

## Chapter 15: Chemical Equilibrium

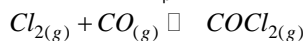
### Kahoot!

1. At eq, the rate of the forward reaction is \_\_\_ the rate of the reverse reaction. **equal to**, slower than, faster than, the reverse of
2. Select the statement that BEST describes a system at equilibrium. The reaction stops since all reactants have become products. The reaction stops since all of the catalyst has been used. **As soon product forms other molecules form reactants**. The reaction stops because equilibrium amounts have been reached.
3. The eq expression for  $4A + 3B_2 \rightleftharpoons 2C + D$  is \_\_\_\_.  $K_c = [C][D]/[A][B_2]$ ,  $K_c = [A][B_2]/[C][D]$ ,  $K_c = [C]^2[D]/[A]^4[B_2]^3$ ,  $K_c = [A]^4[B_2]^3/[C]^2[D]$
4. The reverse eq expression for the  $4A + 3B_2 \rightleftharpoons 2C + D$  is \_\_\_\_.  $K_c = [C][D]/[A][B_2]$ ,  $K_c = [A][B_2]/[C][D]$ ,  $K_c = [C]^2[D]/[A]^4[B_2]^3$ ,  $K_c = [A]^4[B_2]^3/[C]^2[D]$
5. Equilibrium constants typically have units of \_\_\_\_. **M, M<sup>2</sup>, M<sup>-1</sup>**, None of the above
6.  $K_p = K_c$  when \_\_\_\_. the reaction is at eq, the reaction is exothermic, all of the gases present are at the same pressure,  **$n_{\text{gas, products}} = n_{\text{gas, reactants}}$**
7. What is the  $K_p$  of  $\text{Cl}_{2(g)} + \text{CO}_{(g)} \rightleftharpoons \text{COCl}_{2(g)}$  at 325C given  $K_c$  is 5.0? 1.0, 10.0, **0.10**, 0.010
8. What is the  $K_c$  for  $3\text{O}_2 \rightleftharpoons 2\text{O}_3$  if the original  $K_c$  was 25 for  $4\text{O}_3 \rightleftharpoons 6\text{O}_2$ ? 25, **0.2**, 20 5
9. If the value of the  $K_c$  is large, then at equilibrium mostly \_\_\_ will be present. reactants, **products**, catalysts, water
10.  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$   $[\text{HA}] = 1.65 \times 10^{-2} \text{ M}$ , &  $[\text{H}^+] = [\text{A}^-] = 5.44 \times 10^{-4} \text{ M}$  at eq.  $K_c =$  \_\_\_\_.  $1.79 \times 10^{-2}$ ,  $1.79 \times 10^{-3}$ ,  $1.79 \times 10^{-4}$ ,  **$1.79 \times 10^{-5}$**
11. The reaction quotient Q is usually represented by \_\_\_\_.  $[\text{reactants}]/[\text{products}]$ ,  **$[\text{products}]/[\text{reactants}]$** ,  $[\text{reactants}] \times [\text{products}]$ ,  $[\text{reactants}] + [\text{products}]$
12.  $\text{Co}(s) + 2 \text{H}^+(aq) \rightleftharpoons \text{Co}^{2+}(aq) + \text{H}_2(g)$  Which Q is correct?  $Q = [\text{Co}][\text{H}^+]^2/[\text{Co}^{2+}][\text{H}_2]$ ,  **$Q = [\text{Co}^{2+}][\text{H}_2]/[\text{H}^+]^2$** ,  $Q = [\text{Co}^{2+}][\text{H}_2]/[\text{Co}][\text{H}^+]^2$ ,  $Q = [\text{H}^+]^2/[\text{Co}^{2+}][\text{H}_2]$
13. Which of the following is true if reaction quotient Q is at eq?  $Q > K$ ,  $Q < K$ ,  **$Q = K$** ,  $Q^2 = K$
14. If  $K = 2.39$  and  $Q = 5.21$  which direction do we go in to reach equilibrium? **reverse**, forward, remain the same, cannot be predicted.
15. Q for heterogeneous equilibria do not include concentrations of \_\_\_\_. pure liquids, pure solids, **both**, neither
16.  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$  If  $\text{H}_2$  is added,  $[\text{CO}]_{\text{eq}}$  will \_\_\_\_. **increase**, decrease, remain unchanged, disappear
17.  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$  If all species are gases & the container is compressed,  $[\text{CO}]_{\text{eq}}$  will \_\_\_\_. increase, decrease, **remain unchanged**, disappear
18.  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$  If  $\text{H}_2\text{O}$  is added,  $[\text{CO}]_{\text{eq}}$  will \_\_\_\_. increase, **decrease**, remain unchanged, disappear
19.  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$  If  $\text{CO}_2$  is removed,  $[\text{CO}]_{\text{eq}}$  will \_\_\_\_. increase, **decrease**, remain unchanged, disappear
20.  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$  Adding a catalyst will cause  $[\text{CO}]_{\text{eq}}$  to \_\_\_\_. increase, decrease, **remain unchanged**, disappear
21.  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$  If this is an endothermic reaction and T is increased,  $[\text{CO}]_{\text{eq}}$  will \_\_\_\_. **increase**, decrease, remain unchanged, disappear
22.  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$  If this is an endothermic reaction and T is increased, the value of  $K_c$  will \_\_\_\_. **increase**, decrease, remain unchanged, disappear
23.  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$  Adding a Ne to this reaction will cause the will cause  $[\text{CO}]_{\text{eq}}$  to \_\_\_\_. increase, decrease, **remain unchanged**, disappear
24.  $\text{Ni}(\text{CO})_{4(g)} \rightleftharpoons \text{Ni}_{(s)} + 4 \text{CO}_{(g)}$  Adding nickel to this reaction will cause the equilibrium to \_\_\_\_. Shift toward products, shift toward reactants, **remain unchanged**, change based on the amount added

