

Chapter 15-Dang

Chemical Equilibrium

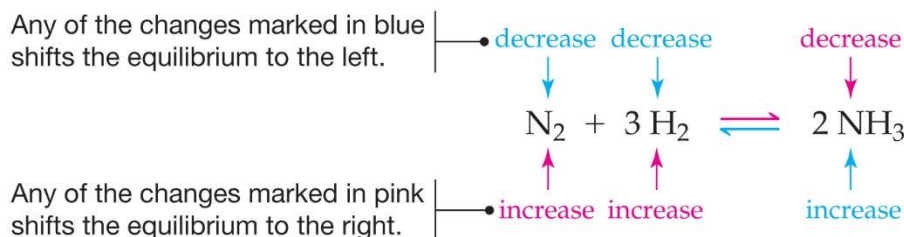
How a System at Equilibrium Responds to Disturbances

Le Châtelier's Principle: If a stress is applied to a reaction mixture *at equilibrium*, net reaction occurs in the direction that relieves the stress.

15.7 Altering an Equilibrium Mixture: Changes in Concentration

- How will this affect the rate of the forward reaction?
- How will it affect the rate of the reverse reaction?
- How will it affect the value of K_c ?

Let's consider the equilibrium that occurs in the Haber process for the synthesis of ammonia:



In general, when an equilibrium is disturbed by the addition or removal of any reactant or product, **Le Châtelier's principle** predicts that

- The concentration stress of **an added reactant or product** is relieved by net reaction in the direction that consumes the added substance.
- The concentration stress of a **removed reactant or product** is relieved by net reaction in the direction that replenishes the removed substance.

Suppose that we have an equilibrium mixture of 0.50 M N_2 , 3.00 M H_2 , and 1.98 M NH_3 at 700 K and that we disturb the equilibrium by increasing the concentration to 1.50 M.

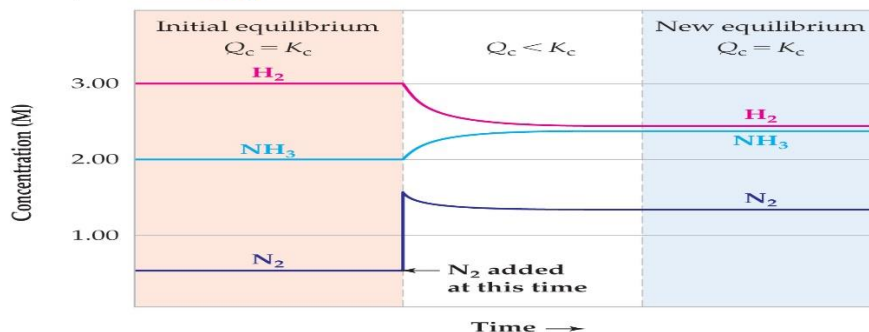
When the system at equilibrium

$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(1.98)^2}{(0.50)(3.00)^3} = 0.29 = K_c$$

For the system to move a new state of equilibrium, Q_c must increase; that is, the numerator of the equilibrium constant expression must increase and the denominator must decrease. This implies the net conversion of N_2 and H_2 to NH_3 , just as predicted by Le Châtelier's principle. When the new equilibrium is established, the concentrations are 1.31 M N_2 , 2.43 M H_2 and 2.36 M NH_3 ,

$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(2.36)^2}{(1.31)(2.43)^3} = 0.296 = K_c$$

Net conversion of N_2 and H_2 to NH_3 occurs until a new equilibrium is established. That is, the N_2 and H_2 concentrations decrease, while the NH_3 concentration increases.



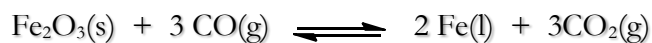
Add reactant – denominator in Q_c expression becomes larger

- $Q_c < K_c$
- To return to equilibrium, Q_c must be increases
- More product must be made => reaction shifts to the right
- Adding a reactant initially increases the rate of the forward reaction, but has no initial effect on the rate of the reverse reaction
- No change in K_c

Remove reactant - denominator in Q_c expression becomes smaller

- $Q_c > K_c$
- To return to equilibrium, Q_c must be decreases
- Less product must be made => reaction shifts to the left
- Removing a reactant initially decreases the rate of the forward reaction, but has no initial effect on the rate of the reverse reaction
- No change in K_c

