI molec. ∴ ↑ over collisions. ∴ ↑ more effective collisions.
How does this affect the fwd and reverse reaction rates?
Temporarily the FWD rate will increase, while the reverse is initially not affected ...
If one rate is temporarily greater than the other, we say a shift is taking place, as concentrations are no longer constant. In the case above, shift to the **right** is taking place because the forward rate is temporarily ___greater___ than the reverse rate.

Therefore, products are being produced faster than they are being used (resulting in a net increase), so during a shift right, we say that products are **favoured**. This is LeChatelier's 'counteraction' (we added more reactant, but now the product concentration is increasing).

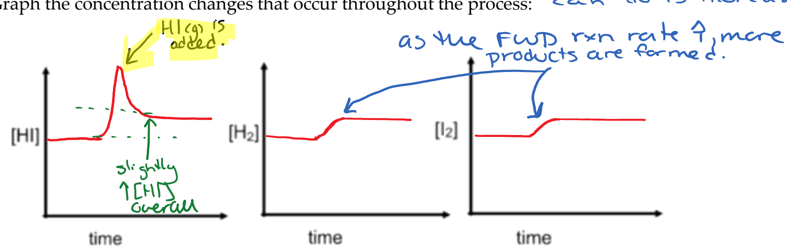
Since products start increasing in concentration, what will happen to the reverse rate? ↑[products] ∴ ↑ effective collisions ∴ ↑ reverse reaction rate.

Concurrently, since the reactant is being used up faster than it is being produced, what starts to happen to the forward rate?
as reactants get used up, the FWD rxn rate ↓

The reverse rate continues to increase and the forward rate continues to decrease until... they become equal, and a new equilibrium is established.

In summary: (b/c we added it)
[HI] initially ___increased___, then due to the shift right it (↑FWD rxn rate) ___decrease___, but overall is slightly ___increase___ (an initial change is always more drastic than a shift change).
[H_2] ___incresed___, and [I_2] ___increased___ due to the shift right. (products are favored)

So how is it possible that all of [HI], [H_2], and [I_2] increased? Because more HI(g) was added initially, there are more particles in the system, so all the [conc.] can do is increase.
Graph the concentration changes that occur throughout the process:



Draw a graph to show how forward and reverse rates change throughout the process:

↑[HIg] when HI(g) was added.

When a quantity of reactant or product is added to an equilibrium system, the system will shift to remove *some* of the added chemical.

When a quantity of reactant or product is removed from an equilibrium system, the system will shift to replace *some* of the removed chemical.

An **equilibrium system** is a reacting system that is at or approaching equilibrium. When we change the concentration of a reactant or a product, we "stress" the equilibrium system by temporarily destroying the equilibrium condition. When a system responds by changing some reactants into products, the response is referred to as a "**shift right**" because the products are on the right side of a chemical equation. When a system responds by changing some products into reactants, the response is called a "**shift left**."

Sample Problem 2.2.1(a) — Predicting How an Equilibrium System Will Respond to the Addition of Reactant or Product

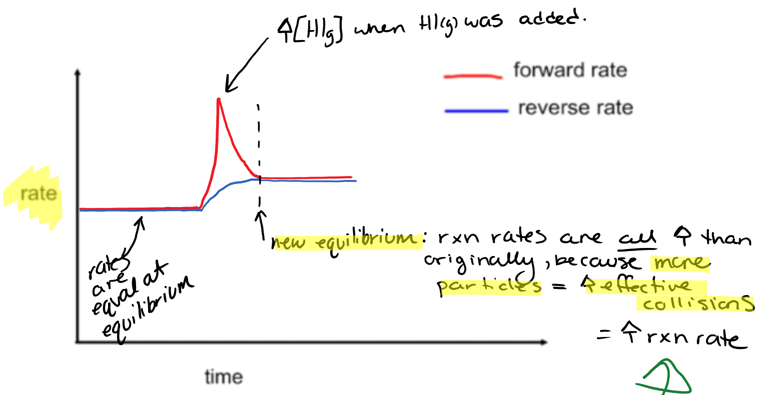
Some HI is added to the system below. In what direction will the system shift to restore equilibrium? When equilibrium is restored, how will the concentration of each substance compare to its concentration before the HI was added?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

What to Think About	How to Do It
1. Using Le Châtelier's principle, determine that the system will shift to remove some of the added HI.	The system must *shift left* (toward reactants) to consume some of the added HI.
2. Infer from Le Châtelier's principle that the shift left produces H_2 and I_2. Note that Le Châtelier's principle doesn't explicitly state what happens to the concentrations of H_2 and I_2, but you can infer what happens from your understanding of the principle	Since not all of the added HI will be removed, the [HI] will increase. The [H_2] and [I_2] will also increase

happens from your understanding of the principle

Draw a graph to show how forward and reverse rates change throughout the process:



How is it possible that both rates are now higher compared to the original equilibrium?

