

Equilibrium

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EQUILIBRIUM INTRODUCTION

- **Dynamic equilibrium:** a balance between forward and reverse processes occurring at the same rate. Requirements for dynamic equilibrium:
 1. The system is a closed system
 2. All components of the chemical system need to be present
 3. The initial concentration of the chemicals stays the same throughout
- **Solubility equilibrium:** a dynamic equilibrium between a solute and a solvent in a saturated solution in a closed system
- **Phase equilibrium:** a dynamic equilibrium between different physical states of a pure substance in a closed system
- **Chemical reaction equilibrium:** a dynamic equilibrium between reactants and products of a chemical reaction in a closed system

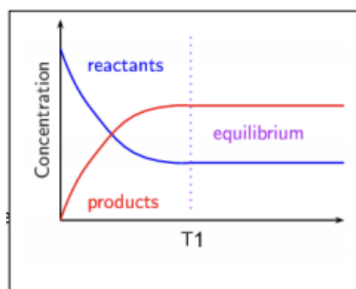


Figure 1: The position of the equilibrium shows that the products are more favoured. This means the percent reaction for reactants is less than 50% and the percent reaction for products is greater than 50%.

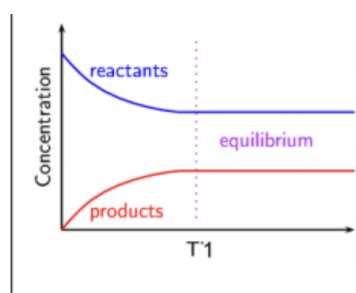


Figure 2: The position of the equilibrium shows that the products are less favoured. This means the percent reaction for reactants is greater than 50% and the percent reaction for products is less than 50%.

Solubility Equilibrium

- For instance, when NaCl is dissolved in water, the ions from the crystal collide with water molecules to dissolve. However, those ions can also collide with the crystal itself, forming ionic bonds, and crystalizing

- Early in the dissolving process, far more ions are entering the dissolved state compared to ions entering the crystal state. At equilibrium, water molecules and ions collide with the crystal at equal rates, hence the rate of dissolution equals the rate of crystalization and no change is observed
- This state is called the **state of dynamic equilibrium**

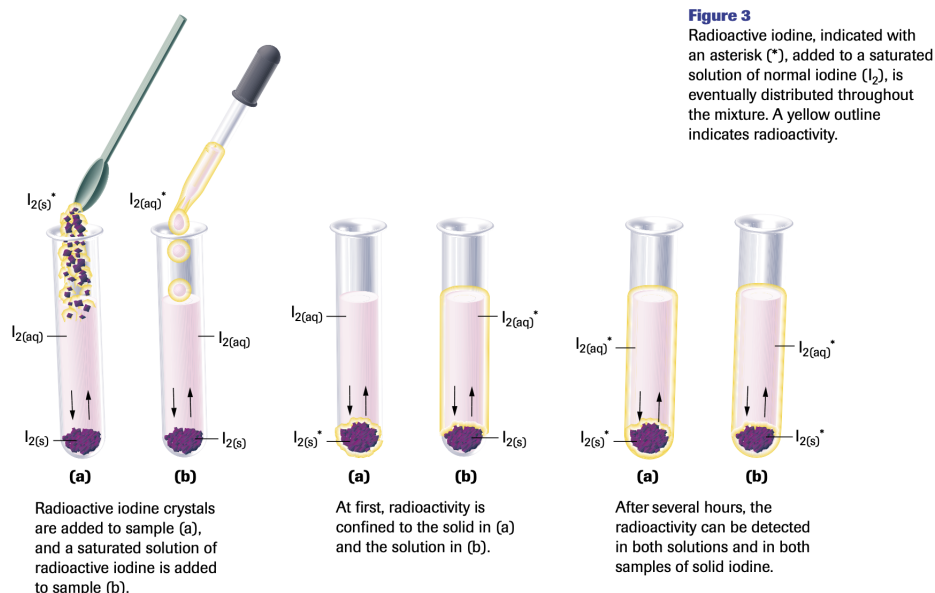


Figure 3: (a) contains solid unsaturated radioactive iodine and (b) contains saturated radioactive iodine. Both are mixed in normal iodine solution. Initially, only the iodine solids in (a) and the solution in (b) are radioactive. However, over time, in both cases (a) and (b), both the solid and solution components are radioactive.