Example: The reaction of iron (III) oxide with carbon monoxide occurs in a blast furnace when iron ore is reduced to iron metal:



Use Le Chatelier's principle to predict **the direction of net reaction** when an equilibrium mixture is disturbed by:

- a. adding Fe_2O_3
- b. Removing CO_2

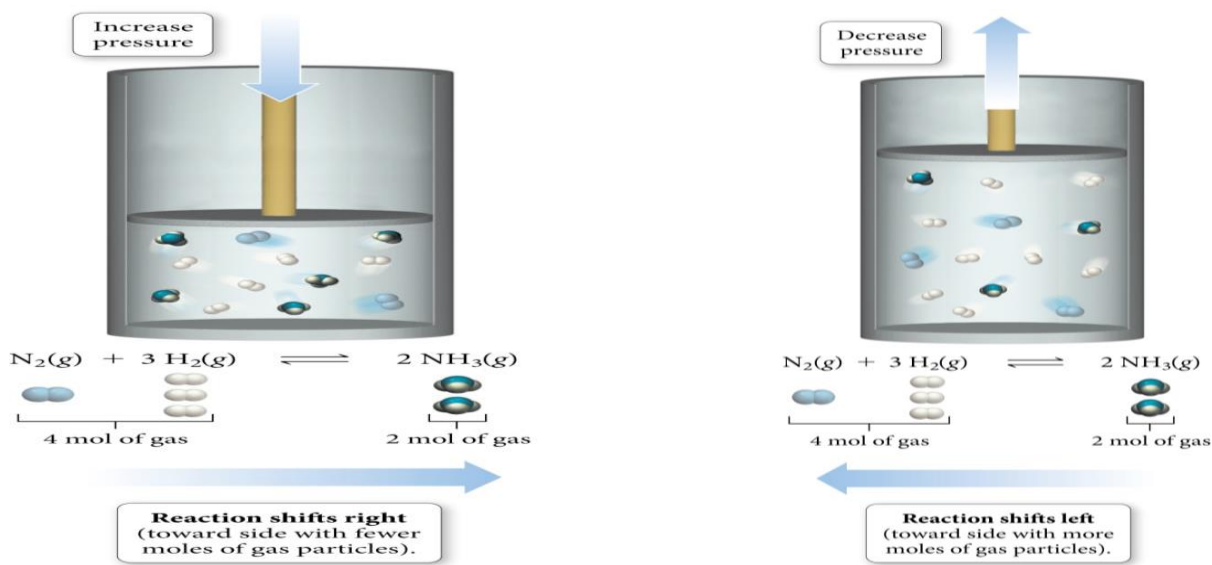
- c. Removing CO; also account for the change using the reaction quotient Q_c .

15.8 Altering an Equilibrium Mixture: Changes in Pressure and Volume

Recall, an increase in pressure by reducing the volume will bring about net reaction in the direction that decreases the number of moles of gas (Boyle's law).

In general, Le Chatelier's principle predicts that:

- An **increase in pressure** by reducing volume will bring about the net reaction in the direction that decreases the number moles of gas.
- An **decrease in pressure** by expand volume will bring about the net reaction in the direction that increase the number moles of gas.
- if the reaction shows the same number moles of gas on both side, then equilibrium does not shift in response to changing pressure.



To see why Le Chatelier's principles works for pressure (volume) changes, let calculate Q_c for the equilibrium mixture of 0.50M N_2 , 3.00 M H_2 and 1.98 M NH_3 at 700K.

$$Q_c = \frac{[NH_3]^2}{[N_2] [H_2]^3} = \frac{(1.98)^2}{(0.50) (3.00)^3} = 0.29 = K_c$$

If we disturb the equilibrium by reducing volume by a factor of 2, we not only double the total pressure, we also double the partial pressure and thus the molar concentration of each reactant and products (because molarity = n/V).

$$Q_c = \frac{[\text{NH}_3]_2}{[\text{N}_2][\text{H}_2]^3} = \frac{(3.96)^2}{(1.00)(6.00)^3} = 0.0726 \ll K_c$$

The increase in the denominator (reactants) in the expression is greater than the increase in the numerator, and the new value Q_c is less than the equilibrium constant K_c . To re-establish the equilibrium, Q_c must increase, which means the net reaction must go to the right, the side with less moles of gas.

