

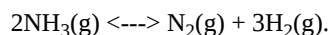
## 6.3: Equilibrium Expressions Involving Pressures

When calculating equilibrium constants of solutions, the concentrations of each component in the solution are used to calculate  $K$ , which is the equilibrium constant. When working with concentrations, the equilibrium constant is designated as  $K_c$ . However, when working with a mixture of gases, concentrations are not used, but instead the gases' partial pressures. By first calculating the equilibrium constant in terms of pressure, designated  $K_p$ ,  $K_c$  can then be calculated by using a simple formula.

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### How do you begin writing the equilibrium constant for a mixture of gases?

To explain this clearly, let us look at a simple example, the reaction:



1) First, each component of the mixture in the equilibrium constant is written in terms of their activities. The activity of each component is the partial pressure of each component divided by their partial pressure "reference-states." Writing the equilibrium constant in terms of partial pressures requires it to be referred to as  $K_p$ .

$$K = (a_{\text{N}_2})(a_{\text{H}_2})^3 / (a_{\text{NH}_3})^2 \text{ eq}$$

$$a_{\text{N}_2} = P_{\text{N}_2}/P^0$$

$$a_{\text{H}_2} = P_{\text{H}_2}/P^0$$

$$a_{\text{NH}_3} = P_{\text{NH}_3}/P^0$$

2) Next, take the activities, showed in terms of pressure, of the products raised to the power of their coefficients, and divided by the activities of the reactants. The activities of the reactants are also raised to the power of their coefficients. To simplify the expression, the partial pressure "reference-state" of each component can be divided out.

$$K_p = (P_{\text{N}_2}/P^0)(P_{\text{H}_2}/P^0)^3 / (P_{\text{NH}_3}/P^0)^2 \text{ eq}$$

$$P^0 (P_{\text{N}_2})(P_{\text{H}_2})^3 / (P_{\text{NH}_3})^2 \text{ eq}$$

3) To relate the pressures of this expression to concentrations, the ideal gas law is used. The ideal gas law is  $PV=nRT$ , where  $P$  is the pressure,  $V$  is the volume,  $n$  is the number of moles of the substance,  $R$  is the constant 0.08206 L atm/K mol, and  $T$  is the temperature in Kelvins. By inverting the ideal gas law equation and solving for the concentration,  $n/V$ , or moles per liter, the concentrations of the gases are expressed by their partial pressures divided by  $RT$ .

$$\{\text{N}_2\} = n/V = P_{\text{N}_2}/RT$$

$$\{\text{H}_2\} = n/V = P_{\text{H}_2}/RT$$

$$\{\text{NH}_3\} = n/V = P_{\text{NH}_3}/RT$$

4) Now, since we have solved for the concentrations of each gas component, we write them in terms of concentration activities. This is the concentrations of each component divided by the concentration reference state.

$$a_{\text{N}_2} = \{\text{N}_2\}/c^0 = (P_{\text{N}_2}/RT)/c^0$$

$$a_{\text{H}_2} = \{\text{H}_2\}/c^0 = (P_{\text{H}_2}/RT)/c^0$$

$$a_{\text{NH}_3} = \{\text{NH}_3\}/c^0 = (P_{\text{NH}_3}/RT)/c^0$$

The last and final step is entering these activities into the expression we earlier derived in step 2 and dividing out  $RT$ .

$$K_p = P^0 ( \{\text{N}_2\}RT ) ( \{\text{H}_2\}RT )^3 / ( \{\text{NH}_3\}RT )^2 \text{ eq}$$

$$K_p = (P^0/RT) ( \{\text{N}_2\} \{\text{H}_2\}^3 / \{\text{NH}_3\}^2 ) \text{ eq}$$

This gives the equilibrium constant expression for a mixture of gases ( $K_p$ ).

$K_p$  and  $K_c$  can be related by setting the two equations equal to each other and divided out the reference states. This gives the simple formula:

$K_p = K_c(RT)^{\text{difference in coefficients of gas components only}}$

**Please Note:**

$P^\circ$  is the partial pressure reference-state and it equals about 1 atm

$c^\circ$  is the concentration reference-state and it equals about 1 mol/L

eq is the term used to indicate that the components are at equilibrium

{x} is the concentration of the component x where x is a variable used to indicate a substance

Equilibrium constant expression do not include those components in a reaction that are pure solids or liquids (please refer to the corresponding internal link below)

## Internal Links

- Writing equilibrium constant expressions involving solids and liquids
- [Gas equilibrium constants,  \$K\_p\$  and  \$K\_c\$ ?](#)
- Meaning of the equilibrium constant, K

## Practice Problems

1) Gas A and Gas B react to form Gas C. The reaction performed can be written as  $A(g)+B(g)$

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C(g). At equilibrium, the partial pressures of A, B, and C are 1 atm, 0.50 atm, and 0.75 atm respectively. Find  $K_p$  for the reaction.

