Chemistry 12

Equilibrium III

Name:
Date:
Block:

1. **The Haber-Bosch Process**
2. **K_{eq}**

The Haber-Bosch Process

It has been called one of the greatest inventions of the 20th Century, and without it almost half the world's population would not be alive today.

Two German chemists, Fritz Haber and Carl Bosch, devised a way to transform nitrogen in the air (78%) into fertilizer, using what became known as the Haber-Bosch process.

$$N_{2(g)} + 3\ H_{2\ (g)} \rightleftharpoons 2\ NH_{3\ (g)} \qquad \Delta H = -92\ kJ/mol$$

In order to form the desired product, you need to generate extreme heat and pressure. To create these conditions the Haber-Bosch process today consumes more than 1% of all the world's energy. (Think about the carbon emissions). Only some of the nitrogen in fertilizer makes its way via crops to humans.

German chemist Fritz Haber developed the equipment and procedures from producing ammonia (NH_3) from its constituent elements (N_2 and H_2) in 1910. In 1918, he received the Nobel Prize in chemistry for his accomplishment. In 1931, another German chemist, Carl Bosch, won the Nobel Prize in chemistry, in part for transforming the process to an industrial scale.

The Equilibrium Constant

Consider the following equation:

$$N_{2(g)} + 3\ H_{2\ (g)} \rightleftharpoons 2\ NH_{3\ (g)}$$

At equilibrium, the forward and reverse rates are equal.

Forward rate: Reverse rate:

Rearranging to isolate the constants, we get:

In this case, $\frac{k_f}{k_r}$ provides a constant that chemists call the equilibrium constant, **K_{eq}.**

$K_{eq} =$

Regardless of the initial concentrations of reactants and products, when equilibrium is achieved and the equilibrium concentrations are substituted into this expression, the calculated value will always be the same.

The equilibrium law states that for the general balanced equation: $$\mathbf{w\,A + x\,B \rightleftharpoons y\,C + z\,D}$$ where w, x, y and z are coefficients to balance the equation.

Balance and write the equilibrium expression for the following reactions:

___ $C_2H_{2(g)}$ + ___ $H_{2\,(g)} \rightleftharpoons$ ___ $CH_{4(g)}$

___ $SO_{2(g)}$ + ___ $O_{2\,(g)} \rightleftharpoons$ ___ $SO_{3\,(g)}$

___ $HCl_{(g)}$ + ___ $O_{2\,(g)} \rightleftharpoons$ ___ $Cl_{2(g)}$ + ___ $H_2O_{\,(g)}$

___ $CH_{4(g)}$ + ___ $H_2O_{\,(g)} \rightleftharpoons$ ___ $CO_{\,(g)}$ + ___ $H_{2\,(g)}$

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1. The following gases are at equilibrium in a flask at 423°C:
4.56×10^{-3} M H_2, 7.4×10^{-4} M I_2, and 1.35×10^{-2} M HI. What is the equilibrium constant for the reaction at this temperature?

___ $H_{2\,(g)}$ + ___ $I_{2\,(g)} \rightleftharpoons$ ___ $HI_{\,(g)}$

2. A quantity of 3.88×10^{-3} M NO_2 is at equilibrium with 1.73×10^{-4} M N_2O_4 at 60°C. What is the equilibrium constant for the reaction?

___ $NO_{2\,(g)} \rightleftharpoons$ ___ $N_2O_{4(g)}$

Chemicals in liquids or solid states are NOT included in the equilibrium expressions!!

- Liquids and solids have a fixed density and therefore, a fixed concentration.
- The only **exception** is when two liquids appear in the same equation, thus each liquids dilutes the other.

Balance and write the equilibrium expression for the following reactions:

___ $Cr_2O_7^{-2}{}_{(aq)}$ + ___ $H_2O_{(l)}$ ⇋ ___ $H^+{}_{(aq)}$ + ____ $CrO_4^{2-}{}_{(aq)}$

___ $NaCl_{(s)}$ ⇋ ___ $Na^+{}_{(aq)}$ + ___ $Cl^-{}_{(aq)}$

___ $H_{2(g)}$ + ___ $Br_{2\,(l)}$ ⇋ ___ $HBr_{(g)}$

___ $B_2H_{6(g)}$ + ___ $O_{2\,(g)}$ ⇋ ___ $B_2O_{3(s)}$ + ___ $H_2O_{(g)}$

Hebden Workbook: Pg. 60 #31, 34, 35:

31. Write the equilibrium expressions for the following.

a) $2\,ICl(g) \rightleftharpoons I_2(g) + Cl_2(g)$
b) $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$
c) $3\,O_2(g) \rightleftharpoons 2\,O_3(g)$
d) $2\,Bi^{3+}(aq) + 3\,H_2S(g) \rightleftharpoons Bi_2S_3(s) + 6\,H^+(aq)$
e) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
f) $CaC_2(s) + 2\,H_2O(l) \rightleftharpoons C_2H_2(g) + Ca(OH)_2(s)$
g) $C_6H_6(l) + Br_2(l) \rightleftharpoons C_6H_5Br(l) + HBr(g)$
h) $Cu(s) + 2\,Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2\,Ag(s)$
i) $4\,NH_3(g) + 5\,O_2(g) \rightleftharpoons 6\,H_2O(g) + 4\,NO(g)$
j) $H_2(g) + 1/2\,O_2(g) \rightleftharpoons H_2O(l)$

34. Which way will the equilibrium $CaCO_3(s) + CO_2(g) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2\,HCO_3^-(aq) + 40\text{ kJ}$ shift if

(a) more $CO_2(g)$ is added?
(b) more $CaCO_3(s)$ is added?
(c) $Ca^{2+}(aq)$ is removed?
(d) heat is added?

35. Rearrange the following equations to solve in terms of the concentrations indicated in bold.

(a) $K_{eq} = \frac{\mathbf{[H_3O^+]}[F^-]}{[HF]}$

(b) $K_{eq} = \frac{[H_3O^+][F^-]}{\mathbf{[HF]}}$

(c) $K_{eq} = \frac{\mathbf{[NO_2]}^2}{[NO]^2[O_2]}$

(d) $K_{eq} = \frac{[NO_2]^2}{\mathbf{[NO]}^2[O_2]}$

(e) $K_{eq} = \frac{[NH_3]^2}{[N_2]\,\mathbf{[H_2]}^3}$

(f) $K_{eq} = \frac{[N_2O_4]}{\mathbf{[NO_2]}^2}$

(g) $K_{eq} = \frac{\mathbf{[NH_3]}^2}{[N_2]\,[H_2]^3}$

(h) $K_{eq} = \frac{[PCl_3]^4}{[P_4]\,\mathbf{[Cl_2]}^6}$

Relative Size of K_{eq}

Recall that…

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$$

$K_{eq}>1$	K_{eq} =	______________ are favoured.
$K_{eq}<1$	K_{eq} =	______________ are favoured.

Which of the following is **least** likely to favour the formation of products?

A. $2H_2O_{(g)} \leftrightharpoons 2\,H_{2(g)} + O_{2(g)}$ $K_{eq} = 7.3 \times 10^{-18}$
B. $N_2O_{(g)} + NO_{2(g)} \leftrightharpoons 3\,NO_{(g)}$ $K_{eq} = 4.2 \times 10^{-4}$
C. $N_2O_{4(g)} \leftrightharpoons 2NO_{2(g)}$ $K_{eq} = 4.5$
D. $SO_{2(g)} + NO_{2(g)} \leftrightharpoons NO_{(g)} + SO_{3(g)}$ $K_{eq} = 85$

Explain your answer to the question above:

Does the value of K_{eq} change when…

Concentration changes?

$$N_{2(g)} + 3\,H_{2\,(g)} \leftrightharpoons 2\,NH_{3\,(g)} \qquad \Delta H = -92\ kJ/mol$$

- What happens to the relative concentrations of each species when…
  - NH_3 is increased?

$$N_{2(g)} + 3\,H_{2\,(g)} \leftrightharpoons 2\,NH_{3\,(g)} \qquad K_{eq} =$$

Overall, the concentration __________ stays the same, so K_{eq} _________________________.

  - H_2 is decreased?

$$N_{2(g)} + 3\,H_{2\,(g)} \leftrightharpoons 2\,NH_{3\,(g)} \qquad K_{eq} =$$

Overall, the concentration __________ stays the same, so K_{eq} _________________________.

Temperature changes?

$N_{2(g)} + 3\ H_{2\,(g)} \rightleftharpoons 2\ NH_{3\,(g)}$ $\Delta H= -92$ kJ/mol

- What happens to the relative concentrations of each species when…
  - Heat is increased?

