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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.

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

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.

Recall: Rxn Rate = $\underbrace{k}_{\text{rate constant}}$ [A] [B]

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:
- Dependent on [ ] of reactants		- Dependent on [ ] of products
$k_f[N_2][H_2]^3$	=	$k_r[NH_3]^2$

Rearranging to isolate the constants, we get:

$$\frac{k_f}{k_r} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

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

$$\boxed{K_{eq} = \frac{[\text{Products}]}{[\text{Reactants}]}}$$

* coefficients become exponents

* no units!

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.

$\frac{2}{3} = \frac{4}{6}$

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.

$$K_{eq} = \frac{[Products]}{[Reactants]} = \frac{[C]^y[D]^z}{[A]^w[B]^x}$$

Balance and write the equilibrium expression for the following reactions: K_{eq}

__ $C_2H_{2(g)}$ + 3 $H_{2\,(g)} \rightleftharpoons$ 2 $CH_{4(g)}$

$$K_{eq} = \frac{[CH_4]^2}{[C_2H_2][H_2]^3}$$

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

$$K_{eq} = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

4 $HCl_{(g)}$ + __ $O_{2\,(g)} \rightleftharpoons$ 2 $Cl_{2(g)}$ + 2 $H_2O_{\,(g)}$

$$K_{eq} = \frac{[Cl_2]^2[H_2O]^2}{[HCl]^4[O_2]}$$

__ $CH_{4(g)}$ + __ $H_2O_{\,(g)} \rightleftharpoons$ __ $CO_{\,(g)}$ + 3 $H_{2\,(g)}$

$$K_{eq} = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$

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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?

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

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.35 \cdot 10^{-2})^2}{(4.56 \cdot 10^{-3})(7.4 \cdot 10^{-4})} = \boxed{54}$$

Show this!

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?

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

$$K_{eq} = \frac{[N_2O_4]}{[NO_2]^2} = \frac{(1.73 \cdot 10^{-4})}{(3.88 \cdot 10^{-3})^2} = \boxed{11.5}$$

include: (g) & (aq) & 2 or more (l)

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:

___ $Cr_2O_7^{-2}{}_{(aq)}$ + ___ $\cancel{H_2O_{(l)}}$ $\rightleftharpoons$ 2 $H^+_{(aq)}$ + 2 $CrO_4^{2-}{}_{(aq)}$

$$K_{eq} = \frac{[H^+]^2[CrO_4^{2-}]^2}{[Cr_2O_7^{-2}]}$$

___ $\cancel{NaCl_{(s)}}$ $\rightleftharpoons$ ___ $Na^+_{(aq)}$ + ___ $Cl^-_{(aq)}$

$$K_{eq} = \frac{[Na^+][Cl^-]}{1}$$

___ $H_{2(g)}$ + ___ $\cancel{Br_{2(l)}}$ $\rightleftharpoons$ 2 $HBr_{(g)}$

$$K_{eq} = \frac{[HBr]^2}{[H_2]}$$

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

$$K_{eq} = \frac{[H_2O]^3}{[B_2H_6][O_2]^3}$$

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…

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

$K_{eq}>1$	$K_{eq} = \frac{[PRODUCTS]}{[REACTANTS]}$	Products are favoured.
$K_{eq}<1$	$K_{eq} = \frac{[PRODUCTS]}{[REACTANTS]}$	Reactants 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. $SO_{2(g)} + NO_{2(g)} \leftrightharpoons NO_{(g)} + SO_{3(g)}$ $K_{eq} = 85$

Smallest Keq
aka most likely to form reactants

Explain your answer to the question above:

Smallest Keq

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?

$$N_{2(g)}\uparrow + 3\ H_{2\,(g)}\uparrow \leftrightharpoons 2\ NH_{3\,(g)}\uparrow\downarrow \qquad K_{eq} = \frac{[Products]\uparrow}{[Reactants]\uparrow}$$

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

  - H_2 is decreased?

$$N_{2(g)}\uparrow + 3\ H_{2(g)}\downarrow\uparrow \leftrightharpoons 2\ NH_{3\,(g)}\downarrow \qquad K_{eq} = \frac{[Products]\downarrow}{[Reactants]\downarrow}$$

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

$\boxed{\therefore \text{No, [ ] doesn't affect Keq}}$

Temperature changes?

