Chapter 15

CHEMICAL EQUILIBRIUM

(Part II)

15.4

The Reaction Quotient and Equilibrium Constant

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

$$K_c = \frac{[COCl_2]_{eq}}{[CO]_{eq}[Cl_2]_{eq}} \qquad Q_c = \frac{[COCl_2]}{[CO][Cl_2]}$$

- $Q_c = K_c$; equilibrium is present.
- $Q_c > K_c$; product conc. > reactant conc. ; some products must convert to reactants in order to reach equilibrium; a net shift to the left should occur ; *the reverse reaction is favored*.
- $Q_c < K_c$; product conc. < reactant conc. ; some reactants must convert to products in order to reach equilibrium ; a net shift to the right should occur ; *the forward reaction is favored*.

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Predicting the Direction of a Reaction

- Exercise:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

K_c @ 375°C is 1.2.

At the start of the reaction the concentrations of N_2, H_2, and NH_3 are 0.071 *M*, 9.2×10^{-3} *M* and 1.83×10^{-4} *M*, respectively.

(a) Is the system at equilibrium?

(b) If not, determine to which direction it must proceed in order to establish equilibrium.

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Calculation Involving Equilibrium Constants

- Knowing the equilibrium constant (K_c or K_P) and/or the initial concentrations of reactants and products for a given reaction allows you to predict several features of that reaction, such as:
  - o whether the reaction tends to occur or not.
  - o whether a given set of concentrations are at equilibrium or not.
  - o the equilibrium concentrations of the reaction mixture.

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Calculation Involving Equilibrium Constants

- Exercise:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

At a certain temperature, a 1.00-L flask initially contained 0.298 mol $PCl_3(g)$ and 8.70×10^{-3} mol $PCl_5(g)$. After the system had reached equilibrium, 2.00×10^{-3} mol $Cl_2(g)$ was found in the flask.

Calculate the equilibrium concentrations of all species and the value of K_c .

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Calculation Involving Equilibrium Constants

- Exercise:

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$$

K_c is 1.15×10^2 at a certain temperature. What will be the concentrations at equilibrium if we start with 2.000 M concentrations of both H_2 and F_2?

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Calculation Involving Equilibrium Constants

- Exercise:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

K_c @ 700 K is 5.10.

Calculate the equilibrium concentrations of all species at 700 K if 1.000 mol of each component is mixed in a 1.000-L flask.

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Calculation Involving Equilibrium Constants

- Exercise: $Br_2(g) \rightleftharpoons 2Br(g)$

K_c is 1.1×10^{-3} at 1280°C. Initially, $[Br_2] = 6.3\times10^{-2}$ M and $[Br] = 1.2 \times 10^{-2}$ M. What are the equilibrium concentrations of Br_2 and Br at 1280°C?

Find the reaction direction; $Q = \dfrac{(1.2 \times 10^{-2})^2}{6.3 \times 10^{-2}} = 2.3 \times 10^{-3}$

$Q > K_c$; the reaction will go in the reverse direction to reestablish the equilibrium.

Conc. (M)	$Br_2(g)$	$\rightleftharpoons$ $2\,Br(g)$
Initial	6.3×10^{-2} M	1.2×10^{-2} M
Change	$+x$	$-2x$
Equilibrium	$(6.3 \times 10^{-2}) + x$	$(1.2 \times 10^{-2}) - 2x$

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$$K_c = \frac{[Br]^2}{[Br_2]} = \underbrace{\frac{[(1.2\times10^{-2}) - 2x]^2}{(6.3\times10^{-2}) + x} = 1.1\times10^{-3}}_{4x^2 - 0.048x + (7.47\times10^{-5}) = 0}$$

Quadratic equation: $ax^2 + bx + c = 0$

Solutions are: $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$x_1 = 1.838\times10^{-3}$; $x_2 = 1.050\times10^{-2}$

Equilibrium conc.	$x_1 = 1.838\times10^{-3}$	~~$x_2 = 1.050\times10^{-2}$~~
$[Br] = (1.2\times10^{-2}) - 2x$	= 0.00832 M	~~$-0.00900\ M$~~
$[Br_2] = (6.3\times10^{-2}) + x$	= 0.0648 M	

impossible

$$\boxed{\begin{array}{ll}[Br] & = 8.3\times10^{-3}\ M \\ [Br_2] & = 6.5\times10^{-2}\ M\end{array}}$$

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Calculation Involving Equilibrium Constants

- Exercise:

$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$

K_c is 1.15×10^2 at a certain temperature. What will be the concentrations at equilibrium if we mix 3.000 mol of H_2 with 6.000 mol of F_2 in a 3.000-L flask?