Important. At equilibrium, the forward rates and reverse reaction rates are equal. How we achieved equilibrium is not relevant. For instance, once equilibrium is achieved, it is impossible to tell if we started with separate solutions of $Ca_{(aq)}^{2+}$ and $SO_{4(aq)}^{2-}$, or with excess $CaSO_{4(aq)}$ added to pure water. Initially, the difference is evident, but once the equilibrium is achieved, assuming that the equilibrium positions are identical, there is no difference.

Phase Equilibrium

- An example of **liquid-gas equilibrium** is having a water bottle with the cap closed. A small percentage of liquid water molecules have enough kinetic energy to change into gaseous state. However, simultaneously, there are also gaseous water molecules that are colliding with the liquid water molecules, causing them to turn also into liquid water molecules. In this case, the rate at which both processes are occurring are identical, thus no change is observed
- If the lid was uncapped however, the system becomes an open system and the liquid water will eventually all become gaseous liquid water molecules

- **Note:** the tendency of any liquid to evaporate increases at higher temperatures, so the concentration and pressure of the vapour is greater if the equilibrium is established at a higher temperature
- An example of **solid-liquid equilibrium** is ice/water slush at 0°C and 101.325 kPa. As the temperature of the water drops, the rate of melting decreases while the rate of freezing increases simultaneously, until a temperature of 0°C, where the rates become equal and the mixture will remain constant

Chemical Reaction Equilibrium

- **Quantitative reaction:** a chemical reaction in which virtually all of the limiting reagent is consumed. Often occurs in an **open system**
- A synthesis/decomposition reaction are common types of reversible reactions
- **Reversible reaction:** a reaction that can achieve equilibrium in the forward or reverse direction. Occurs in a **closed system**

Percent Reaction at Chemical Equilibrium

Percent reaction: the yield of product measured at equilibrium compared to the maximum possible yield of product.

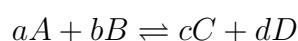
All chemical reactions are considered reversible; the only thing to consider is the extent to which they are reversible. Reactions fall loosely into three categories

- Reactions that favour reactants strongly; the percent reaction is less than 1%. In these reactions, mixing the reactants has no observable effect
- Reactions that favour products very strongly; where the percent reaction is greater than 99%. These reactions are observed to be quantitative reactions. These reactions are typically written with an arrow that has only one direction, to show that their reverse reaction is negligible
- Reactions that achieve noticeable equilibrium; the percent reaction lies somewhere between 1% and 99%. Only occurs in a closed system. If the percent reaction is less than 50%, reactants are favoured; if the percent reaction is more than 50%, the products are favoured
- An ICE table, standing for initial, change, and equilibrium, is useful for calculating stoichiometry involving dynamic equilibrium

EQUILIBRIUM CONSTANT

A ratio involving equilibrium constants between the reactants and products has a constant value, independent of how the equilibrium is reached. The ratio can be derived using the BCE. This ratio is called the equilibrium constant expression and denoted by K_{eq} .

In the hypothetical reaction



The value for K_{eq} , determined **empirically**, is given mathematically as

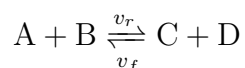
$$K = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

Where the exponents are the same as the coefficients in the BCE.

- When calculating the equilibrium conditions for homogeneous equilibrium, the expression is very straight forward. However, many equilibria involve more than one phase and are called heterogeneous
- When writing the equilibrium constant expression, it is essential to note that the position of the equilibrium **does not depend on the amounts of solid or liquid components present**. This is because, fundamentally, the “concentrations” of pure solids and liquids do not change. Therefore, the “concentrations” of these components are not included in the equilibrium constant expression
- In other words, since solids and liquids generally do not change concentrations, they are **not included** in the equilibrium constant equation

Derivation of the Equilibrium Constant

Given equilibrium equation



Where v_f is the rate of the forward reaction and v_r is the rate of the reverse reaction, we can derive two equations

$$v_f = k_f[\text{A}][\text{B}]$$

$$v_r = k_r[\text{C}][\text{D}]$$

During equilibrium, the forward reaction rate is equivalent to the reverse reaction rate. That is, $v_f = v_r$

$$\begin{aligned} v_f &= v_r \\ k_f[\text{A}][\text{B}] &= k_r[\text{C}][\text{D}] \\ \frac{k_f}{k_r} &= \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} \\ K &= \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} \end{aligned}$$

