Le Chatelier's Principle

- changes in factors such as temperature, pressure, concentration & catalyst can **upset the balance in rates** of the forward and reverse reactions of a system in equilibrium

Factors that upset an equilibrium system are referred to as STRESSES.

- stresses cause **changes to the reactant and product concentrations**
- net increase in [product] is called a **"shift to the right"**
- net increase in [reactant] is called a **"shift to the left"**
- Henri Louis Le Châtelier (1850-1936) studied the effects of changing conditions on equilibrium systems

Le Chatelier's Principle
When a stress is applied to a system **at equilibrium**, the system readjusts to **relieve or offset** the stress and the system reaches a **new state of equilibrium**.

- in other words, whatever we do to an equilibrium, the equilibrium will try to undo

Consider the following reaction:

$$2NO(g) + Cl_2(g) \rightleftarrows 2NOCl(g) + 76\ kJ$$

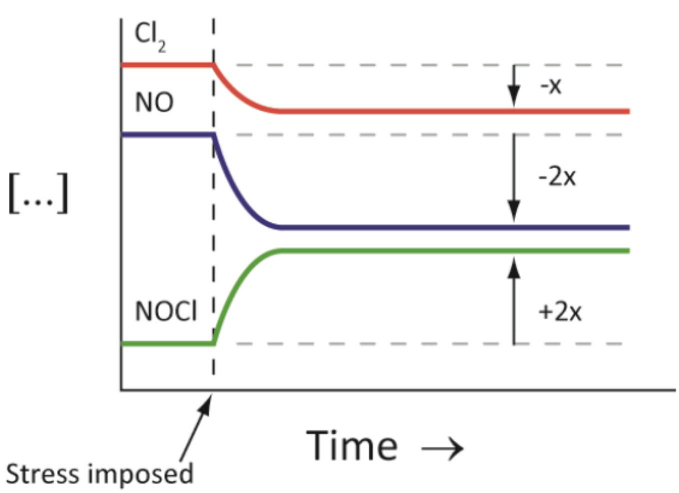
The effects of various **stresses** on a system at equilibrium can be summarized as follows:

1. **<u>Temperature</u>**

- if the temperature of the equilibrium is **decreased**, LCP predicts that the equilibrium **shifts to the right**

$$2NO(g) + Cl_2(g) \rightleftarrows 2NOCl(g) + \boxed{76\ kJ \downarrow}$$

- exothermic reaction **shifts to the right** to produce more heat
- the reverse reaction rate initially experiences a greater decrease because heat is a "reactant" in the reverse reaction
- as equilibrium is reversed, the reverse rate increases and forward rate decreases
- the net change is that both forward and reverse rates decrease



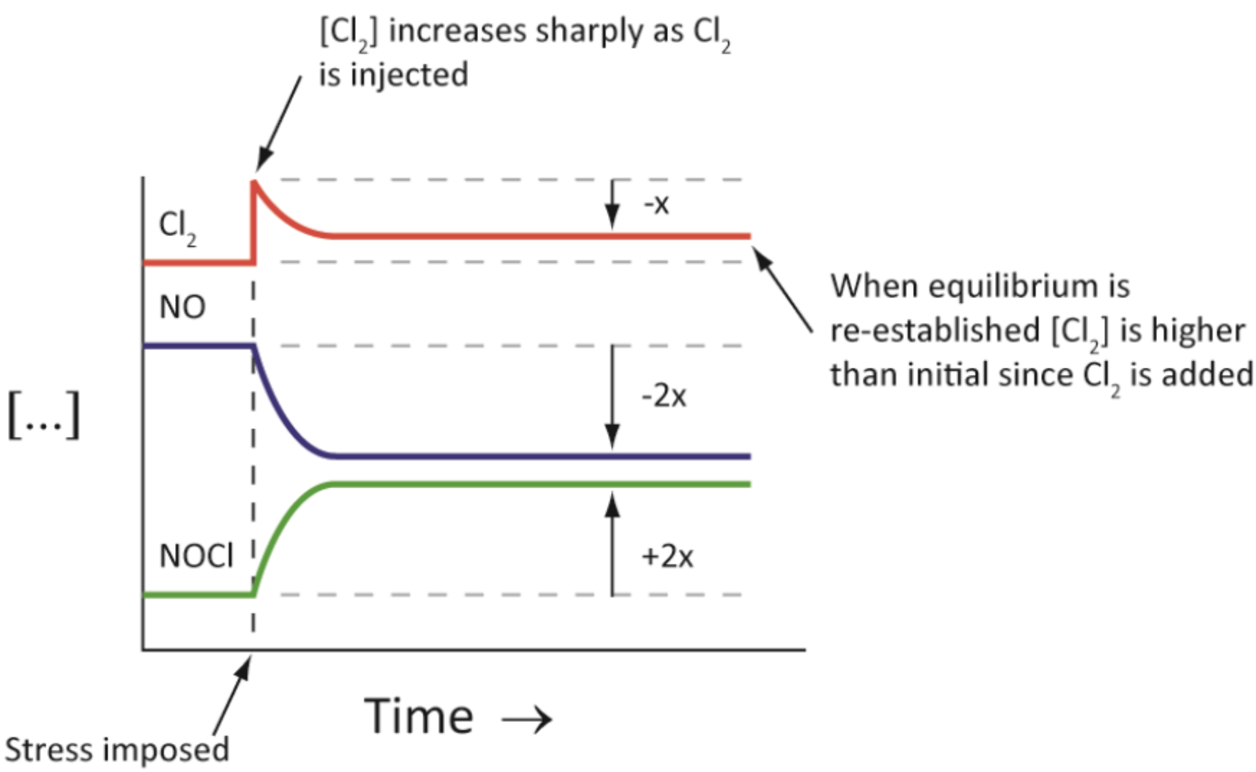
[NO] decreases twice as much as $[Cl_2]$ since 2:1 ratio from balanced equation

