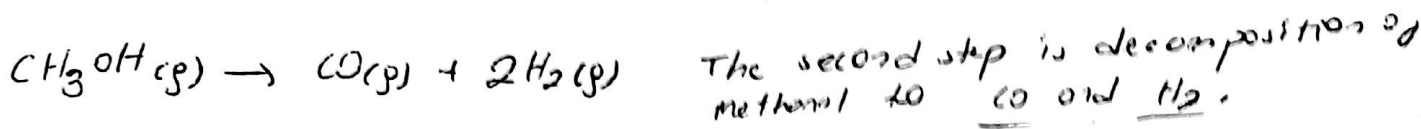
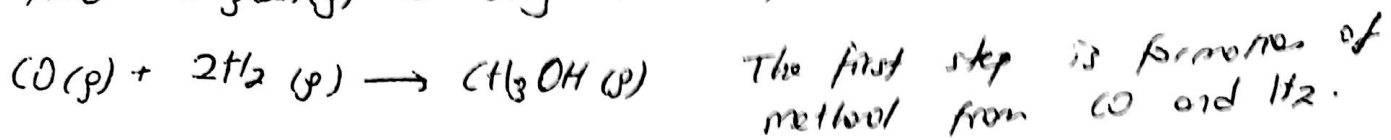


CHP 11 CHEMICAL EQUILIBRIUM 1

Let's examine a simple rxn.

- Methanol synthesis is a reversible rxn, which means that at the same time $\text{CH}_3\text{OH}(g)$ is being formed,

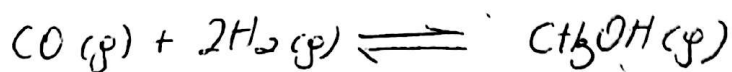


* If a rxn involving both a forward and a reverse rxns it is called reversible rxn.

1) Initially, only the forward rxn occurs, but as soon as some CH_3OH forms, the reverse rxn begins.

2) With passing time the forward rxn slows because of decreases concentrations of reactant and the reverse rxn speeds up.

3) Finally, the forward and reverse rxns proceed at equal rates. We can say that there is a dynamic equilibrium, and represent it with a double arrow \rightleftharpoons .



* The amounts of reactants and products remain constant during the equilibrium.

For the methanol synthesis rxn the ratio of equilibrium concentration is represented by following equation.

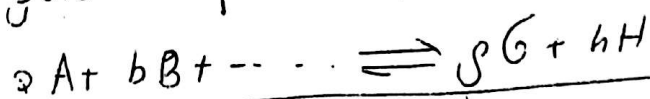
$$K = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2}$$

equilibrium constant

* The ratio of equilibrium concentrations is called equilibrium constant expression and its numerical value is the equilibrium constant.

\Rightarrow equilibrium constant expression.

- A general expression for K:



$K = \frac{(a_G)^g (a_H)^h}{(a_A)^a (a_B)^b}$	$= \frac{[\text{G}]^g [\text{H}]^h}{[\text{A}]^a [\text{B}]^b}$	<p>products</p> <p>reactants</p>
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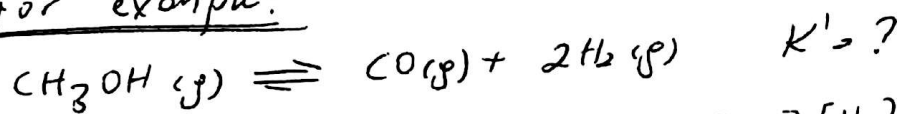
initial amounts of reactant and products.

The value of eq. constant depends only on the particular rxn and on the temperature.

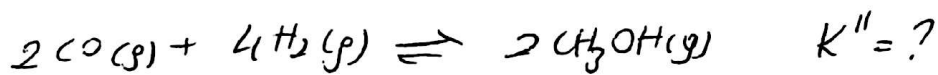
Relationships Involving Equilibrium Constant

- 1) When we reverse an equation, we invert the value of K .
- 2) When we multiply coefficients in a balanced equation by a common factor, we raise the eq. constant to the corresponding power.
- 3) When we divide the coefficients by a common factor, we take the correspondingly root of the K .

for example:



— We should write: $K' = \frac{[\text{CO}][\text{H}_2]^2}{[\text{CH}_3\text{OH}]} = \frac{1}{\frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2}} = \frac{1}{K} //$

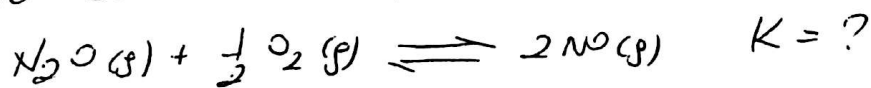


Here $K'' = K^2$ That is:

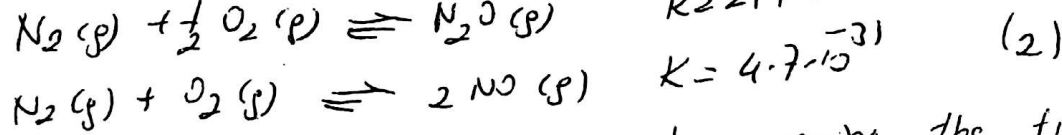
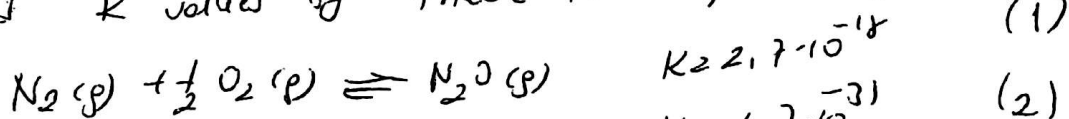
$$K'' = \frac{[\text{CH}_3\text{OH}]^2}{[\text{CO}]^2[\text{H}_2]^4} = \left(\frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} \right)^2 = \underline{\underline{K^2}}$$

- 4) When individual equations are combined, their eq. constants are multiplied to obtain the eq. constant for the overall rxn.

Ex. We search the eq. const. for the rxn:

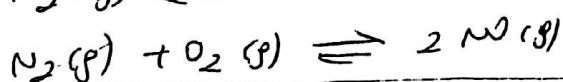
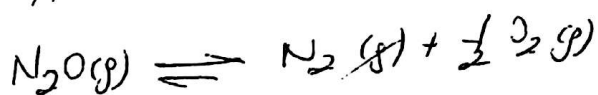


and K values of these two equilibria:



Our desired equation is obtained by reversing the first equation and

adding it to second equation.



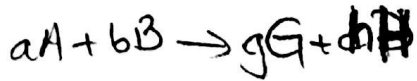
$$K(1) = 1/K_1 = 1/2.7 \cdot 10^{-18} = 3.7 \cdot 10^{17}$$

$$K(2) = 4.7 \cdot 10^{-31}$$

$$K_{overall} = \frac{[NO]^2}{[N_2O][O_2]^{1/2}} = \underbrace{\frac{[N_2][O_2]^{1/2}}{[N_2O]}}_{K(a)} \times \underbrace{\frac{[NO]^2}{[N_2][O_2]}}_{K(b)} = K_a \times K_b = 1.1 \times 10^{13}$$

5) For a general rxn, the eq. constant is expressed
 $* a, b, g, h \Rightarrow$ are the coefficients in balanced chemical equation.

$$K_c = \frac{[G]^g [H]^h}{[A]^a [B]^b}$$



* The subscript c on the K indicates that concentration expressed in molarity (mol/L) are used to evaluate the constant.

* When the reactants and products in a chemical rxn are gases we can formulate the eq-constant expression in molar concentration or in terms of partial pressures. When partial pressures in atmospheres are used in the expression, we can denote the equilibrium constant as K_p .

$K_c \rightarrow$ If molar concentration of gases are used in expression

$K_p \rightarrow$ If partial pressure of

The expression for K_p is:

$$K_p = \frac{(P_G)^g (P_H)^h}{(P_A)^a (P_B)^b}$$

EX: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ for this rxn the equation K_c

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

$$\frac{P}{n} = \frac{nRT}{V} \Rightarrow P = \frac{nRT}{V}$$

- using the ideal gas law $PV = nRT$ to relate gas concentrations and partial pressures

$$[SO_3] = \frac{n_{SO_3}}{V} = \frac{P_{SO_3}}{RT}, \quad [SO_2] = \frac{n_{SO_2}}{V} = \frac{P_{SO_2}}{RT}, \quad [O_2] = \frac{n_{O_2}}{V} = \frac{P_{O_2}}{RT}$$

$$K_c = \frac{(P_{SO_3}/RT)^2}{(P_{SO_2}/RT)^2 (P_{O_2}/RT)} = \frac{(P_{SO_3})^2}{(P_{SO_2})^2 (P_{O_2})} \cdot RT \Rightarrow K_c = K_p \cdot RT \text{ or } K_p = K_c \cdot (RT)^{-1}$$