**Numeric Example:** A reaction vessel contains an eq mix of the following:  $P_{\text{SO}_2} = 0.0018$  atm,  $P_{\text{O}_2} = 0.0032$  atm, and  $P_{\text{SO}_3} = 0.0166$  atm. What is the eq constant for the following reaction?  $2\text{SO}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{SO}_{3(g)}$

$$K_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}} = \frac{(0.0166 \text{ atm})^2}{(0.0018 \text{ atm})^2 (0.0032 \text{ atm})} = 2.66 \times 10^4$$

**Another Example:** What is the  $K_p$  of the reaction below at 325°C given  $K_c = 5.0$ ?



$$K_c = \frac{[COCl_2]}{[Cl_2][CO]} \rightarrow \therefore K_c \text{ units are } \frac{L}{mol}$$

$$K_p = K_c (RT)^{\Delta n} = 5.0 \frac{L}{mol} \left( 0.08206 \frac{L \cdot atm}{mol \cdot K} \times (325 + 273.15) K \right)^{(1-2)}$$

$$K_p = 0.10$$

**Application of Mass Action Rules I:** Calculate the eq const for  $2D \rightleftharpoons A + 2B$  given the info below.



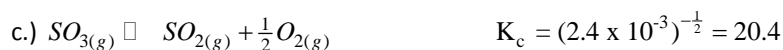
- we need to look from the reverse direction for both of these reactions

$$C \rightleftharpoons A + 2B \quad K_c = \frac{1}{3.3} = 0.303$$

$$2D \rightleftharpoons C \quad K_c = \frac{1}{0.041} = 24.4$$

$$2D \rightleftharpoons A + 2B \quad K_c = 0.303 \times 24.4 = 7.39$$

**Application of Mass Action Rules II:** If the eq. constant at a given temperature is  $2.4 \times 10^{-3}$  for  $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$  what is the eq. constant for the reactions below?



**Calculating Equilibrium Constant when all eq concentrations are known:** What is the  $K_c$  for  $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$  if their equilibrium concentrations are  $[SO_2]=0.15 \text{ M}$ ,  $[O_2]=0.68$ ,  $[SO_3]=1.5$

1. Write down the equilibrium expression symbolically:

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

2. Plug the give equilibrium values into the expression and solve:

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} = \frac{[1.5]^2}{[0.15]^2 [0.68]} = 1.5 \times 10^2$$

**Calculating Eq Constant with both initial and some eq concentrations known:** we use an "ICE" table, "I"nitial, "C"hange, "E"q & stoichiometry

-- Ex: What is the  $K_c$  for  $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$  if the initial concentrations of reactants were  $[SO_2]=0.150 \text{ M}$  and  $[O_2]=0.680 \text{ M}$  and the equilibrium concentration of the product is  $[SO_3]=0.050 \text{ M}$ ?

1. Setup the ICE table

	SO <sub>2</sub>	O <sub>2</sub>	SO <sub>3</sub>
Initial	0.15	0.68	0.0
Change	-2x	-x	+2x
Eq	?	?	0.05

- Use the given equilibrium concentration to identify  $x$   
 $2x = 0.050 \rightarrow x = 0.025$
- Plug  $x$  into the table to get the missing equilibrium concentrations

	SO <sub>2</sub>	O <sub>2</sub>	SO <sub>3</sub>
Initial	0.150	0.680	0.00
Change	-2(0.025)	-0.025	+2x
Eq	0.100	0.655	0.05

- Write down the equilibrium expression symbolically and plug in values

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} = \frac{[0.05]^2}{[0.10]^2 [0.655]} = 3.8 \times 10^{-1}$$

**Calculating Equilibrium constant when the initial concentrations and %dissociation is known:**

-- Ex: What is the  $K_c$  for  $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$  if 0.500M of both reactants will be 0.5% dissociated in order to reach equilibrium?