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Factors that Affect Chemical Equilibrium

- The chemical equilibria can be affected by several factors. Affecting the chemical equilibrium of a chemical reaction may result with an increase or decrease of the amount of its products.

- ***Le Châtelier's principle*** can be used to predict the effect of a change in conditions on a chemical equilibrium.

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Le Châtelier's Principle

- ***Le Châtelier's principle*** states that:

  If a change is imposed on a system at equilibrium, the system will respond by *shifting* in the (*forward or reverse*) direction that minimizes the effect of that change. As a result, a new equilibrium position will be reestablished. Changes made on the system can be:

  - Addition or removal of a reactant or product.
  - change in the volume and pressure of the system.
  - change in temperature.

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Addition of a Substance

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

- Consider the following equilibrium concentrations:

  $[N_2]_{eq} = 2.05\ M$; $[H_2]_{eq} = 1.56\ M$; $[NH_3]_{eq} = 1.52\ M$

$$K_c = \frac{[NH_3]^2_{eq}}{[N_2]_{eq}\,[H_2]^3_{eq}} = 0.297$$

- Let' s add more N_2 by increasing its conc. from 2.05 *M* to 3.51 *M*. How do you think the system will respond to this change?

$$Q_c = \frac{(1.52)^2}{(3.51)\,(1.56)^3} = 0.173 \quad < K_c$$

The system *responds* by shifting to the right in order to reestablish equilibrium.

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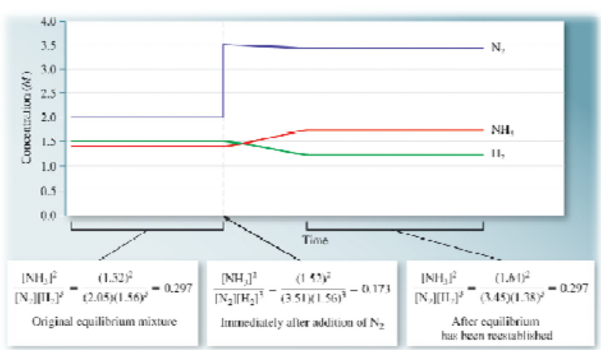
Addition of a Substance

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The system *responds* by shifting to the right in order to reestablish equilibrium.



There will be a net decrease in $[N_2]$ and $[H_2]$, and an increase in $[NH_3]$ until Q_c becomes again equal to K_c .

A change has happened to the *equilibrium position*, not to the equilibrium constant .

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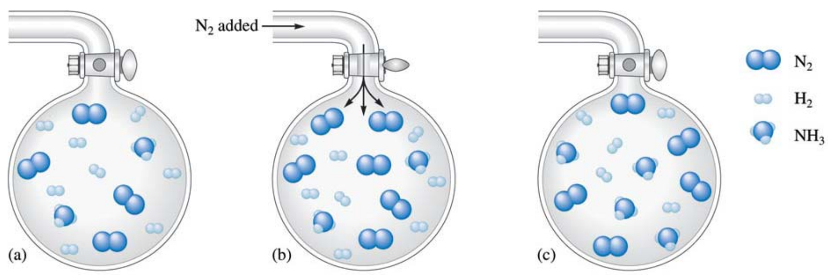
Addition of a Substance

- To the initial equilibrium mixture of N_2, H_2, and NH_3 (case: a) , some N_2 is added (case: b). The *new equilibrium position* for the system (case: c) contains more N_2 (due to Less H_2), and more NH_3 than in case a.



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Addition of a Substance

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

- What do you think will happen if more H_2 is added?

