

American Chemical Society



USNCO Coaching Session Tutorial Notes: Equilibrium

Angela Wilden, Philip Pietrangelo, Johanna Foley
20 November 2020

Disclaimer



- ACS is providing a remake of these tutorials and images as a courtesy to and for the convenience of the reader. It makes no representations or warranties, express or implied, relative to the accuracy, veracity, ownership, or authority contained within the information provided therein. In accessing these slides, the reader knowingly, willingly, and voluntarily accepts the information's remake “as is”.

Completion vs Equilibrium



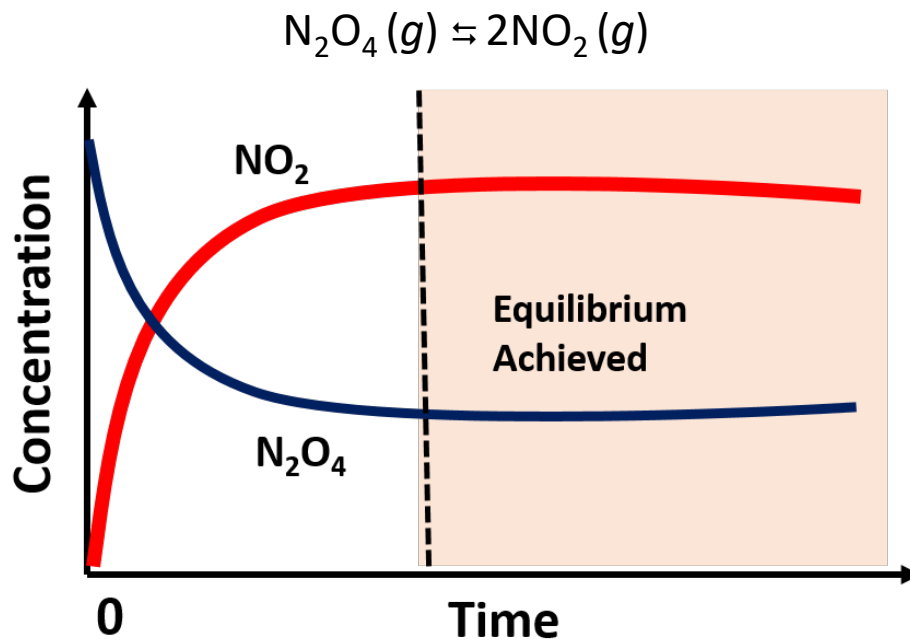
- Reactions that go to completion are governed by the consumption of the limiting reactant. When the limiting reactant is used up, the reaction STOPS.
- Many reactions, however, do not go to completion. Instead, after some products are made, they can be converted back into the reactants. Any reaction performed in a closed vessel will go to equilibrium.

Dynamic Equilibrium



- Equilibrium, does NOT mean the reaction has stopped OR that we have equal amounts of Products and Reactants.
- Equilibrium occurs when the RATE of the forward reaction and the RATE of the reverse reaction are EQUAL and there is no net change in the concentration of the products or the reactants.

Graphing Equilibrium



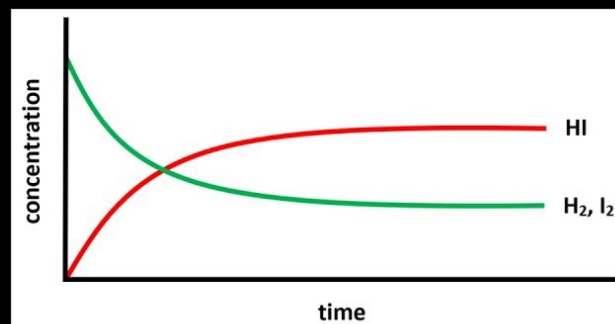
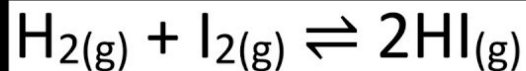
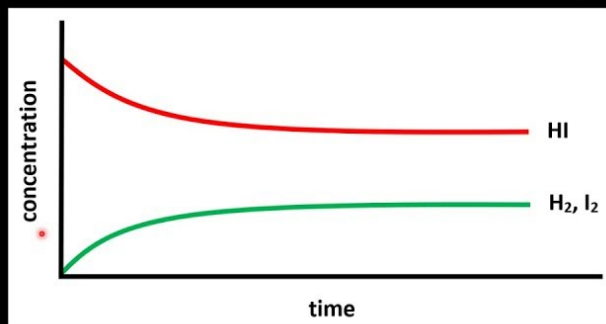
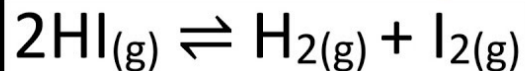
Dynamic Equilibrium