Of course, this applies to the case where the reactants have different coefficients as well

$$K = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

THE REACTION QUOTIENT

Equilibrium Establishment

- When the reactants and products for a particular chemical reaction are combined, it is useful to know whether the mixture is at equilibrium or not. When it is not, it is necessary to know how the system will change in order to establish equilibrium
- This change in equilibrium is typically referred to as a *shift*
- A shift **to the right** means that the concentration of the **products** will increase to reach equilibrium
- A shift **to the left** means that the concentration of the **reactants** will increase to reach equilibrium

Determining the *shift* in position is very simple if the concentration of any one of the reactants or products is 0:

- The system must shift in the direction of the missing component(s)
- This is because it is impossible to reach equilibrium if one of the components is missing

The Reaction Quotient

- When all of the initial concentrations are non-zero, then the reaction quotient, denoted by Q , is used to determine the shift that is required to establish equilibrium
- The reaction quotient uses the equilibrium constant expression for the reaction; however, the **initial concentrations** are used in the equation, rather than the equilibrium concentrations

For instance, in the reaction $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$

$$Q = \frac{[\text{NH}_3]_o^2}{[\text{N}_2]_o[\text{H}_2]_o^3}$$

Where the subscripted o denotes that it is the **initial concentration**.

Recalling that Q and K measure the ratio between the concentrations of the products to reactants, we can compare the values of Q to K to assert the following

- When $Q > K$
 - The initial concentration ratio between products to reactants is **too large**
 - Some products will be consumed to form reactants in equilibrium
 - The system shifts **left** to reach a state of equilibrium
- When $Q < K$
 - The initial concentration ratio between products to reactants is **too little**
 - Some reactants will be consumed to form products in equilibrium

- The system shift **right** to reach a state of equilibrium
- When $Q = K$
 - The initial concentration represents a system that is already in a state of equilibrium
 - The system will undergo no shift

Sample: For the synthesis of ammonia at 500°C , the equilibrium constant is $K = 6.0 \times 10^{-2}$. Predict the direction that the system must shift in order to establish equilibrium for the following “initial concentration” scenarios.

Experiment	$[\text{N}_2]$	$[\text{H}_2]$	$[\text{NH}_3]$
1	1.0×10^{-5}	2.0×10^{-3}	1.0×10^{-3}
2	1.5×10^{-5}	3.54×10^{-1}	2.0×10^{-4}
3	5.0	1.0×10^{-2}	1.0×10^{-4}

Answer: For experiment 1, the value for Q is

$$\begin{aligned}
 Q &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \\
 &= \frac{(1.0 \times 10^{-3})^2}{(1.0 \times 10^{-5})(2.0 \times 10^{-3})^3} \\
 &= 1.25 \times 10^7
 \end{aligned}$$

Since $Q > K$, the reaction shifts to the left.

For experiment 2, the value for Q is

$$\begin{aligned}
 Q &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \\
 &= \frac{(2.0 \times 10^{-4})^2}{(1.5 \times 10^{-5})(3.54 \times 10^{-1})^3} \\
 &= 0.06
 \end{aligned}$$

Since $Q \approx K$, the reaction has no shift.

For experiment, 3, the value for Q is

$$\begin{aligned}
 Q &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \\
 &= \frac{(1.0 \times 10^{-4})^2}{(5.0)(1.0 \times 10^{-2})^3} \\
 &= 0.002
 \end{aligned}$$

Since $Q < K$, the reaction will shift right.

QUALITATIVE CHANGES IN EQUILIBRIUM SYSTEMS

Le Chatelier's Principle

When a chemical system at equilibrium is disturbed by a change in property, the system adjusts in a way that opposes the change.