- Setup the ICE table

	SO <sub>2</sub>	O <sub>2</sub>	SO <sub>3</sub>
Initial	0.500	0.500	0.0
Change	-2x	-x	+2x
Eq	?	?	?

- Use the given %dissociation to identify  $x$

$$x = \frac{\% \text{ dissociation}}{100} [\text{initial concentration}] \rightarrow x = \frac{0.5}{100} [0.5] = 0.0025$$

- Plug  $x$  into the table to get the missing equilibrium concentrations

	SO <sub>2</sub>	O <sub>2</sub>	SO <sub>3</sub>
Initial	0.500	0.500	0.00
Change	-2(0.0025)	-0.0025	+2x
Eq	0.4950	0.4975	0.0050

- Write down the equilibrium expression symbolically and plug in values

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} = \frac{[0.0050]^2}{[0.4950]^2 [0.4975]} = 2.05 \times 10^{-4}$$

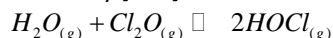
**Example with Q:** Given the data below is the reaction in equilibrium and if not in which direction will need to go in order to reach eq?

$A \rightleftharpoons B$   $K = 22$ ,  $[A] = 0.10 \text{ M}$ ,  $[B] = 2.0 \text{ M}$

$$Q = \frac{[B]}{[A]} = \frac{2.0}{0.1} = 20 < 22 = K \text{ therefore it will go in the forward direction}$$

**Calculating Equilibrium Concentrations using "ICE" table, "I"nitial, "C"hange, "E"q**

**ICE Example I:** The value of  $K_c = 0.0900$  at 298K for the reaction below, determine the eq concentrations if initially  $[H_2O] = 0.00432 \text{ M}$  and  $[Cl_2O] = 0.00442 \text{ M}$ .



- Write down the ICE table

	H <sub>2</sub> O	Cl <sub>2</sub> O	HOCl
Initial	0.00432	0.00442	0.0
Change	-x	-x	+2x
Eq	0.00432-x	0.00442-x	+2x

- Write down the equilibrium expression symbolically

$$K_c = \frac{[HOCl]^2}{[H_2O][Cl_2O]}$$

- Fill in the expression and get the quadratic equation

$$K_c = \frac{(2x)^2}{(0.00432 - x)(0.00442 - x)} = \frac{4x^2}{1.9094 \times 10^{-5} - 8.74 \times 10^{-2}x + x^2} = 0.0900$$

$$0.0900(1.9094 \times 10^{-5} - 8.74 \times 10^{-2}x + x^2) = 4x^2$$

$$1.1785 \times 10^{-6} - 7.866 \times 10^{-4}x + 0.0900x^2 = 4x^2$$

$$0 = 3.9100x^2 + 7.866 \times 10^{-4}x - 1.1785 \times 10^{-6}$$

4. Use the quadratic equation to find x (choose the positive value)

Recall the quadratic equation:

$$\text{for } ax^2 + bx + c = 0 \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

in our case, a = 3.9100, b = 7.866 × 10<sup>-4</sup>, c = 1.1785 × 10<sup>-6</sup>

$$x = \frac{-7.866 \times 10^{-4} \pm \sqrt{(7.866 \times 10^{-4})^2 - 4 \times 3.9100 \times (-1.1785 \times 10^{-6})}}{2 \times 3.9100}$$

$$x = \frac{-7.866 \times 10^{-4} \pm \sqrt{6.187 \times 10^{-7} + 2.688 \times 10^{-5}}}{7.82}$$

$$x = \frac{-7.866 \times 10^{-4} \pm 0.005244}{7.82} \rightarrow x = 5.70 \times 10^{-4} \quad \text{or} \quad x = -7.71 \times 10^{-4}$$

5. Plug the x value into the E row of the table and find the concentrations:

x must be greater than zero therefore x = 5.70 × 10<sup>-4</sup>

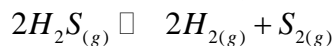
Using this value we can determine what the concentrations are at eq:

$$[\text{H}_2\text{O}] = 0.00432 - x = 0.00432 - 0.00057 = 0.00375 \text{ M}$$

$$[\text{Cl}_2\text{O}] = 0.00442 - x = 0.00385 \text{ M}$$

$$[\text{HOCl}] = 2x = 0.00114 \text{ M}$$

**ICE Example II:** The value of K<sub>c</sub> for the thermal decomposition of hydrogen sulfide



is 2.2 × 10<sup>-6</sup> at 1400K. A sample of gas in which [H<sub>2</sub>S] = 0.600M is heated to 1400K in a sealed vessel. After chemical eq has been achieved, what is the value of [H<sub>2</sub>S]? Assume no H<sub>2</sub> and S<sub>2</sub> was present in the original sample.