ACS
Chemistry for Life®

MSJChem
Tutorials for IB Chemistry

Dynamic equilibrium



**Equilibrium can be reached from either direction.
Concentrations of reactants and products are constant
(not equal).**

<https://www.msjchem.com/>

The Equilibrium Constant



The condition of the reaction

(\uparrow [P] or \uparrow [R])

at equilibrium can be described using the **equilibrium constant expression**, sometimes called the **law of mass action**.

Equilibrium Constants

- The equilibrium constant describes the equilibrium position of a chemical system, or the degree to which the forward and reverse reaction is favored
- Given a reaction $aA + bB \rightleftharpoons cC + dD$, the equilibrium constant K_c , also called K or K_{eq} , is defined as follows:

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

- For $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, $K_c = \frac{[NO_2]^2}{[N_2O_4]}$

The Meaning of K

- The magnitude of K gives us information about the relative amounts of reactants and products at equilibrium for a given reaction (at a given temperature).

Magnitude of K	Favors
> 1	Products
$= 1$	Both
< 1	Reactants

The Magnitude and Meaning of K

- Reactions that go essentially to completion have very large K_{eq} values. Therefore, large K values indicate an equilibrium position that lies far to the right. Much higher [P] than [R]

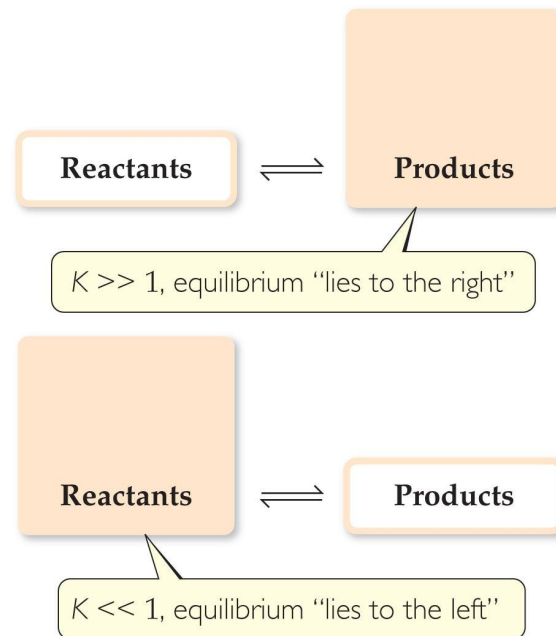
Strong acid or strong base dissociation



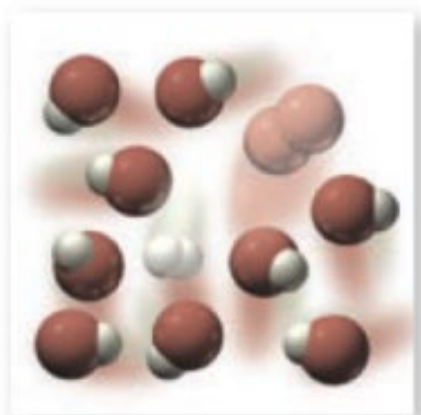
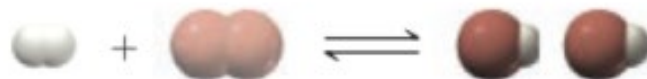
Combustion reactions



Acid + base neutralization



The Magnitude and Meaning of K



$$K = \frac{[\text{HBr}]^2}{[\text{H}_2][\text{Br}_2]} = \text{large number}$$

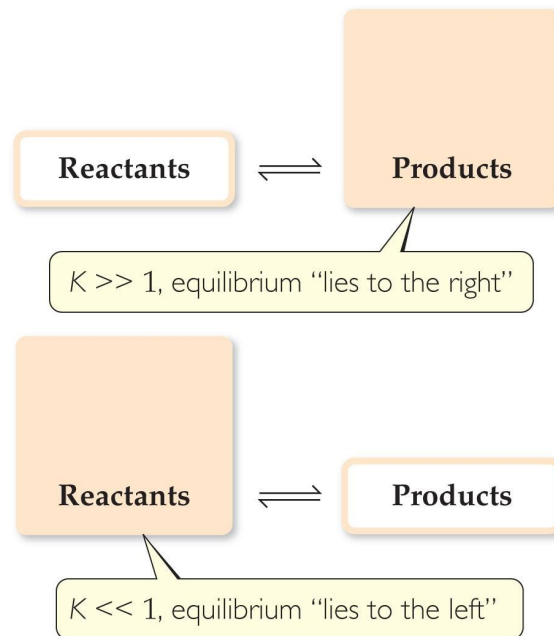
The Magnitude and Meaning of K

- Reactions with very small K values indicate that the equilibrium position lies far to the left. Much higher [R] than [P].