- **Equilibrium shift:** movement of a system at equilibrium, resulting in a change in the concentrations of reactants and products
- Keep in mind that any increase/decrease in concentration is **gradual**

Le Chatelier's Principle and Concentration Changes

- In most industrial chemical processes, we want to ensure that equilibrium is not achieved. That is, the reverse reaction is not allowed to occur, for maximum efficiency and profit. For instance, the synthesis of ammonia in the Haber process
- To ensure the maximum efficiency, reactants are constantly added while products are simultaneously removed to utilize Le Chatelier's Principle in order to minimize the reverse reaction
- When you add particles to a reaction system, the rates at the new equilibrium state will be greater than before, because the system now contains a large number of particles. Likewise, if particles were removed, the rates at the new equilibrium state will be less than before

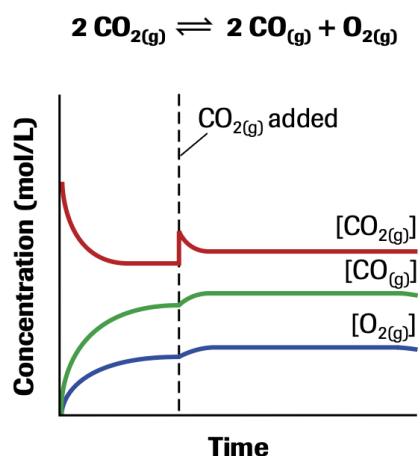


Figure 4: In this case, because reactants are being added, to achieve equilibrium, there will be a shift to the right to produce more products. This results in a concentration increase (till eventual decrease until equilibrium) in $[\text{CO}_{2(g)}]$ and a slight increase in $[\text{CO}_{(g)}]$ and $[\text{O}_{2(g)}]$. Initially, the forward reaction rate is significantly faster than the reverse reaction rate, until they eventually equal once they reach a state of equilibrium once the reverse reaction rate begins to speed up.

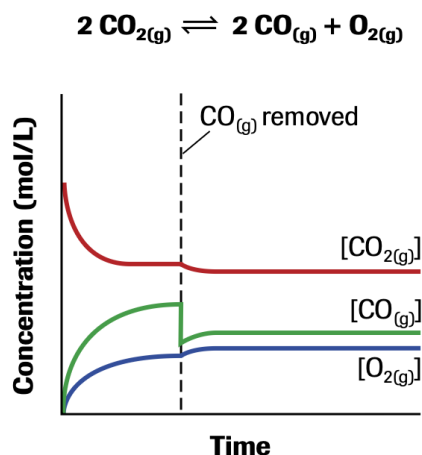


Figure 5: In this case, because products are being removed, to achieve equilibrium, there will be a shift to the right to produce more products. This results in a concentration decrease in $[\text{CO}_{2(g)}]$ and a slight increase in $[\text{CO}_{(g)}]$ and $[\text{O}_{2(g)}]$. Initially, the forward reaction rate is significantly faster than the reverse reaction rate, until they eventually equal once they reach a state of equilibrium once the reverse reaction rate begins to speed up.