The system will respond by shifting to the right in order to reestablish equilibrium. (Bringing back $Q_c = K_c$)

- What do you think will happen if more NH_3 is added?

The equilibrium of system will be disturbed, and $Q_c > K_c$.

In order for the system to reestablish equilibrium, more NH_3 must be consumed and more H_2 and N_2 must be produced until $Q_c = K_c$.

- o In general, a system at equilibrium will respond to addition of a species by consuming some of that species.

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Removal of a Substance

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

- What do you think will happen if H_2 or N_2 is removed?

  The equilibrium of system will be again disturbed, and $Q_c > K_c$.

  The system will shift to the left to reestablish equilibrium. Some NH_3 must be consumed and some H_2 and N_2 must be produced until $Q_c = K_c$.

- What do you think will happen if more NH_3 is removed?

  - In general, a system at equilibrium will respond to the removal of a species by producing more of that species.

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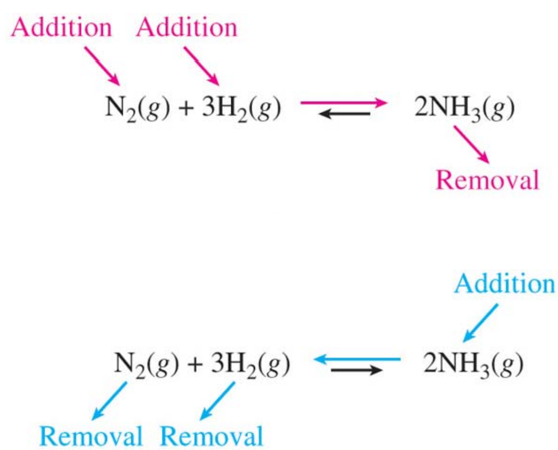
Addition or Removal of a Substance



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Addition or Removal of a Substance

- Exercise:

$$2H_2S(g) + O_2(g) \rightleftharpoons 2S(s) + 2H_2O(g)$$

(a) For the reaction above, determine its response when O_2 is added, when H_2S is removed, when H_2O is removed, and when S is added.

(b) The reaction above is commonly used to get red of hydrogen sulfide (H_2S) contaminant exist in natural gas and produce sulfur. How can it be made industrially more efficient, i.e. making it consuming more H_2S?

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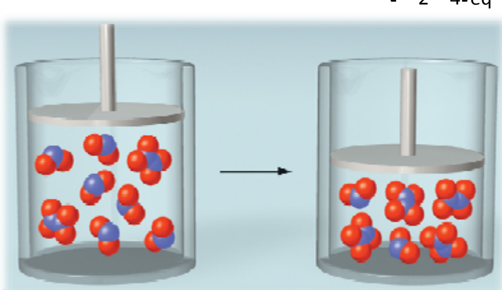
Change in Volume and Pressure

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

- Consider the following equilibrium concentrations:

$[N_2O_4]_{eq} = 0.643\ M$; $[NO_2] = 0.0547\ M$

$$K_c = \frac{[NO_2]^2_{eq}}{[N_2O_4]_{eq}} = 4.63\times10^{-3}$$



Suppose that a pressure is applied and the volume is decreased by one-half.

As a result, the concentrations of N_2O_4 and NO_2 will be *doubled*.

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Change in Volume and Pressure

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

- Consider the following equilibrium concentrations:

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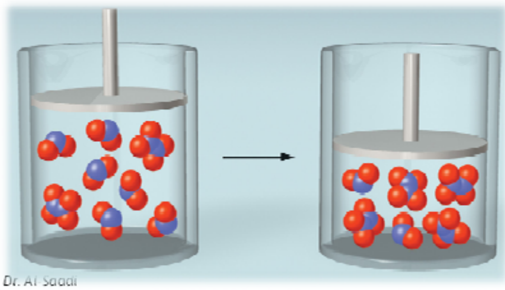

$$Q_c = \frac{(0.1094)^2}{1.286} = 9.31\times10^{-3} > K_c$$

The system *responds* by shifting to the left (*producing more of N_2O_4 and consuming more of NO_2*) in order to reestablish equilibrium.

