

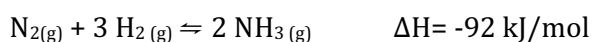
1. The Haber-Bosch Process
2. K_{eq}

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.



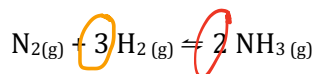
In order to form the desired product, you need to generate extreme heat and pressure. To create these conditions the Haber-Bosch process today consumes more than 1% of all the world's energy. (Think about the carbon emissions). Only some of the nitrogen in fertilizer makes its way via crops to humans.

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: $R_{xn} \text{ Rate} = k [A] [B]$

The Equilibrium Constant

Consider the following equation:



rate constant

At equilibrium, the forward and reverse rates are equal.

Forward rate:

- Dependent on [] of reactants

$$k_f [N_2] [H_2]^3$$

Reverse rate:

- Dependent on [] of products

$$k_r [NH_3]^2$$

$$k_f [N_2] [H_2]^3 = k_r [NH_3]^2$$

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} .

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

* 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.

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

The equilibrium law states that for the general balanced equation:

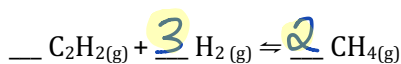
$$w A + x B \rightleftharpoons y C + z D$$

where w, x, y and z are coefficients to balance the equation.

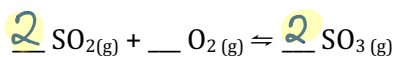
$$K_{eq} = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[C]^y [D]^z}{[A]^w [B]^x}$$

K_{eq}

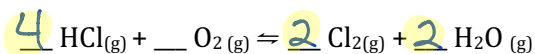
Balance and write the equilibrium expression for the following reactions:



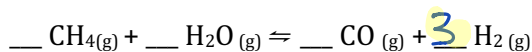
$$K_{eq} = \frac{[CH_4]^2}{[C_2H_2][H_2]^3}$$



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



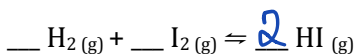
$$K_{eq} = \frac{[Cl_2]^2 [H_2O]^2}{[HCl]^4 [O_2]}$$



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

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?

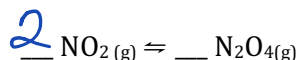


$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.35 \cdot 10^{-2})^2}{(4.56 \cdot 10^{-3})(7.4 \cdot 10^{-4})}$$

Show this!

$$= \boxed{54}$$

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?



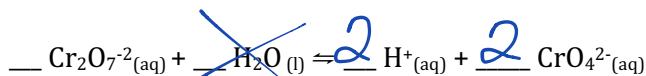
$$K_{eq} = \frac{[N_2O_4]}{[NO_2]^2} = \frac{(1.73 \cdot 10^{-4})}{(3.88 \cdot 10^{-3})^2} = \boxed{11.5}$$

include: (g) & (aq) & ^{2 or more} (l)

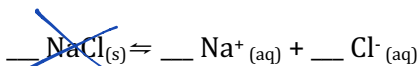
Chemicals in liquids or solid states are NOT included in the equilibrium expressions!!

- 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 liquid dilutes the other.

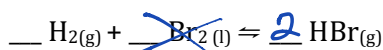
Balance and write the equilibrium expression for the following reactions:



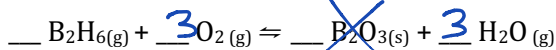
$$K_{\text{eq}} = \frac{[\text{H}^+]^2 [\text{CrO}_4^{2-}]^2}{[\text{Cr}_2\text{O}_7^{2-}]}$$



