Le Chatelier's Principle states that a system at equilibrium will adjust to relieve stress when there are changes in the concentration of a reactant or product, the partial pressures of components, the volume of the system, and the temperature of reaction. There are three ways to change the pressure of a constant-temperature reaction system involving gaseous components:

1. **Add or remove a gaseous reactant or product:** Adding or removing a gaseous reactant or product changes the concentrations. If the concentration of reactant or product is increased, the system will shift away from the side in which concentration was increased (i.e., if the concentration of reactants is increased, the system will shift toward the products. If more products are added, the system will shift to form more reactants). Conversely, if the concentration of reactant or product is decreased, the system will shift toward the side in which concentration was decreased (i.e., if reactants are removed, the system will shift to form more reactants. If the concentration of products is decreased, the equilibrium will shift toward the products).

2. **Add an inert gas (one that is not involved in the reaction) to the constant-volume reaction mixture:** This will increase the total pressure of the system, but will have no effect on the equilibrium condition. That is, there will be no effect on the concentrations or the partial pressures of reactants or products.

3. **Change the volume of the system:** When the volume is changed, the concentrations and the partial pressures of both reactants and products are changed. If the volume is decreased, the reaction will shift towards the side of the reaction that has fewer gaseous particles. If the volume is increased, the reaction will shift towards the side of the reaction that has more gaseous particles.

When a system at equilibrium undergoes a change in pressure, the equilibrium of the system will shift to offset the change and establish a new equilibrium. The system can shift in one of two ways:

- Toward the reactants (i.e., in favor of the reverse reaction)
- Toward the products (i.e., in favor of the forward reaction)

The effects of changes in pressure can be described as follows (this only applies to reactions involving gases):

- When there is an increase in pressure, the equilibrium will shift towards the side of the reaction with fewer moles of gas.
- When there is a decrease in pressure, the equilibrium will shift towards the side of the reaction with more moles of gas.

Pressure is inversely related to volume. Therefore, the effects of changes in pressure are opposite of the effects of changes in volume. Additionally, this does not apply to a change in the pressure in the system due to the addition of an inert gas.

References

Problems

1. Consider the decomposition of NOCl: \[2\text{NOCl}_{(g)} \rightleftharpoons 2\text{NO}_{(g)} + \text{Cl}_{2 (g)}\]
   In which direction will the reaction shift if the overall pressure is decreased? Does this favor the forward reaction or the reverse reaction?

2. Consider the decomposition of HBr: \[2\text{HBr}_{(g)} \rightleftharpoons \text{H}_{2 (g)} + \text{Br}_{2 (g)}\]
   In which direction will the reaction shift when overall pressure is increased? Which direction will it shift when overall pressure is decreased?

3. Consider the reaction: \[\text{C}_{(s)} + 2\text{H}_{2 (g)} \rightleftharpoons \text{CH}_{4 (g)}\]
   What will happen to the equilibrium if the overall pressure is increased? (In which direction will the reaction shift? Does it favor reactants or products? Does this favor the formation of CH₄? Is the rate of the forward reaction greater than the rate of the reverse reaction?)

4. Consider the decomposition of MgCO₃: \[\text{MgCO}_3_{(s)} \rightleftharpoons \text{MgO}_{(s)} + \text{CO}_{2 (g)}\]
   Will the formation of CaCO₃ or the decomposition of CaCO₃ occur faster if the overall pressure is increased?

5. Consider the reaction in a closed container: \[2\text{SO}_{2 (g)} + \text{O}_{2 (g)} \rightleftharpoons 2\text{SO}_{3 (g)}\]
   You want the reaction to favor the formation of SO₃. You have two options: decrease the overall volume of the container, or increase the overall volume. Which should you choose?

Solutions

1. There are 2 moles of gas particles on the side of the reactants, and 3 moles of gas particles on the side of the products. (Note: 2 moles on the reactant's side come from 2 moles NOCl; 3 moles on the product's comes from 2 moles NO + 1 mole Cl₂.). A decrease in pressure favors the side with more particles.
   \[\therefore \text{The reaction will shift towards the products, and will favor the forward reaction.}\]

2. There are 2 moles of gas particles on the side of the reactants, and 2 moles of gas particles on the side of the products. Increasing pressure favors the side with fewer particles, and decreasing pressure favors the side with more particles. However, because there is an equal number of particles on both sides, change in pressure will have no effect on the system.
   \[\therefore \text{No effect - the reaction will not shift in either direction regardless of pressure changes.}\]

3. There are 2 moles of gas particles on the side of the reactants, and 1 mole of gas particles on the side of the products. Increasing pressure favors the side with fewer particles.
   \[\therefore \text{The reaction will shift towards the products. This means that the reaction will favor the forward reaction, which means that it favors the formation of CH}_4, \text{ and that the rate of the forward reaction is greater than the rate of the reverse reaction.}\]

4. There are 0 moles of gas particles on the side of the reactants, and 1 mole of gas particles on the side of the products.
   Increasing the pressure favors the side with fewer particles, so the reaction favors the reactants. The products are the decomposition of MgCO₃, while the reactants are the formation of MgCO₃.
   \[\therefore \text{The formation of MgCO}_3 \text{ is favored, meaning that the formation of MgCO}_3 \text{ will occur faster than its decomposition.}\]

5. There are 3 moles of gas particles on the side of the reactants, and 2 moles of gas particles on the side of the products.
   Because you want the reaction to favor the formation SO₃, you want the reaction to favor the forward reaction/shift
to the right, which is the side with fewer moles of gas particles. For a system to shift towards the side of a reaction with fewer moles of gas, you need to increase the overall pressure. Recall that pressure and volume are inversely related, so in order to increase the overall pressure, you need to decrease the overall volume.

∴ You should decrease the overall volume.

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