1. Write down the ICE table

	H <sub>2</sub> S	H <sub>2</sub>	S <sub>2</sub>
Initial	0.600	0.0	0.0
Change	-2x	+2x	+x
Eq	0.600-2x	+2x	+x

2. Write down the equilibrium expression symbolically:

$$K_c = \frac{[\text{H}_2][\text{S}_2]}{[\text{H}_2\text{S}]^2}$$

3. Fill in the expression

$$K_c = \frac{(2x)^2(x)}{(0.600 - 2x)^2} = \frac{4x^3}{(0.600 - 2x)^2} = 2.2 \times 10^{-6}$$

4. Here we cannot use quadratic so instead we must use an assumption to find x:

$$\text{assume } 0.600 \gg 2x \therefore 0.600 - 2x \approx 0.600$$

$$\frac{4x^3}{(0.600 - 2x)^2} = 2.2 \times 10^{-6} \approx \frac{4x^3}{0.36} \rightarrow x = 0.00583\text{M}$$

5. Verify assumption:

$$\frac{0.00583 \times 2}{0.600} \times 100\% = 1.94\% < 5\% \therefore \text{valid}$$

6. Use the E row to find the equilibrium concentrations:

Using  $x = 0.00734 \text{ M}$  we can determine what the concentrations are at eq:

$$[\text{H}_2\text{S}] = 0.600 - 2x = 0.600 - 2 \cdot 0.00734 = 0.585 \text{ M}$$

$$[\text{H}_2] = 2x = 0.01468 \text{ M and } [\text{S}_2] = 0.00367 \text{ M}$$

**ICE Example III:** What are the eq concentrations of each of the species in the following reaction, given the  $K_c = 5.1$  at 700K and the initial concentration of all species is 0.050 M?



	CO	H <sub>2</sub> O	CO <sub>2</sub>	H <sub>2</sub>
Initial	0.050	0.050	0.050	0.050
Change	-x	-x	+x	+x
Eq	0.050-x	0.050-x	0.050+x	0.050+x

$$K_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(0.050+x)(0.050+x)}{(0.050-x)(0.050-x)} = \frac{(0.050+x)^2}{(0.050-x)^2} = 5.1$$

$$\frac{(0.050+x)^2}{(0.050-x)^2} = 5.1 \rightarrow \frac{(0.050+x)}{(0.050-x)} = 2.258$$

$$2.258(0.050-x) = 0.050+x$$

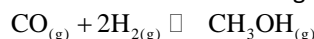
$$0.1129 - 2.258x = 0.050+x \rightarrow x = 0.0193 \text{ M}$$

using this value we determine the concentrations:

$$[\text{CO}] = [\text{H}_2\text{O}] = (0.050-0.0193)\text{M} = 0.031 \text{ M}$$

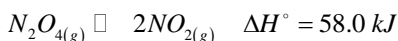
$$[\text{CO}_2] = [\text{H}_2] = (0.050+0.0193)\text{M} = 0.069 \text{ M}$$

**LCP Example I:** For each scenario predict the direction the reaction goes to attain eq:



- CO is added ..... reaction goes toward product (forward)
- CH<sub>3</sub>OH is added ..... reaction goes toward reactants (reverse)
- Pressure is reduced .....  $\Delta n_{\text{reactants}} = 3$ ,  $\Delta n_{\text{products}} = 1$  reaction goes toward reactants (reverse)
- Volume is increased ..... reaction goes toward reactant (forward)

**LCP Example II:** In what direction will the eq shift when each of the following changes are made to the system at eq?



- $\text{N}_2\text{O}_{4(g)}$  is added ..... reaction goes toward product
- $\text{NO}_{2(g)}$  is removed ..... reaction goes toward product
- the total pressure is increased by adding  $\text{N}_{2(g)}$  ..... reaction remains unchanged since the partial pressures of the reacting species is constant at constant volume
- the volume is decreased ..... reaction goes toward reactant since  $\Delta n_{\text{reactants}} = 1$ ,  $\Delta n_{\text{products}} = 2$
- the temperature is decreased ..... reaction goes toward reactant since the process is endothermic or  $\text{N}_2\text{O}_{4(g)} + 58.0 \text{ kJ} \rightleftharpoons 2\text{NO}_{2(g)}$