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

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

$$N_{2(g)} + 3\,H_{2\,(g)} \rightleftharpoons 2\,NH_{3\,(g)} + \text{heat} \qquad K_{eq} = \frac{[\text{Products}]\downarrow}{[\text{Reactants}]\uparrow}$$

Concentration of reactants increased.

Concentration of products decreased.

Therefore, K_{eq} will decrease. (favouring reactants)

  - Heat is decreased?

$$N_{2(g)} + 3\,H_{2\,(g)} \rightleftharpoons 2\,NH_{3\,(g)} + \text{heat} \qquad K_{eq} = \frac{[\text{Products}]\uparrow}{[\text{Reactants}]\downarrow}$$

Concentration of reactants decreased.

Concentration of products increased.

Therefore, K_{eq} will increase. (favouring products)

$\boxed{\therefore \text{Yes, temp affects } K_{eq}}$

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

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

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

start here

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

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 $G + H \rightleftharpoons J + heat$	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 $N + M + heat \rightleftharpoons P$	Increased	↑

Practice Questions:

1. Balance and write the equilibrium expression for each of the following:

   a. ____ $\cancel{Fe_{(s)}}$ + <u>2</u> $H^+_{(aq)} \rightleftharpoons$ ____ $H_{2\,(g)}$ + ____ $Fe^{2+}_{(aq)}$

   $$K_{eq} = \frac{[H_2][Fe^{2+}]}{[H^+]^2}$$

   b. <u>2</u> $I^-_{(aq)}$ + ____ $Cl_{2\,(aq)} \rightleftharpoons$ ____ $\cancel{I_{2\,(s)}}$ + <u>2</u> $Cl^-_{(aq)}$

   $$K_{eq} = \frac{[Cl^-]^2}{[I^-]^2[Cl_2]}$$

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

   $$K_{eq} = \frac{1}{[CO_2]}$$

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

   $$K_{eq} = \frac{[CO_2]}{[CO_2]}$$

   e. <u>2</u> $\cancel{Na_2O_{(s)}} \rightleftharpoons$ <u>4</u> $\cancel{Na_{(l)}}$ + ____ $O_{2\,(g)}$

   $$K_{eq} = [O_2]$$

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:
   $2\,CH_{4(g)} \rightleftharpoons C_2H_{2\,(g)} + 3\,H_{2\,(g)}$

   $$[CH_4] = \frac{0.38\,mol}{2.0\,L} = 0.19\,M \qquad [C_2H_2] = \frac{0.59\,mol}{2.0\,L} = 0.30\,M \qquad [H_2] = \frac{1.4\,mol}{2.0\,L} = 0.70\,M$$

   $$K_{eq} = \frac{[C_2H_2][H_2]^3}{[CH_4]^2}$$

   $$= \frac{(0.30)(0.70)^3}{(0.19)^2}$$

   $$= \boxed{2.9}$$

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.

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

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

$[COBr_2] = \frac{0.12M}{2} = 0.060M$ $\quad [CO] = \frac{0.060M}{2} = 0.030M$ $\quad [Br_2] = \frac{0.080M}{2} = 0.040M$

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

$$\underset{1}{COBr_2(g)} \rightleftharpoons \underset{2}{CO(g) + Br_2(g)}$$

V↑ = P↓ conc↓

↳ shift to the side w/ higher pressure (more particles)

↳ shift right

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

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

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.017$$

$$\frac{[NH_3]^2}{(0.65)(0.85)^3} = 0.017$$

$$[NH_3] = \sqrt{(0.65)(0.85)^3(0.017)}$$

$$= \boxed{0.082M}$$

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