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



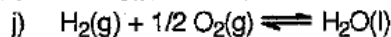
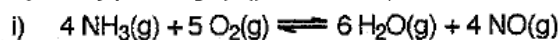
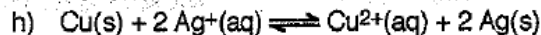
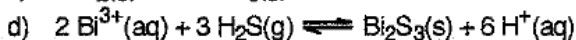
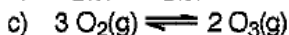
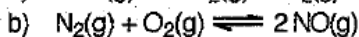
$$K_{\text{eq}} = \frac{[\text{HBr}]^2}{[\text{H}_2]}$$



$$K_{\text{eq}} = \frac{[\text{H}_2\text{O}]^3}{[\text{B}_2\text{H}_6][\text{O}_2]^3}$$

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

31. Write the equilibrium expressions for the following.



34. Which way will the equilibrium $\text{CaCO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2 \text{HCO}_3^-(\text{aq}) + 40 \text{ kJ}$ shift if

(a) more $\text{CO}_2(\text{g})$ is added?

(c) $\text{Ca}^{2+}(\text{aq})$ is removed?

(b) more $\text{CaCO}_3(\text{s})$ is added?

(d) heat is added?

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

(a) $K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$

(d) $K_{\text{eq}} = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$

(g) $K_{\text{eq}} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$

(b) $K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$

(e) $K_{\text{eq}} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$

(h) $K_{\text{eq}} = \frac{[\text{PCl}_3]^4}{[\text{P}_4][\text{Cl}_2]^6}$

(c) $K_{\text{eq}} = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$

(f) $K_{\text{eq}} = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$

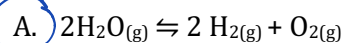
Relative Size of K_{eq}

Recall that...

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

$K_{eq} > 1$	$K_{eq} = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$	<u>Products</u> are favoured.
$K_{eq} < 1$	$K_{eq} = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$	<u>Reactants</u> are favoured.

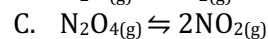
Which of the following is least likely to favour the formation of products?



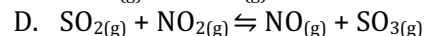
$$K_{eq} = 7.3 \times 10^{-18}$$



$$K_{eq} = 4.2 \times 10^{-4}$$



$$K_{eq} = 4.5$$



$$K_{eq} = 85$$

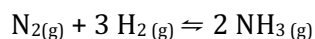
Smallest K_{eq}
aka most likely
to form
reactants

Explain your answer to the question above:

Smallest K_{eq}

Does the value of K_{eq} change when...

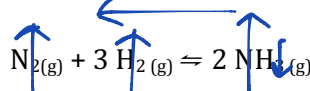
Concentration changes?



$$\Delta H = -92 \text{ kJ/mol}$$

- What happens to the relative concentrations of each species when...

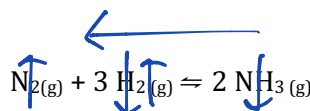
- o NH_3 is increased?



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

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

- o H_2 is decreased?

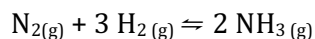


$$K_{eq} = \frac{[\text{Products}] \downarrow}{[\text{Reactants}] \downarrow}$$

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

∴ No, $[\]$ doesn't affect K_{eq}

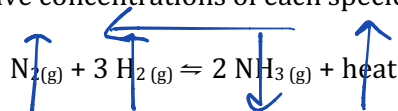
Temperature changes?



$$\Delta H = -92 \text{ kJ/mol}$$

- What happens to the relative concentrations of each species when...

- Heat is increased?



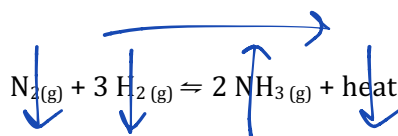
$$K_{\text{eq}} = \frac{[\text{Products}] \downarrow}{[\text{Reactants}] \uparrow}$$

Concentration of reactants increased.

Concentration of products decreased.

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

- Heat is decreased?



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

Concentration of reactants decreased.

Concentration of products increased.