For a general equation:

$$* K_p = K_c \cdot (RT)^{\Delta n_{gas}}$$

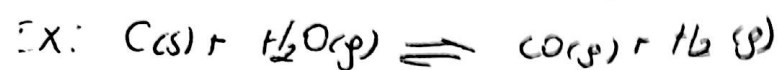
K_p

Δn_{gas} = the total number of gas in products - the total number of gas in reactants

Δn_{gas} is the difference in the number of gaseous products and reactants, that is $\Delta n_{\text{gas}} = (p + \dots) - (a + \dots)$

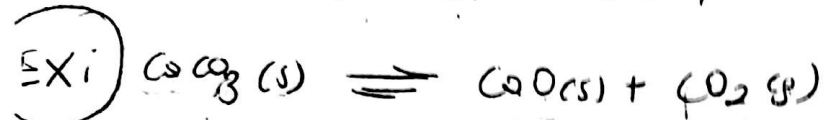
* In summary, there are mobility for K_c expressions and pressure in atmospheres for K_p expressions.

*) Eq.-constant-expressions do not contain concentration terms for Solid or liquid phases of a single component.



$$K_c = \frac{a_{\text{CO}} \cdot a_{\text{H}_2}}{a_{\text{C(s)}} \cdot a_{\text{H}_2\text{O(g)}}} = \frac{[\text{CO}][\text{H}_2]}{[\text{H}_2\text{O}]}$$

The activity of solids and liquids are 1.
 $a_{\text{C(s)}} = 1$



$$K_c = \frac{a_{\text{CaO}} \cdot a_{\text{CO}_2}}{a_{\text{CaCO}_3}} = [\text{CO}_2]$$

$$K_p = K_c (RT)^{\Delta n_{\text{gas}}} \quad \Delta n_{\text{gas}} = 1$$

$$K_p = K_c \cdot RT = [\text{CO}_2] \cdot RT$$

* Introduction of additional CaCO_3 , CaO has no effect on the partial pressure of the $\text{CO}_2\text{(g)}$.

The Reaction Quotient, Q , Predicting the Direction of Next Change:

The reaction quotient Q , is the number obtained by using reactant and product concentrations or partial pressures at any point during a rxn into an eq.-constant-expression. Therefore for the general rxn:

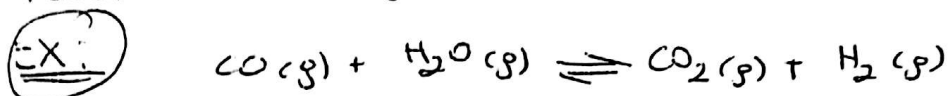
$$Q = \frac{(a_{\text{G}}^{\text{g}})^s (a_{\text{H}}^{\text{h}})^h}{(a_{\text{A}}^{\text{a}})^a (a_{\text{B}}^{\text{b}})^b} = \frac{[\text{G}]^s [\text{H}]^h}{[\text{A}]^a [\text{B}]^b}$$

reaction goes

! If $Q = K$ a rxn is at equilibrium.

! If $Q > K$ The concentration of products is too large and that of reactants too small. Thus, substances on the right side of the chemical equation will react to form substances of the left side. The rxn moves from right to left in approaching equilibrium.

if $Q < K$: The concentration of products is too small and that of reactants too large. The rxn moves from left to right. \rightarrow



$K_c = 1.0$ at about 1100 K . The following amounts of substances are brought together and allowed to react at this temperature. 1 mol CO, 1 mol H_2O , 2 mol CO_2 and 2 mol H_2 . Compared with their initial amounts, which of the substances will be present in a greater amount and which in a lesser amount when equilibrium is established?

Solution:

Our task is to determine the direction of net change by evaluating Q_c .

$$Q_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(2\text{ mol/v})(2\text{ mol/v})}{(1\text{ mol/v})(1\text{ mol/v})} = 4$$

Compare Q_c and K_c

$$Q_c = 4 > K_c = 1$$

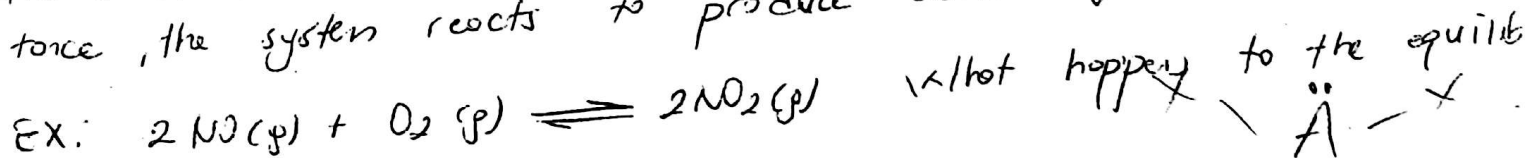
Because $Q_c > K_c$, a net change occurs to the left. When equilibrium is established the amounts of CO and H_2O will be greater than the initials quantified and the amount of CO_2 and H_2 will be less. SOR

LE CHATELIER'S PRINCIPLE:

If a system at equilibrium is disturbed by a change in temperature, pressure or the concentration of one of the components, the system responds by a new equilibrium that partially offsets the impact of the change. This is called Le Chatelier's principle.