Figure 4

Disturbing the iron(III) thiocyanate equilibrium

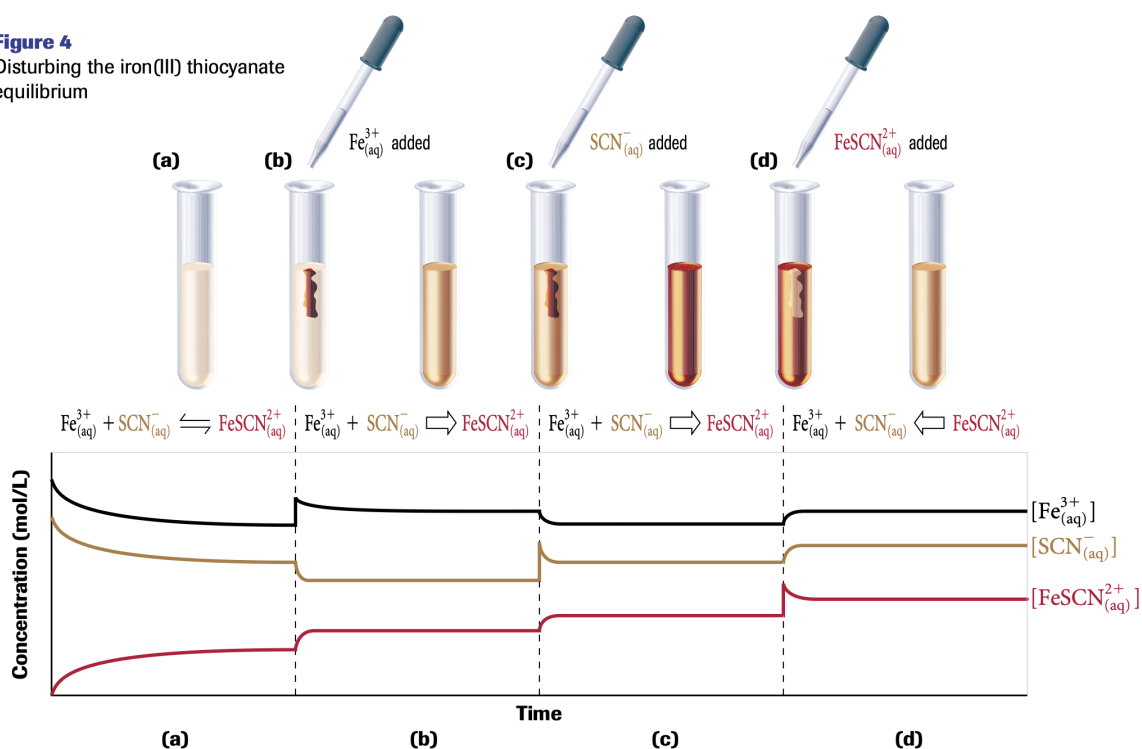


Figure 6: An example of the effects of concentration change on equilibrium shift.

Le Chatelier's Principle and Temperature Changes

The two types of reactions to consider are endothermic and exothermic reactions

endothermic reaction: reactants + energy \rightleftharpoons products

exothermic reaction: reactants \rightleftharpoons products + energy

- Energy can be added or removed to a system by heating or cooling the container. The

equilibrium shifts, according to Le Chatelier's Principle, to minimize the changes

- If the system is **cooled**, the system tries to **warm itself up** by shifting the equilibrium in a direction that produces heat. If heat is added, the equilibrium position will shift such that heat is absorbed by the system
- For instance, in the decomposition of dinitrogen tetroxide



When the system at equilibrium is heated, the reaction shifts to the right, increasing the concentration of $\text{NO}_{2(g)}$. This is made visible by the intensification of the reddish-brown colour. You can almost think of energy as a **chemical entity** partaking in the reaction

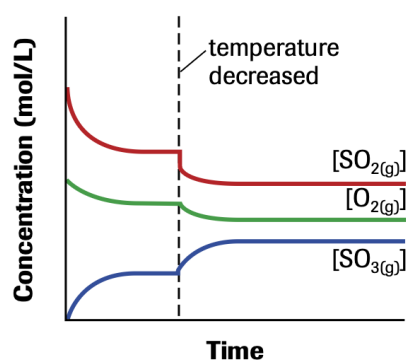
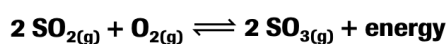


Figure 7: In this example, when the temperature is cooled, the system will counteract this change according to Le Chatelier's Principle by producing more heat. Thus, a right shift is observed by increasing the products via the consumption of reactants. Note that the forward rate is faster than the reverse rate initially, so that the system can produce more heat to counteract the decrease in temperature until equilibrium is achieved.

Important. Temperature change is the only factor that will **change the equilibrium constant value**. This is because the equilibrium constant depends on the fact that the closed system has constant temperature and pressure.

Le Chatelier's Principle and Gas Volume Changes

- According to Boyle's Law, the volume and pressure are inversely proportional. That is, if the volume decreases by half, the pressure increases by a factor of two
- Changing the volume of any equilibrium system **may** cause a shift in the equilibrium. If all the reactants and products are aqueous, then the shift in equilibrium is negligible. However, if there are chemical entities in the gaseous state, then a shift in equilibrium will be observed

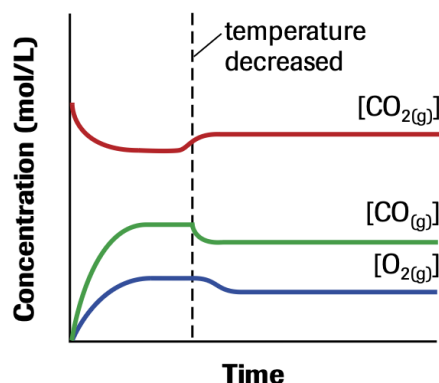
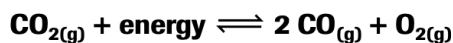


Figure 8: In this example, when the temperature is cooled the system will counteract this change by consuming less heat. Thus, a left shift is observed. Note that the reverse rate is faster than the forward rate initially, so that the system consumes less heat to counteract the decrease in temperature until equilibrium is achieved.