2. **<u>Concentration</u>**

- if the concentration of Cl_2 increases, LCP predicts that the equilibrium will shift to the right to use up the added Cl_2

$$2NO(g) + \boxed{Cl_2(g)\uparrow} \rightleftarrows 2NOCl(g) + 76\ kJ$$

- in terms of reaction rate, Cl_2 is a reactant in the forward reaction; increase $[Cl_2]$ increases forward reaction initially
- as equilibrium is re-established, forward rate decreases and reverse rate increases
- overall, both rates increase

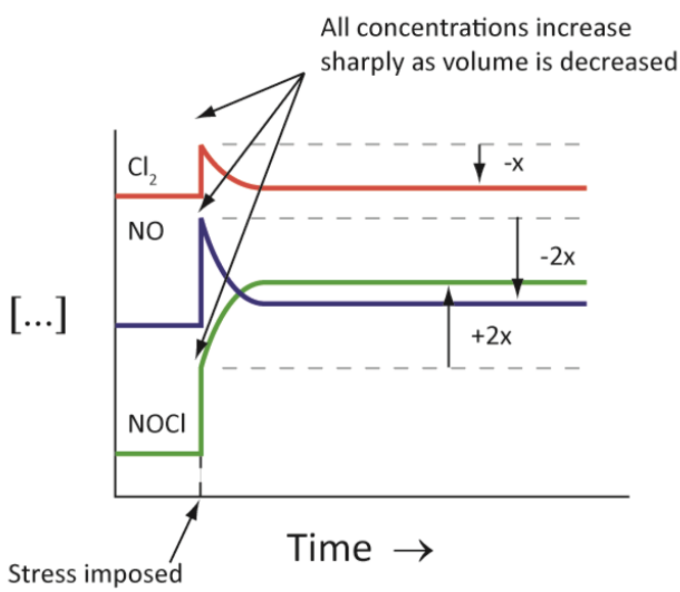


3. **Pressure**

- increasing the partial pressure of a gas has the **same effect as increasing its concentration**
- pressure can also be increased **by decreasing the volume of the container**
- a **decrease** in volume simultaneously **increases** the partial pressure and concentration of **ALL gases present in the system**
- shift to reduce the overall pressure - this results in a shift towards the side of the reaction with the **fewest moles of gas present**

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) + 76\ kJ$$

- the direction that involves the greater number of gas moles will experience a greater increase in rate initially
- for this reaction, the forward reaction rate would increase initially
- as equilibrium is re-established, forward rate decreases and reverse rate increases
- when the number of **moles of gas are equal** on both sides of the equilibrium, **no shift is observed**



4. **<u>Catalyst</u>**

- a catalyst lowers the Ea for a reaction, however, it decreases the Ea of both the forward and reverse reactions and **speeds up the forward and reverse rates by an equivalent amount**
- adding a catalyst to a reaction already **<u>at equilibrium</u>** will increase the rates of both forward and reverse reactions but will have **no effect on reactant and product concentrations**
- adding a catalyst to a reaction that is not at equilibrium will allow it to be **reached faster**

Consider the following reaction:

$$N_2(g) + 2H_2(g) \rightleftarrows 2NH_3(g) + 92\ kJ$$

Predict the direction of shift and the effect on the amount of $H_2(g)$ resulting from the following stresses:

1. increase $[N_2]$ shifts right, $[H_2]$ decreases
2. increase $[NH_3]$ shifts left, $[H_2]$ increases
3. increase temperature shifts left, $[H_2]$ increases
4. increase volume shifts left, $[H_2]$ increases