1) Change in Reactant or Product Concentration:

If a chemical system is at equilibrium and we increase the concentration of a substance, the system reacts to consume some of the substance. Conversely, if we decrease the concentration of a substance, the system reacts to produce some of the substance.



a) if O_2 is added

b) if NO is removed

c) If O_2 is added, the net change occurs to the right. NO and O_2 react to form NO_2 .

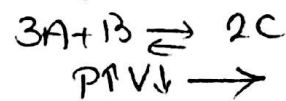
d) If NO is removed, a net change occurs to the left. NO_2 from the new equilibrium.

Ex. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ predict the effect of adding more $H_2(g)$ to the constant-volume equilibrium mixture of N_2 , H_2 and NH_3 .

Solution: Increasing H_2 stimulates the forward rxn and a shift in the equilibrium condition to the right. When the equilibrium is reestablished there will be more H_2 than was present originally and also more NH_3 , but the amount of N_2 will be smaller. Because some of the original N_2 must be consumed in converting some of the added H_2 to NH_3 .

2) Effect of changes in Pressure or Volume on Equilibrium:

When the volume of an equilibrium mixture of gases is reduced a net change occurs in the direction that reduces the number of moles of gas. Conversely, increasing the volume causes a shift in the direction that produces more gas molecules.



Let's consider the formation of SO_3 from SO_2 and O_2 . $P \downarrow \leftarrow$



What happens if the volume reduced to one-tenth of its original value by increasing the external pressure?

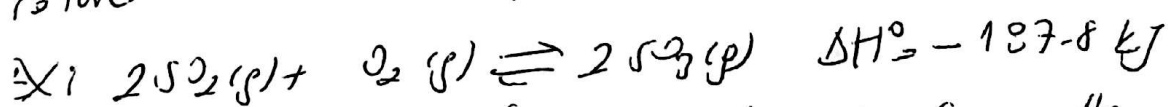
Let's first rearrange the eq. const. expression to form:

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} = \frac{(n_{SO_3}/V)^2}{\left(\frac{n_{SO_2}}{V}\right)^2 \left(\frac{n_{O_2}}{V}\right)} = \frac{n_{SO_3}^2 \uparrow}{n_{SO_2}^2 \cdot n_{O_2} \downarrow} \times V = 2.8 \cdot 10^2 \quad \therefore V = nRT$$

If V is reduced by a factor of 10, the ratio (of moles) must increase by a factor of 10. In this way, the value of K_c is restored. There is only one way for increasing the ratio of moles. The number of moles of SO_3 must increase and the numbers of moles of SO_2 and O_2 must decrease.

3) Effect of Temperature on Equilibrium:

Raising the temperature of an equilibrium mixture shifts the eq. condition in the direction of the endothermic rxn. Lowering the temperature causes a shift in the direction of the exothermic rxn.



Will the amount of SO_3 formed from the given amounts of

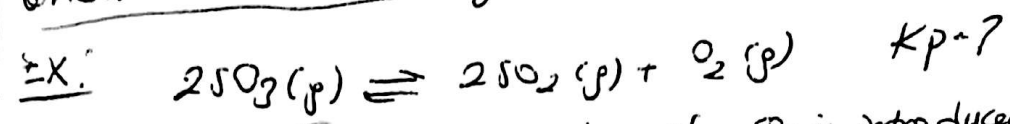
SO₂ and O₂ are gases

Solution:

Raising the temp. favors the endothermic rxn, the reverse rxn.
Lowering the temp. favors the forward (exothermic) rxn. Therefore the amount of SO₂ will be greater at lower temp.

Effect of a Catalyst on Equilibrium

Adding a catalyst speeds up both the forward and reverse rxns. Equilibrium is achieved more rapidly, but the equilibrium amounts are unchanged by the catalyst.



When a 0.02 mol sample of SO₃ is introduced into an evacuated vessel at 800 K, 0.0142 mol SO₂ is present at equilibrium. What is the value of K_p for the dissociation of SO₃(g) at 800 K?