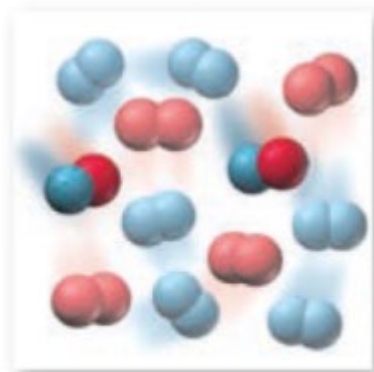
Weak acid or weak base dissociation



Dissolution of slightly soluble salts



The Magnitude and Meaning of K



$$K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \text{small number}$$

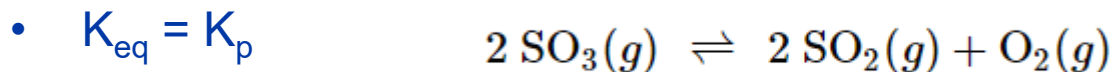
K_c vs K_p



- Equilibrium involving concentrations of aqueous solutions is described using K_c for the equilibrium constant.
- $K_{eq} = K_c$ when the species are in aqueous solution

K_c vs K_p

- Equilibria involving gases can also be described in terms of pressures.
- Instead of using concentration, we could use the partial pressures of each gaseous species.



$$K_c = \frac{[\text{SO}_2]^2 [\text{O}_2]}{[\text{SO}_3]^2} \qquad K_p = \frac{(P_{\text{SO}_2})^2 P_{\text{O}_2}}{(P_{\text{SO}_3})^2}$$

K_c vs K_p

- Using the Ideal Gas Law, we can derive a relationship between K_p and K_c .

$$K_p = K_c (RT)^{\Delta n}$$

K_c vs K_p

- Using the Ideal Gas Law, we can derive a relationship between K_p and K_c .

$$P_A V = n_A RT$$
$$P_A = \frac{n_A}{V} RT$$

Since $[A] = n_A/V$, we can write:

[16.1]

$$P_A = [A] RT \quad \text{or} \quad [A] = \frac{P_A}{RT}$$

K_c vs K_p

- Using the Ideal Gas Law, we can derive a relationship between K_p and K_c .

Substituting $[X] = P_X/RT$ for each concentration term, we get:

$$\begin{aligned}K_c &= \frac{\left(\frac{P_C}{RT}\right)^c \left(\frac{P_D}{RT}\right)^d}{\left(\frac{P_A}{RT}\right)^a \left(\frac{P_B}{RT}\right)^b} = \frac{P_C^c P_D^d \left(\frac{1}{RT}\right)^{c+d}}{P_A^a P_B^b \left(\frac{1}{RT}\right)^{a+b}} = \frac{P_C^c P_D^d}{P_A^a P_B^b} \left(\frac{1}{RT}\right)^{c+d-(a+b)} \\ &= K_p \left(\frac{1}{RT}\right)^{c+d-(a+b)}\end{aligned}$$