Summary using LeChatelier's Principle:
If an equilibrium is subjected to a change (stress: an ↑[HI]),
processes occur to counteract the change (shift RIGHT; ↓[HI]), until a
new equilibrium is established (rates are higher but equal again.)

Consider the same system at equilibrium: $2HI_{(g)} \Leftrightarrow H_{2(g)} + I_{2(g)}$
Explain what would occur if some $HI_{(g)}$ is removed from the system.
HI collisions would decrease.
Forward rate would decrease (less effective collisions)
Thus, reverse rate will be temporarily higher than the forward rate.
This will cause a shift LEFT •counteract the stress, meaning reactants (in order to produce more HI(g) and ↑FWD rate) will be favoured .
So for a time, due to the shift, [HI] will increase and $[H_2]$ and $[I_2]$ will decrease.
Eventually, the forward rate will start to increase and the reverse rate will decrease until they become equal
At this point, a new EQUILIBRIUM has been established.

In summary, [HI] initially decreased, then increased, but overall slightly decreased.
$[H_2]$ decreased and $[I_2]$ decreased.

How is it that all concentrations decrease?
Particles were removed originally (↓HI(g)) so the system has less particles overall
∴ all concentrations decrease.

Sample Problem 2.2.1(b) — Predicting How an Equilibrium System Will Respond to the Removal of Reactant or Product

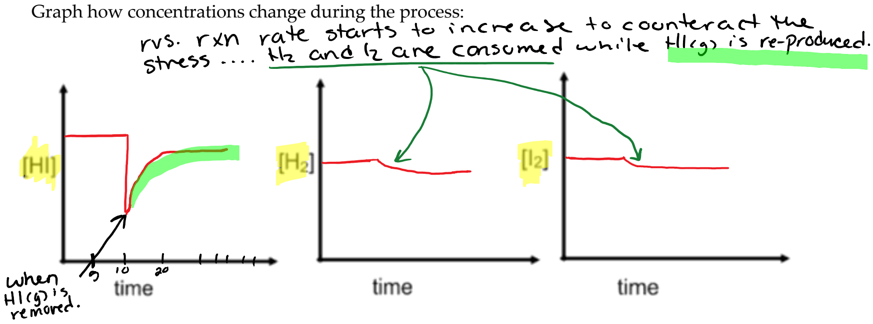
Some solid calcium hydroxide is in equilibrium with a saturated solution of its ions.

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,OH^-(aq)$$

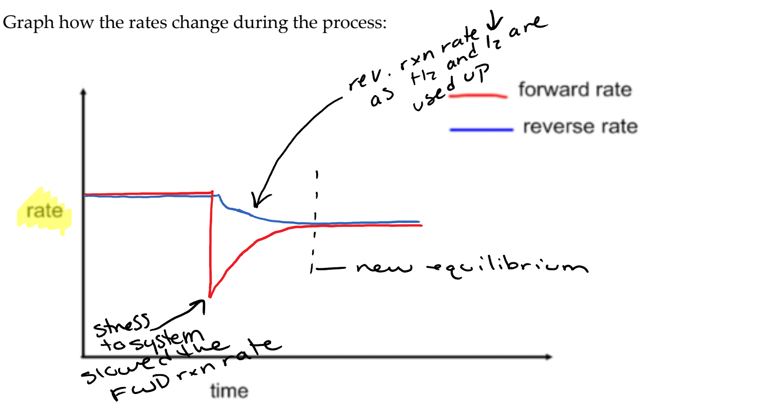
This is a solubility equilibrium. The rate of dissolving equals the rate of recrystallizing. Some OH^- is removed by adding some hydrochloric acid to the solution. (The H^+ in the acid neutralizes some OH^- to produce H_2O.) In what direction will the equilibrium shift? When equilibrium is restored, how will the calcium ion and the hydroxide ion concentrations compare to their concentrations before the acid was added?

What to Think About	How to Do It
1. Using Le Châtelier's principle, determine that the system will shift to replace some of the removed OH^-.	The system must shift right (towards products) to replace some of the removed OH^-.
2. Determine the effect of the shift right. The shift right also produces some Ca^{2+} and causes more of the $Ca(OH)_2(s)$ to dissolve.	Since not all of the removed OH^- is replaced, the $[OH^-]$ will decrease. The $[Ca^{2+}]$ will increase.

Graph how concentrations change during the process:



Graph how the rates change during the process:



LeChatelier's Principle:

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What was the initial change? decrease in $[HI]_{(g)}$ "reactant"
stress

What was the 'counteraction'? shift LEFT to favor reactants to temporarily produce more $HI_{(g)}$ (to ↑FWD rxn rate)
shift

Why was it a 'new' equilibrium? the new rates are slightly lower, but equal and the concentrations are constant.

Note: The 'counteraction' is always the… shift that is the result of the initial stress/disturbance.

Conclusion: Increasing the concentration of a substance causes a shift to the opposite side. Decreasing the concentration of a substance causes a shift to the same side.