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

Initial amount =	0.02 mol	-	-
changes =	-0.0058 mol	+0.0058	0.0029
eqm. amounts =	0.0142 mol	0.0058	0.0029
eqm. conc. =	$\frac{0.0142 \text{ mol}}{1.52 \text{ L}}$	$\frac{0.0058}{1.52}$	$\frac{0.0029}{1.52}$

1.52 L

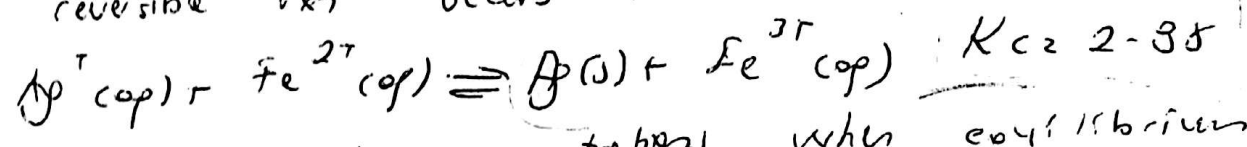
$[SO_3] = 9.34 \cdot 10^{-3} M$
 $[SO_2] = 3.8 \cdot 10^{-3} M$
 $[O_2] = 1.9 \cdot 10^{-3} M$

$$K_{c2} = \frac{[SO_2]^2 [O_2]}{[SO_3]^2} = \frac{(3.8 \cdot 10^{-3})^2 (1.9 \cdot 10^{-3})}{(9.34 \cdot 10^{-3})^2}$$

$K_p = K_c (RT)^{\Delta n_{\text{gas}}}$ antamadin!

$\Delta n_{\text{gas}} = 3 - 2 = 1 \Rightarrow K_p = 3 \cdot 10^{-4} \frac{\text{mol}}{\text{L}} \cdot (0.08206 \frac{\text{K atm}}{\text{K mol}} \cdot 800 \text{ K}) = 2.3 \cdot 10^{-2}$

EX: Solid silver is added to a solution with these initial concentrations: $[Ag^+] = 0.2 M$, $[Fe^{2+}] = 0.1 M$ and $[Fe^{3+}] = 0.3 M$. The following reversible rxn occurs.

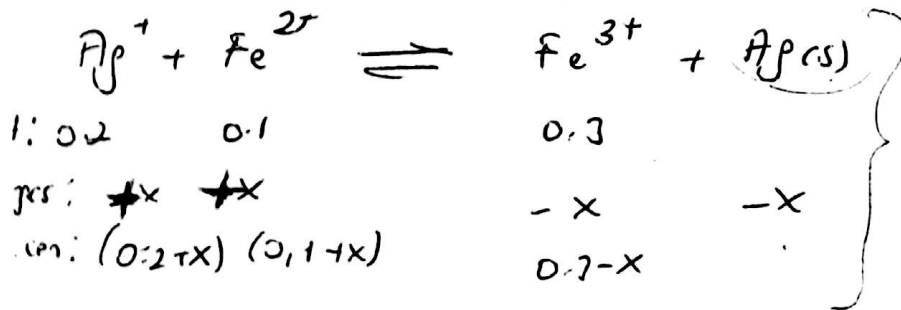


What are the ion concentrations when equilibrium is established?

we need to use the reaction quotient Q_c to determine the direction in which a net change occurs.

$$Q_c = \frac{[Fe^{3+}]_{init.}}{[Fe^{2+}]_{init.} [Ag^+]_{init.}} = \frac{0.3}{(0.2)(0.1)} = 15$$

Because $Q_c > K_c$
a net change occurs to the left.



Bunlar (aq) solutions

$$K_c = \frac{0.3-x}{(0.2+x)(0.1+x)} = 2.98 \Rightarrow x = 0.11$$

$$\begin{aligned} [Ag^+] &= 0.2 + 0.11 = 0.31 \\ [Fe^{2+}] &= 0.1 + 0.11 = 0.21 \\ [Fe^{3+}] &= 0.3 - 0.11 = 0.19 \end{aligned}$$

To find the root:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-b \pm \sqrt{b^2 - 40c}}{20}$$

antlamadim!!
Kitaptan bakmalym!

$$(-1)^2 + (-1)^2 = 2$$

$$(2x^2 + 5x + c = 0)$$

$$(-1)^2 + (-1)^2 = 2$$

$$2.98 (0.2+x)(0.1+x) = 0.3-x$$

$$a + b + c = 0$$

$$a(0.1 + ax + 0.1001) = 0.12x^2$$

$$A + B + C = 0$$

$$\begin{array}{r} 0.0142 \\ \times 0.0058 \\ \hline 0.0008316 \end{array}$$