Rearranging,

$$K_p = K_c (RT)^{c+d-(a+b)}$$

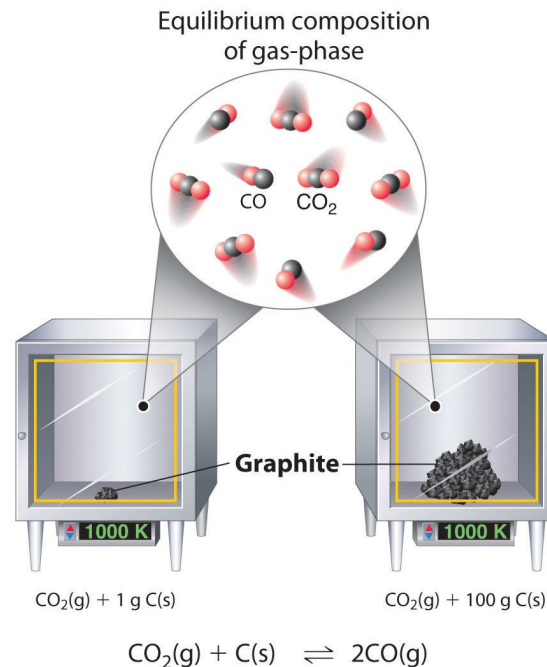
Heterogeneous Equilibria



- If all reactants and products are gaseous or in aqueous solution, they are all included in the K_{eq} expression,
- BUT ...
- ... experiments have shown that equilibrium does not depend on the amount of solids or liquids present, so they are omitted from the K_{eq} expression.

Heterogeneous Equilibria

- Pure solids and liquids are not included in equilibrium expressions because their **concentrations are constant**. In other words, their concentrations are already factored into the equilibrium constant.
- **Practice:** Write the equilibrium expression for the system shown on the right?



Calculating K from Measured Concentrations

Table 16.1 Initial and Equilibrium Concentrations for the Reaction $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g)$ at 445 °C

Initial Concentrations			Equilibrium Concentrations			Equilibrium Constant
$[\text{H}_2]$	$[\text{I}_2]$	$[\text{HI}]$	$[\text{H}_2]$	$[\text{I}_2]$	$[\text{HI}]$	$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$
0.50	0.50	0.0	0.11	0.11	0.78	$\frac{(0.78)^2}{(0.11)(0.11)} = 50$
0.0	0.0	0.50	0.055	0.055	0.39	$\frac{(0.39)^2}{(0.055)(0.055)} = 50$
0.50	0.50	0.50	0.165	0.165	1.17	$\frac{(1.17)^2}{(0.165)(0.165)} = 50$
1.0	0.50	0.0	0.53	0.033	0.934	$\frac{(0.934)^2}{(0.53)(0.033)} = 50$
0.50	1.0	0.0	0.033	0.53	0.934	$\frac{(0.934)^2}{(0.033)(0.53)} = 50$

Calculating K (ICE Tables)

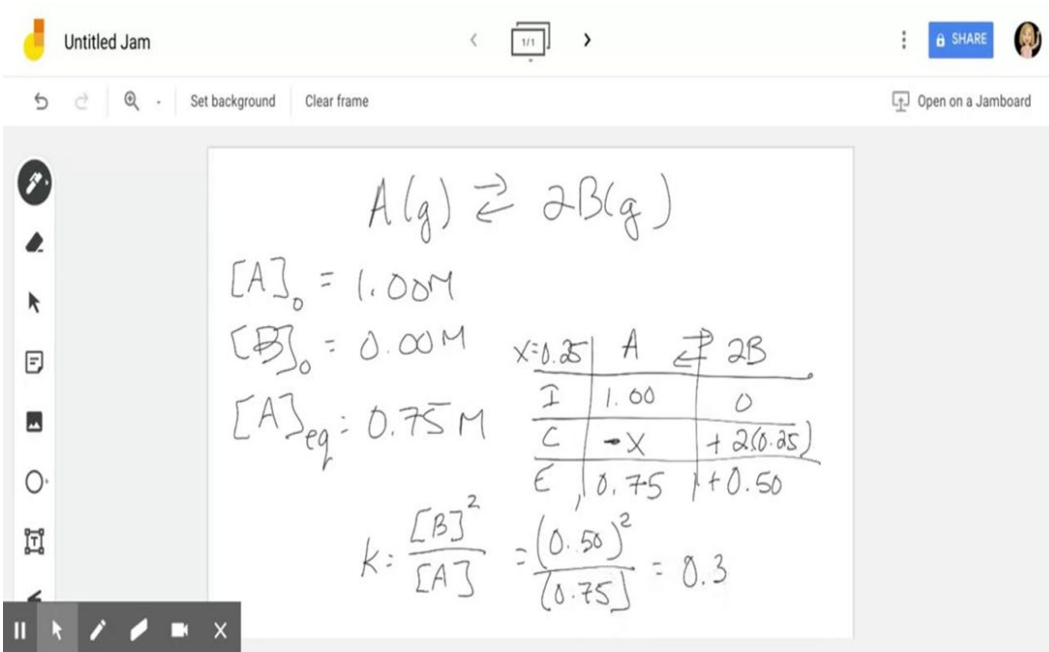
- Suppose that we have a reaction:



- In a reaction at 25°C, the initial concentration of A is 1.00 M and the initial concentration of B is 0. If the equilibrium concentration of A is 0.75 M, what is the K for this reaction?