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

\therefore Yes, temp affects K_{eq}

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

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

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

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

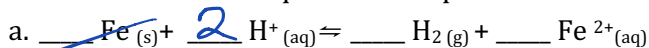
Start here (arrow pointing to K_{eq} column)

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

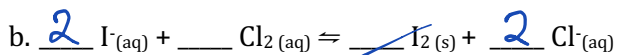
Equation:	K_{eq} result:	Temperature change:
$G + H \rightleftharpoons J$ $\Delta H = -92 \text{ kJ/mol}$ $G + H \rightleftharpoons J + \text{heat}$ (down arrow)	Increased (right arrow)	↓
$A + B + \text{heat} \rightleftharpoons C$ (down arrow)	Decreased (left arrow)	↓
$P + Q + 150 \text{ kJ} \rightleftharpoons R + S$ (up arrow)	Increased (right arrow)	↑
$W + X + 100 \text{ kJ} \rightleftharpoons Y + Z$ (down arrow)	Decreased (left arrow)	↓
$N + M \rightleftharpoons P$ $\Delta H = +125 \text{ kJ/mol}$ $N + M + \text{heat} \rightleftharpoons P$ (up arrow)	Increased (right arrow)	↑

Practice Questions:

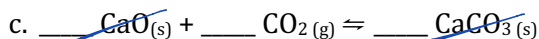
1. Balance and write the equilibrium expression for each of the following:



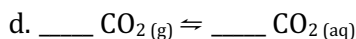
$$K_{eq} = \frac{[H_2][Fe^{2+}]}{[H^+]^2}$$



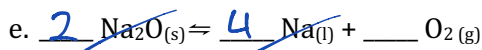
$$K_{eq} = \frac{[Cl^-]^2}{[I^-]^2 [Cl_2]}$$



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



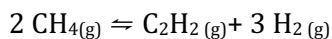
$$K_{eq} = \frac{[CO_2]}{[CO_2]}$$



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

2. A 2.0 L flask contains 0.38 mol CH_{4(g)}, 0.59 mol C₂H_{2(g)}, and 1.4 mol H_{2(g)} at equilibrium.

Calculate the equilibrium constant for the reaction:



$$[CH_4] = \frac{0.38 \text{ mol}}{2.0 \text{ L}} \\ = 0.19 \text{ M}$$

$$[C_2H_2] = \frac{0.59 \text{ mol}}{2.0 \text{ L}} \\ = 0.30 \text{ M}$$

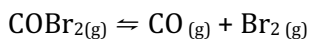
$$[H_2] = \frac{1.4 \text{ mol}}{2.0 \text{ L}} \\ = 0.70 \text{ M}$$

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

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

$$= \boxed{2.9}$$

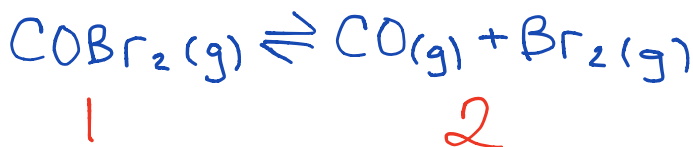
3. A cylinder contains 0.12 M CoBr_2 , 0.060 M CO , and 0.080 M Br_2 at equilibrium. The volume of the cylinder is suddenly doubled.



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

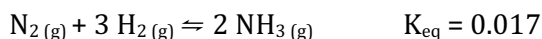
$$\begin{aligned} [\text{CoBr}_2] &= \frac{0.12\text{M}}{2} & [\text{CO}] &= \frac{0.060\text{M}}{2} & [\text{Br}_2] &= \frac{0.080\text{M}}{2} \\ &= 0.060\text{M} & &= 0.030\text{M} & &= 0.040\text{M} \end{aligned}$$

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



*VT = 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 $[\text{NH}_3]$?



$$K_{\text{eq}} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = 0.017$$

$$\frac{[\text{NH}_3]^2}{(0.65)(0.85)^3} = 0.017$$

$$\begin{aligned} [\text{NH}_3] &= \sqrt{(0.65)(0.85)^3(0.017)} \\ &= \boxed{0.082\text{M}} \end{aligned}$$