Solution:

First, write out the equilibrium constant expression for  $K_p$ .  $K_p = P^\circ($

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)eq

Remember that  $P^\circ = 1$  bar which is essentially equal to 1 atm. Next, plug in the partial pressures for the corresponding gases.

$K_p =$

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)

$=1.5$

2) A(g), at 750 mmHg, reacts with B(g), at 760 mmHg, to form C(g).  $K_p$  for the reaction is  $1.5 \times 10^{-5}$  and the reaction at equilibrium can be written  $A(g)+B(g)$

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2C(g). Find the partial pressure of C.

Solution

First set up the equilibrium constant expression for  $K_p$ .  $K_p = P^\circ($

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eq

C is raised to the power of 2 since 2 is the coefficient of C. Since we know  $K_p$  we can substitute that into the equation. Also, convert the partial pressure of A and B to atm.  $P_A = 750 \text{ mmHg} \times$

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$= 0.98684$  &  $P_B = 1 \text{ atm}$

$$1.5 \times 10^5 =$$

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$$(1.5 \times 10^{-5})(0.98684) = C^2$$

$$\sqrt{1.48026 \times 10^{-5}} = C$$

$$C = 3.8474147 \times 10^{-3} \text{ or } C = 3.9 \times 10^{-3}$$

3) For the following reaction at equilibrium  $2\text{SO}_2(\text{g}) + \text{O}_2$

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$2\text{SO}_3(\text{g})$   $K_p$  is 3.4 at 1000K. What is  $K_c$  for the reaction?

Solution:

We know that  $K_p = K_c(RT)^{(\text{Difference in coefficients of gaseous products and reactants})}$

We also know  $K_p = 3.4$ , R is a constant which is  $0.08206 \text{ L atm mol}^{-1}\text{K}^{-1}$ ,  $T = 1000\text{K}$

(RT) is raised to the power of (Difference in coefficients of gaseous products and reactants) so since  $2\text{SO}_2(\text{g}) + \text{O}_2$

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$2\text{SO}_3(\text{g})$  (Difference in coefficients of gaseous products and reactants) =  $(2) - (2+1) = -1$

Rewrite the equation,  $K_p = K_c(RT)^{(\text{Difference in coefficients of gaseous products and reactants})}$ , to solve for  $K_c$  and substitute in the values.  $K_c =$

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$$K_c = 2.79 \times 10^2$$

4) For the following reaction at equilibrium,  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$

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$2\text{NH}_3(\text{g})$ ,  $K_p$  is  $2.25 \times 10^{-6}$ . If the values of the partial pressures of  $\text{N}_2$  and  $\text{NH}_3$  are  $3.5 \times 10^{-3}$  and  $2.0 \times 10^{-5}$  respectively, what is the partial pressure of  $\text{H}_2$ ?

Solution

Set up the equilibrium constant expression for  $K_p$ .  $K_p = K_p = P^0$

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eq

Substitute the values in to the correct places.

$$2.25 \times 10^{-6} =$$

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$$= 0.0507936508$$

Take the cubed root of the number to find the Partial pressure of  $H_2$

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$$= 0.37 \text{ atm}$$

5) 1 mol of A and 1 mol of B are placed in a 2.0 L flask. The following reaction at equilibrium is established at 500K.  $A(g) + B(g)$

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$C(g)$   $K_p = 15.0$  For the equilibrium established, find the partial pressure of C.

#### Solution

First, we must find the partial pressures of A and B. We know that by using  $P =$

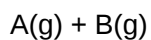
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, we can say  $P_A = P_B =$

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$$= 20.515$$

Now create an ICE table.



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C(g)

I 20.515 20.515 0

C -x -x +x

E (20.515-x) (20.515-x) (x)

Now set up the equilibrium constant expression for  $K_p = 15.0 =$

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$15(20.515-x)^2 = x$  Use FOIL

$15(420.865225 - 41.03x + x^2) = x$  distribute & multiply by 15

$15x^2 - 615.45x + 6312.978375 = x$  subtract the x to make the equation equal to 0

$15x^2 - 616.45x + 6312.978375 = 0$  Use the quadratic formula

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and

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$a=15$   $b=-616.45$   $c= 6312.978375$

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and

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We find that there are two solutions.  $P_C = 19.38$  or  $21.7$

$19.38$  is the correct solution since  $21.7$  is too large.

## References

1. Petrucci, Ralph H., et al. General Chemistry: Principles and Modern Applications. Upper Saddle River, NJ: Prentice Hall, 2007.

## Contributors and Attributions

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