Calculating K (ICE Tables)

- Often, we do not have any information on the equilibrium concentrations and must use what we know about the initial concentrations and the balanced reaction to determine the equilibrium concentrations.



Untitled Jam

Set background Clear frame

Open on a Jamboard

$$A(g) \rightleftharpoons 2B(g)$$

$$[A]_0 = 1.00 M$$

$$[B]_0 = 0.00 M$$

$$[A]_{eq} = 0.75 M$$

x=0.25	A	\rightleftharpoons	2B
I	1.00		0
C	-x		+2(0.25)
E	0.75		+0.50

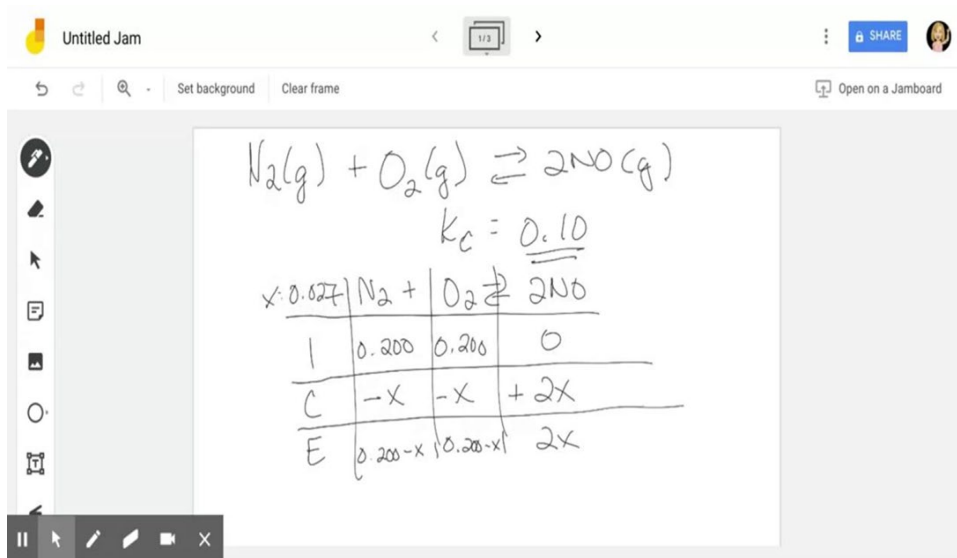
$$K = \frac{[B]^2}{[A]} = \frac{(0.50)^2}{(0.75)} = 0.3$$

Calculating K (ICE Tables)

- Consider this reaction:

$$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$$

$$K_c = 0.10 \text{ (at } 2000^\circ\text{C)}$$
- A reaction mixture at 2000°C , initially contains 0.200 M N_2 and 0.200 M O_2 . Find the equilibrium concentrations of the reactants and products at this temperature.