- For instance, consider $\text{N}_{2(g)} + 3 \text{H}_{2(g)} \rightleftharpoons 2 \text{NH}_{3(g)}$. On the reactants side, there are a total of 4 moles molecules, while on the product side, there are a total of 2 moles of molecules. When there is an increase in pressure, Le Chatlier's Principle suggests that the system will counteract the increase in pressure by reducing the pressure. In this case, the equilibrium will shift to the right, since there will be less moles of molecules in the system
- A system with equal number of gas molecules on each side of the equation will not have an equilibrium shift
- Particles in the **solid, liquid, or aqueous state** are not of significance when it comes to determining equilibrium shift. This is because substances in these condensed states are virtually incompressible, and so reactions involving them cannot counteract pressure change
- Kinetic theory explains the effects of a decrease in volume by assuming that both the forward and reverse reaction rates increase because the concentrations (partial pressures) of reactants and products increase. However, the forward reaction rate increases more than the reverse reaction rate because there are more particles involved in the forward reaction. The shift causes concentration changes that eventually increase the reverse rate and decrease the forward rate until they become equal

Changes That Do Not Affect The Position of Equilibrium Systems

- **Adding Catalysts**
 - The presence of a catalyst in a chemical reaction system lowers the activation energy for both forward and reverse reactions by an equal amount, so the equilibrium state is established much quicker but at the **same position** as it would without a catalyst

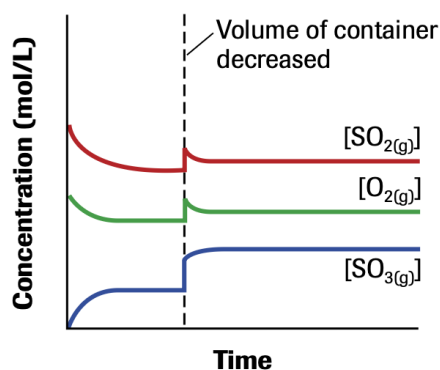
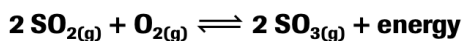
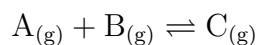
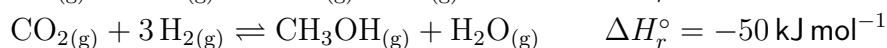
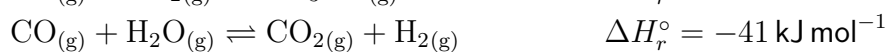


Figure 9: The equilibrium is disturbed by a decrease in volume. The equilibrium shifts forward to counteract the increase in pressure.

- Forward and reverse reaction rates are increased equally
- The value of catalysts in industrial processes is to decrease the time required for equilibrium shifts to occur, allowing a more rapid overall production of the desired product

• Adding Inert Gases

- Adding inert gases, such as noble gases, which will not partake in the reaction of the system, does not affect the equilibrium position
- It may, however, affect the speed at which the equilibrium position is established, similar to the catalyst
- According to kinetic theory, the presence of inert gas changes the probability of a successful collision for both the reactants and products equally, resulting in no shift in the equilibrium system



$$K_{\text{eq}} = \frac{P_{\text{C}}}{P_{\text{A}} \cdot P_{\text{B}}}$$

$$P_{\text{A}} = x_{\text{A}} \cdot P_{\text{total}}$$

$$P_{\text{B}} = x_{\text{B}} \cdot P_{\text{total}}$$

$$P_{\text{C}} = x_{\text{C}} \cdot P_{\text{total}}$$

$$K_{\text{eq}} = \frac{P_{\text{C}}}{P_{\text{A}} \cdot P_{\text{B}}} = \frac{1}{1 \cdot 1} = 1$$