- If reactant side has more moles of gas
 - Denominator will be larger
 - $Q_c < K_c$
 - To return to equilibrium, Q_c must be increased
 - Reaction shifts toward fewer moles of gas (to the product)
- If product side has more moles of gas
 - Numerator will be larger
 - $Q_c > K_c$
 - To return to equilibrium, Q_c must be decreased
 - Reaction shifts toward fewer moles of gas (to the reactant)

- Reaction involves no change in the number moles of gas
 - No effect on composition of equilibrium mixture
- For heterogeneous equilibrium mixture
 - Effect of pressure changes on solids and liquids can be ignored
 - Volume is nearly independent of pressure
- Change in pressure due to addition of inert gas
 - No change in the molar concentration of reactants or products
 - No effect on composition

Example: Consider the following reaction at chemical equilibrium



- a. In which direction will the equilibrium shift when decreasing the volume of the reaction mixture? How does it affect the concentration of $\text{O}_2(\text{g})$?
- b. Increasing the volume of the reaction mixture?
- c. Adding inert gas at constant volume?

15.9 Alternating Change in Temperature

Consistent with the law of mass action, an equilibrium stressed by a change in concentration will shift to re-establish equilibrium without any change in the value of the equilibrium constant, K . When an equilibrium shifts in response to a temperature change, however, it is re-established with a different relative composition that exhibits a different value for the equilibrium constant.

To understand this phenomenon, consider the elementary reaction



Since this is an elementary reaction, the rates laws for the forward and reverse may be derived directly from the balanced equation's stoichiometry:

$$\text{Rate forward} = k_f[A] \quad \text{rate reverse} = k_r[B]$$

When the system is at equilibrium,

$$\text{Rate reverse} = \text{rate forward}$$

Substituting the rate laws into this equality and rearranging gives

$$k_f[A] = k_r[B]$$

$$\frac{[B]}{[A]} = \frac{k_f}{k_r} = K_c$$

The equilibrium constant is seen to be a mathematical function of the rate constants for the forward and reverse reactions. Since the rate constants vary with temperature as described by the Arrhenius equation, it stands to reason that the equilibrium constant will likewise vary with temperature (assuming the rate constants are affected to different extents by the temperature change).

Heat can be considered a reactant in an endothermic reaction and a product in an exothermic reaction.

Endothermic ($\Delta H > 0$) Reactants + **Heat** \rightarrow Products

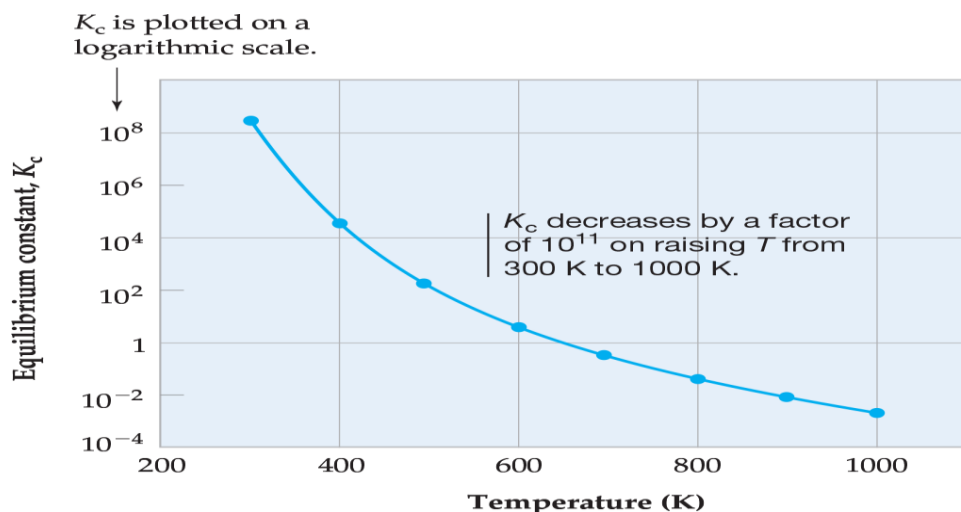
Exothermic ($\Delta H < 0$) Reactant \rightarrow Products + **Heat**