Untitled Jam

Set background Clear frame

Open on a Jamboard

$$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$$

$$K_c = 0.10$$

$x: 0.027$	N_2	O_2	2NO
I	0.200	0.200	0
C	-x	-x	+2x
E	0.200-x	0.200-x	2x

Q vs K

Predicting the Direction of a Reaction

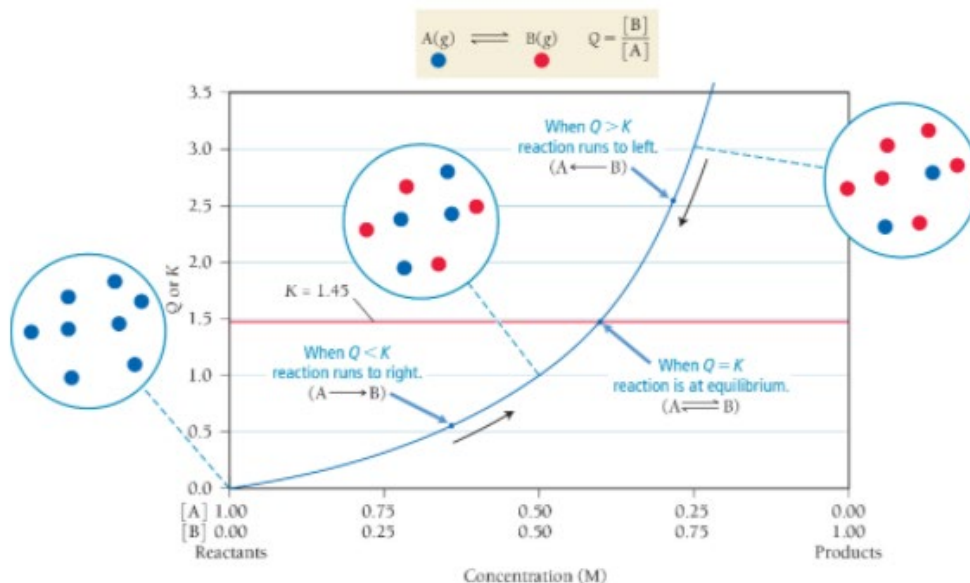


- Q_c = the reaction quotient
- It is calculated the same way as K but can use concentrations from any point during the reaction, not just equilibrium concentrations.

Q vs K

Predicting the Direction of a Reaction

Q, K, and the Direction of a Reaction

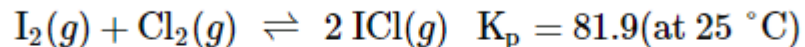


Q vs K

Predicting the Direction of a Reaction



Consider the reaction:



A reaction mixture at 25°C initially contains $P_{\text{I}_2} = 0.100 \text{ atm}$, $P_{\text{Cl}_2} = 0.100 \text{ atm}$, and $P_{\text{ICl}} = 0.100 \text{ atm}$. Find the equilibrium partial pressures of I_2 , Cl_2 , and ICl at this temperature.

Calculate Q to see where these conditions are in relation to equilibrium conditions,

- if $Q > K$, your products will be decreasing while your reactants are increasing (reaction proceeding to the left).
- if $Q < K$, your reactants will be decreasing while your reactants are increasing (reaction proceeding to the right).

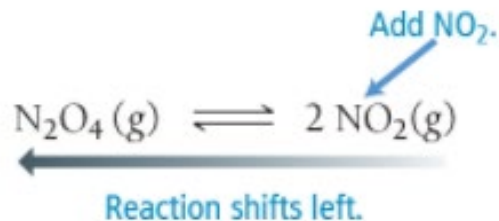
Le Chatelier's Principle



- When a chemical system at equilibrium is disturbed, the system shifts in a direction that minimizes the disturbance.

Concentration Changes

Consider $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$



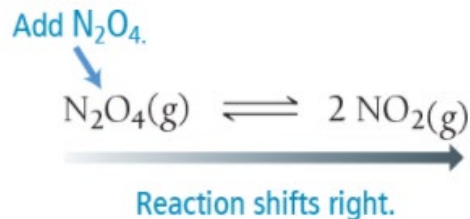
Before addition of NO_2 : $Q = K$

Immediately after addition of NO_2 : $Q > K$

Reaction shifts left (toward the reactants) to reestablish equilibrium.

Concentration Changes

Consider $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

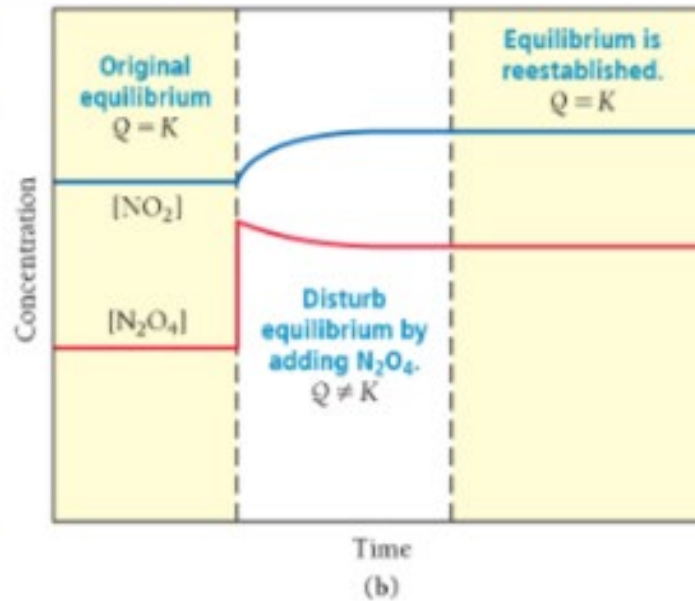
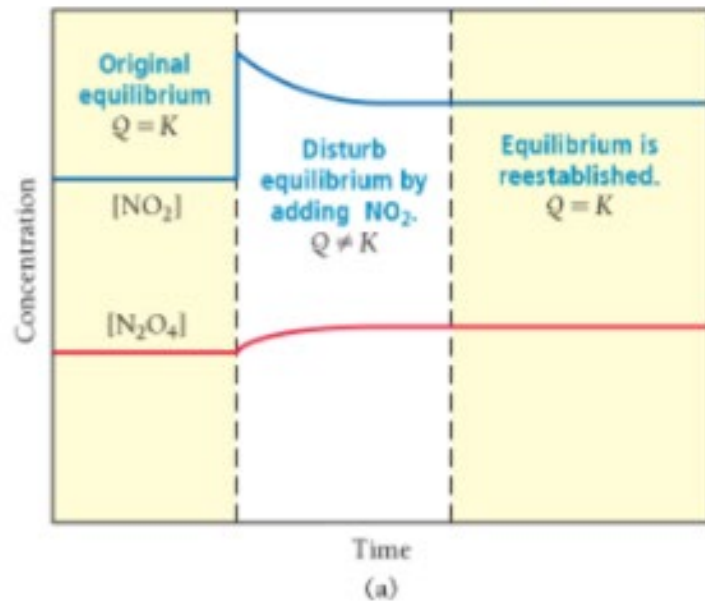