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Change in Volume and Pressure

- Generally,
  - A *decrease* in the volume of a reaction vessel will cause a shift in the equilibrium in the direction that *minimizes the total number of moles of gaseous species*.
  - An *increase* in the volume of a reaction vessel will cause a shift in the equilibrium in the direction that *maximizes the total number of moles of gaseous species*.

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Change in Volume and Pressure

- Exercise:

  Predict the change in direction of the following reactions:

  (a) $PCl_5(g) \rightleftharpoons Cl_2(g) + PCl_3(g)$

  (Volume decreased) Shift to the left

  (b) $2PbS(s) + 3O_2(g) \rightleftharpoons 2PbO(s) + 2SO_2(g)$

  (Volume increased) Shift to the left

  (c) $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$

  (Volume increased) No shift

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Change in Temperature

- Unlike the case with concentration and pressure changes, the change in temperature of a chemical reaction can *change the value of the equilibrium constant*.

  It makes the reaction faster or slower, depending on the enthalpy change (ΔH) *"heat"* accompanying the reaction.

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Change in Temperature

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H° = 58.0 \text{ kJ/mol}$$

- Let's apply here Le Châtelier's principle to the heat absorbed as a reactant.

$$\text{Heat} + N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Adding heat means the reaction will be shifted to the right. Also, addition of heat means an increase in temperature.

- In general, increasing the temperature of endothermic reactions shifts it to the right. While decreasing the temperature of endothermic reactions shifts it to the left.

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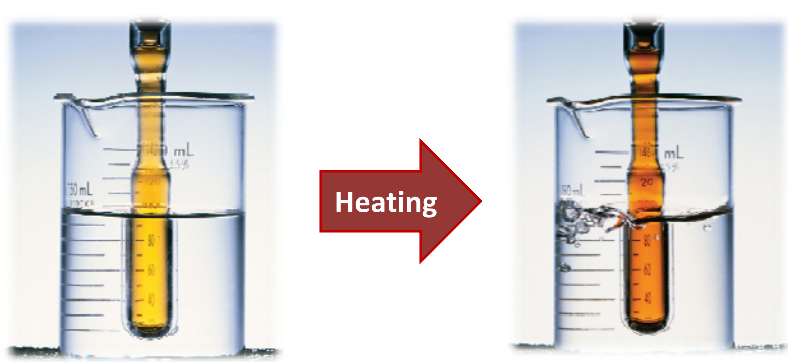
Change in Temperature

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H° = 58.0 \text{ kJ/mol}$$

yellow brown



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Change in Temperature

- Consider the following *exothermic* reaction:

$CoCl_4^{2-} + 6H_2O \rightleftharpoons Co(H_2O)_6^{2+} + 4Cl^- +$ Heat

blue pink

$CoCl_4^{2-}$ and $Co(H_2O)_6^{2+}$ ions at equilibrium

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Change in Temperature

- The increase in temperature favors endothermic reactions.
- The decrease in temperature favors exothermic reactions.
- The change in temperature not only affects the equilibrium position, but also alters the value of the equilibrium constant.

TABLE 13.3 Observed Value of *K* for the Ammonia Synthesis Reaction as a Function of Temperature*

Temperature (K)	*K*
500	90
600	3
700	0.3
800	0.04

*For this exothermic reaction, the value of *K* decreases as the temperature increases, as predicted by Le Châtelier's principle.

A Summary of Le Châtelier's Principle

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H^\circ = 58.0$ kJ/mol

Change	Shift
Addition of $N_2O_4(g)$	
Addition of $NO_2(g)$	
Removal of $N_2O_4(g)$	
Removal of $NO_2(g)$	
Decrease container volume	
Increase container volume	
Increase temperature	
Decrease temperature	

Does a Catalyst Affect the Equilibrium?

- A catalyst
  - speeds up a reaction by lowering its activation energy,
  - lowers the activation energy of the forward and backward reactions to the same extent,
  - neither changes the value of the equilibrium constant nor the equilibrium position, and
  - causes a reaction mixture that is not at equilibrium to reach equilibrium faster.