    $N_{2(g)} + 3\ H_{2\,(g)} \rightleftharpoons 2\ NH_{3\,(g)} + \text{heat}$ $K_{eq} =$

    Concentration of reactants _________________.

    Concentration of products _________________.

    Therefore, K_{eq} will _________________.

  - Heat is decreased?

    $N_{2(g)} + 3\ H_{2\,(g)} \rightleftharpoons 2\ NH_{3\,(g)} + \text{heat}$ $K_{eq} =$

    Concentration of reactants _________________.

    Concentration of products _________________.

    Therefore, K_{eq} will _________________.

For the following equations, state whether the K_{eq} would increase or decrease:

Equation:	**Temperature change:**	**K_{eq} result:**
$G + H \rightleftharpoons J$ $\Delta H= -92$ kJ/mol	Increase	
$A + B + \text{heat} \rightleftharpoons C$	Increase	
$P + Q \rightleftharpoons R + S + 150$ kJ	Decrease	
$W + X + 100$ kJ $\rightleftharpoons Y + Z$	Decrease	
$N + M \rightleftharpoons P$ $\Delta H= +125$ kJ/mol	Increase	

For the following equations, determine whether the reaction is endothermic or exothermic from the observations:

Equation:	**Temperature Change:**	**K_{eq}:**	**Exo or Endo:**
$A + B \rightleftharpoons C + D$	Increase	Increases	
$E + F \rightleftharpoons G + H$	Decrease	Decrease	
$I + J \rightleftharpoons K + L$	Increase	Decrease	
$M + N \rightleftharpoons O + P$	Decrease	Increase	
$Q + R \rightleftharpoons S + T$	Increase	Decrease	

For the following equations, determine whether the temperature has increased or decreased:

Equation:	**K_{eq} result:**	**Temperature change:**
$G + H \rightleftharpoons J$ $\Delta H = -92$ kJ/mol	Increased	
$A + B + heat \rightleftharpoons C$	Decreased	
$P + Q + 150$ kJ $\rightleftharpoons R + S$	Increased	
$W + X + 100$ kJ $\rightleftharpoons Y + Z$	Decreased	
$N + M \rightleftharpoons P$ $\Delta H = +125$ kJ/mol	Increased	

Practice Questions:

1. Balance and write the equilibrium expression for each of the following:
   a. ____ $Fe_{(s)}$ + ____ $H^+_{(aq)}$ ⇋ ____ $H_{2\,(g)}$ + ____ $Fe^{2+}_{(aq)}$

   b. ____ $I^-_{(aq)}$ + ____ $Cl_{2\,(aq)}$ ⇋ ____ $I_{2\,(s)}$ + ____ $Cl^-_{(aq)}$

   c. ____ $CaO_{(s)}$ + ____ $CO_{2\,(g)}$ ⇋ ____ $CaCO_{3\,(s)}$

   d. ____ $CO_{2\,(g)}$ ⇋ ____ $CO_{2\,(aq)}$

   e. ____ $Na_2O_{(s)}$ ⇋ ____ $Na_{(l)}$ + ____ $O_{2\,(g)}$

2. A 2.0 L flask contains 0.38 mol $CH_{4(g)}$, 0.59 mol $C_2H_{2(g)}$, and 1.4 mol $H_{2(g)}$ at equilibrium. Calculate the equilibrium constant for the reaction:
   $2\ CH_{4(g)} \rightleftharpoons C_2H_{2\,(g)} + 3\ H_{2\,(g)}$

3. A cylinder contains 0.12 M $CoBr_2$, 0.060 M CO, and 0.080 M Br_2 at equilibrium. The volume of the cylinder is suddenly doubled.

$$COBr_{2(g)} \leftrightharpoons CO_{(g)} + Br_{2\,(g)}$$

a) What is the molar concentration of each gas immediately after the volume of the cylinder is doubled?

b) Explain, in terms of Le Chatelier's principle, why the system shifts right to restore equilibrium.

4. A closed flask contains 0.65 mol/L N_2 and 0.85 mol/L H_2 at equilibrium. What is the $[NH_3]$?

$$N_{2\,(g)} + 3\,H_{2\,(g)} \leftrightharpoons 2\,NH_{3\,(g)} \qquad K_{eq} = 0.017$$

<u>Hebden Workbook: Pg. 62 #36-46</u>