When an equilibrium is disturbed by a change in temperature, the internal energy changes, Le Châtelier's principle predicts that

- the equilibrium constant for an **exothermic** reaction (negative ΔH°) **decreases** as the temperature **increases**.
 - Contains more reactant than product
 - K_c **decreases** with **increasing** temperature

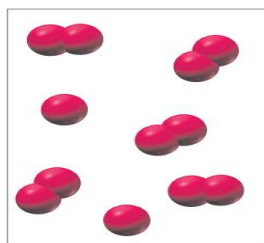
- the equilibrium constant for an **endothermic** reaction (positive ΔH°) **increases** as the temperature **increases**.
 - Contains more product than reactant
 - K_c **increases** with **increasing** temperature

For the synthesis of ammonia in Haber process, equilibrium constant K_c decreases by a factor of 1011 over the temperature range 300 – 1000K



Temp (K)	K_c
300	2.6×10^8
400	3.9×10^4
500	1.7×10^2
600	4.2
700	2.9×10^{-1}
800	3.9×10^{-2}
900	8.1×10^{-3}
1000	2.3×10^{-3}

The pictures represent the composition of the equilibrium mixture at 600 K and 650 K for the combination of two A molecules.



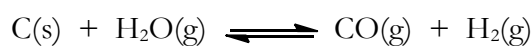
$T = 600 \text{ K}$



$T = 650 \text{ K}$

Is this reaction endothermic or exothermic? Explain using Le Chatelier's principle.

Example: Coal can be used to generate hydrogen gas (a potential fuel) by the endothermic reaction:



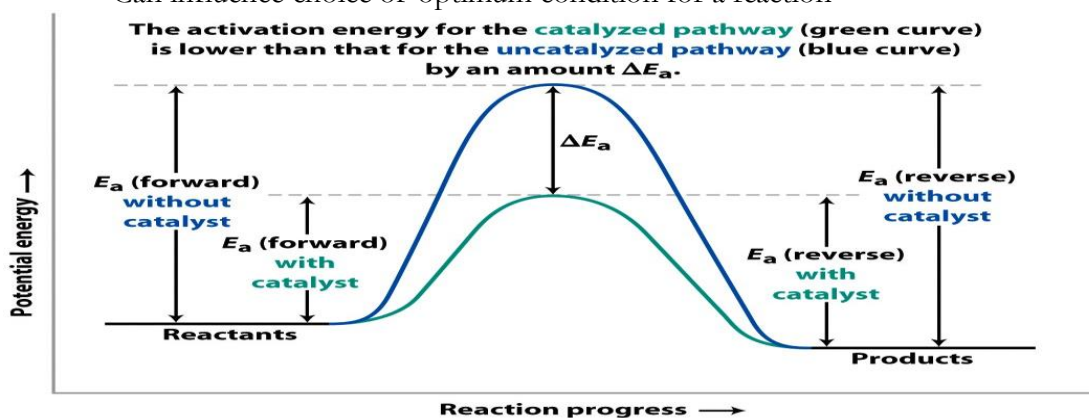
If this reaction is at equilibrium, predict whether each disturbance will result in the formation of additional hydrogen gas or less hydrogen gas or no effect.

- Adding more $\text{C}(\text{s})$ to the reaction mixture

- b. Adding more CO(g) to the reaction mixture
- c. Removing H_2O from reaction mixture, account for Q_c
- d. Decreasing total pressure
- e. Raising the temperature, account for the value of K_c

The Effect of a Catalyst on Equilibrium

- Catalyst increases the rate of a chemical reaction
 - Provide a new, lower energy pathway
 - Forward and reverse reactions pass through the same transition state
 - Rate for forward and reverse reactions increase by the same factor
 - Does not affect the composition of the equilibrium mixture
 - Does not appear in the balance chemical equation
 - Can influence choice of optimum condition for a reaction



Because the forward and reverse reactions pass through the same transition state, the catalyst lowers the activation energy barrier for the forward and reverse reactions by the same amount. The catalyst therefore accelerates the forward and reverse reactions by the same factor, and the composition of the equilibrium mixture is unchanged.