$$x_A = \frac{n_A}{n_{\text{total}}}$$

$$x_B = \frac{n_B}{n_{\text{total}}}$$

$$x_C = \frac{n_C}{n_{\text{total}}}$$

$$P_A = 1 \text{ atm}, P_B = 1 \text{ atm}, P_C = 1 \text{ atm}, P_{\text{total}} = 3 \text{ atm}$$

$$n_I = 1 \text{ mol}, P_I = 1 \text{ atm}, P_{\text{total (new)}} = 4 \text{ atm}$$

$$P_{A(\text{new})} = x_{A(\text{new})} \cdot P_{\text{total (new)}}$$

$$= \frac{1 \text{ mol}}{4 \text{ mol}} \cdot (4 \text{ atm})$$

$$= 1 \text{ atm}$$

$$= P_A$$

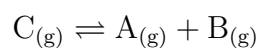
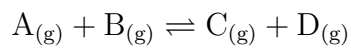
$$Q = \frac{P_{C(\text{new})}}{P_{A(\text{new})} \cdot P_{B(\text{new})}}$$

$$= \frac{P_C}{P_A \cdot P_B}$$

$$= \frac{1}{1 \cdot 1}$$

$$= 1$$

$$= K_{\text{eq}}$$



$$n_A = 1 \text{ mol}$$

$$n_B = 1 \text{ mol}$$

$$n_C = 1 \text{ mol}$$

$$n_D = 1 \text{ mol}$$

$$V = 2 \text{ L}$$

$$[A] = \frac{1}{2} \text{ mol L}^{-1}$$

$$[B] = \frac{1}{2} \text{ mol L}^{-1}$$

$$[C] = \frac{1}{2} \text{ mol L}^{-1}$$

$$[D] = \frac{1}{2} \text{ mol L}^{-1}$$

$$\begin{aligned}
 K_{\text{eq}} &= \frac{[\text{C}]}{[\text{A}][\text{B}]} \\
 &= \frac{\frac{1}{2}}{(\frac{1}{2})(\frac{1}{2})} \\
 &= 2
 \end{aligned}$$

$$n_{\text{I}} = 1 \text{ mol}, V_{\text{new}} = 3 \text{ L}$$

$$\begin{aligned}
 [\text{A}]_{\text{new}} &= \frac{1}{3} \text{ mol L}^{-1} \\
 [\text{B}]_{\text{new}} &= \frac{1}{3} \text{ mol L}^{-1} \\
 [\text{C}]_{\text{new}} &= \frac{1}{3} \text{ mol L}^{-1} \\
 [\text{D}]_{\text{new}} &= \frac{1}{3} \text{ mol L}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 Q &= \frac{[\text{C}]_{\text{new}}}{[\text{A}]_{\text{new}}[\text{B}]_{\text{new}}} \\
 &= \frac{\frac{1}{3}}{(\frac{1}{3})(\frac{1}{3})} \\
 &= 3 \\
 Q &> K_{\text{eq}}
 \end{aligned}$$

$$\begin{aligned}
 K_{\text{eq}} &= \frac{[\text{A}][\text{B}]}{[\text{C}]} \\
 &= \frac{(\frac{1}{2})(\frac{1}{2})}{\frac{1}{2}} \\
 &= \frac{1}{2}
 \end{aligned}$$

$$\begin{aligned}
 Q &= \frac{[\text{A}]_{\text{new}}[\text{B}]_{\text{new}}}{[\text{C}]_{\text{new}}} \\
 &= \frac{(\frac{1}{3})(\frac{1}{3})}{\frac{1}{3}} \\
 &= \frac{1}{3} \\
 Q &< K_{\text{eq}}
 \end{aligned}$$

$$\begin{aligned}
 K_{\text{eq}} &= \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} \\
 &= \frac{(\frac{1}{2})(\frac{1}{2})}{(\frac{1}{2})(\frac{1}{2})} \\
 &= 1
 \end{aligned}$$

$$\begin{aligned}
 Q &= \frac{[\text{C}]_{\text{new}}[\text{D}]_{\text{new}}}{[\text{A}]_{\text{new}}[\text{B}]_{\text{new}}} \\
 &= \frac{(\frac{1}{3})(\frac{1}{3})}{(\frac{1}{3})(\frac{1}{3})} \\
 &= 1 \\
 &= K_{\text{eq}}
 \end{aligned}$$