Before addition of N_2O_4 : $Q = K$

Immediately after addition of N_2O_4 : $Q < K$

Reaction shifts right (toward the products) to reestablish equilibrium.

Le Chatelier's Principle: Graphical Representation



Summarizing the Effect of a Concentration Change on Equilibrium



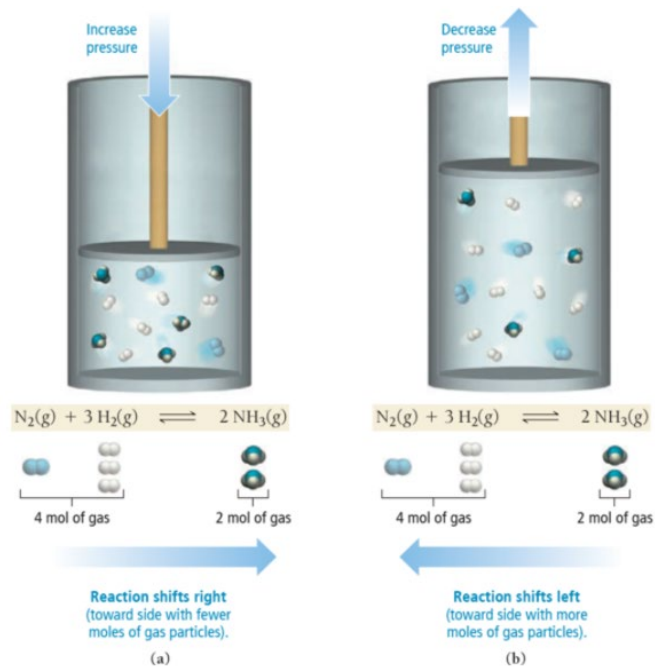
If a chemical system is at equilibrium:

- *Increasing* the concentration of one or more of the *reactants* (which makes $Q < K$) causes the reaction to *shift to the right* (in the direction of the products).
- *Increasing* the concentration of one or more of the *products* (which makes $Q > K$) causes the reaction to *shift to the left* (in the direction of the reactants).
- *Decreasing* the concentration of one or more of the *reactants* (which makes $Q > K$) causes the reaction to *shift to the left* (in the direction of the reactants).
- *Decreasing* the concentration of one or more of the *products* (which makes $Q < K$) causes the reaction to *shift to the right* (in the direction of the products).

Volume or Pressure Changes

- Consider the following reaction that takes place in a container with a moveable piston.
- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
- If the piston is lowered, volume is decreased (pressure increases)
- Since pressure is directly proportional to moles, if we lower the moles of gas produced, the pressure will decrease.
- Reaction Shifts Right

Volume or Pressure Changes



Summarizing the Effect of Volume Change on Equilibrium



If a chemical system is at equilibrium:

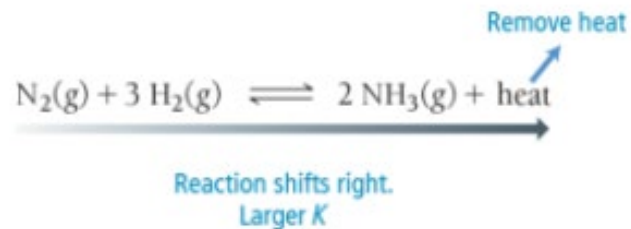
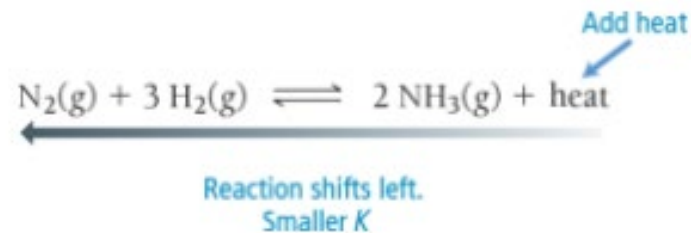
- *Decreasing* the volume causes the reaction to shift in the direction that has *the fewer moles of gas particles*.
- *Increasing* the volume causes the reaction to shift in the direction that has *the greater number of moles of gas particles*.
- If a reaction has an equal number of moles of gas on both sides of the chemical equation, then a change in volume produces no effect on the equilibrium.
- Adding an inert gas to the mixture at a fixed volume has no effect on the equilibrium.

Temperature Changes



- Unlike pressure and concentration changes, temperature changes impact the value of K_{eq} and not the value of Q .
 - Temperature changes that increase K , will cause the reaction to shift right as Q is increased to bring it back equal to K .
 - Temperature changes that decrease K , will cause the reaction to shift left as Q is decreased to bring it back equal to K .

Exothermic Reactions



Summarizing the Effect of a Temperature Change on Equilibrium



In an *exothermic* chemical reaction, heat is a product.

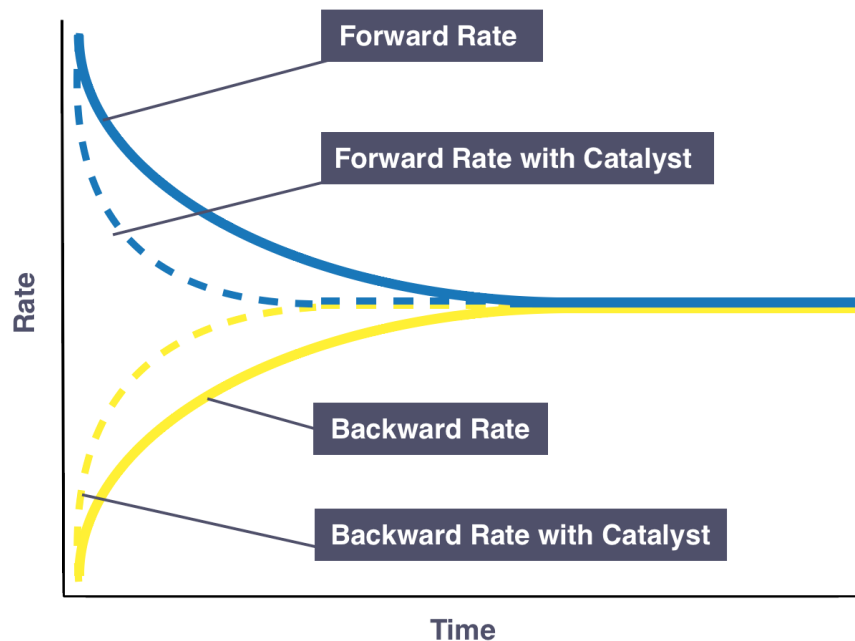
- *Increasing* the temperature causes an exothermic reaction to *shift left* (in the direction of the reactants); the value of the equilibrium constant decreases.
- *Decreasing* the temperature causes an exothermic reaction to *shift right* (in the direction of the products); the value of the equilibrium constant increases.

In an *endothermic* chemical reaction, heat is a reactant.

- *Increasing* the temperature causes an endothermic reaction to *shift right* (in the direction of the products); the equilibrium constant increases.
- *Decreasing* the temperature causes an endothermic reaction to *shift left* (in the direction of the reactants); the equilibrium constant decreases.

The Effect of Catalysts

- Adding a catalyst will increase the rate of BOTH the forward and the reverse reaction equally.
- The reaction will reach equilibrium faster, but the equilibrium position will be unchanged.



Sample Questions



- Local Exam 2019, #33
- National Exam 2019, #31
- National Exam 2019, #32