

ALE 7. Equilibrium Constants(Reference: 17.3 Silberberg 5th edition)**Why does a chemical reaction have more than one equilibrium constant?****The Model: Relationship Between K_c and K_p**

Many of the systems in which there is a reversible reaction involve gases. Assuming that a gas behaves ideally (*i.e.*, $n/V = P/RT$) and that the temperature is constant, then the molar concentration of a gas is directly proportional to the partial pressure of the gas in the reaction mixture. Therefore it is often convenient to monitor the pressures of gases rather than their molar concentrations. The problem with this is that it requires more than one equilibrium constant to describe where the masses (of reactants and products) will be when the reversible reaction reaches equilibrium. If we are interested in the equilibrium molar concentrations, then we need K_c , in which the law of mass action involves a ratio of concentrations. And if we are interested in the equilibrium partial pressures, then we need K_p , in which the law of mass action involves a ratio of pressures. The relationship between K_c and K_p is shown in equation 1.

$$K_c = K_p(RT)^{-\Delta n} \quad (1)$$

Here Δn is the difference between the stoichiometric coefficients of the gaseous products and reactants, T is the absolute temperature of the reaction mixture, and $R = 0.08206 \text{ K}^{-1}$. (We assume that partial pressures of the gases are in atm and the units of the gas constant are simplified so that *equilibrium constants remain unitless.*)

As an example, consider the decomposition reaction of dinitrogen tetroxide to become nitrogen dioxide.



The laws of mass action in terms of molar concentrations (eqn 2a) and in terms of partial pressures (eqn 2b) are as follows.

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \quad (2a) \qquad K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} \quad (2b)$$

Since $[\text{NO}_2] = \frac{P_{\text{NO}_2}}{RT}$ and $[\text{N}_2\text{O}_4] = \frac{P_{\text{N}_2\text{O}_4}}{RT}$, eqn 2a can be written as eqn 2c.

$$K_c = \frac{\left(\frac{P_{\text{NO}_2}}{RT}\right)^2}{\frac{P_{\text{N}_2\text{O}_4}}{RT}} \quad (2c)$$

Algebraically simplifying eqn 2c and using eqn 2b as a substitution in eqn 2c leads to eqn 2d. For

$$K_c = K_p(RT)^{-1} \quad (2d)$$

Key Questions

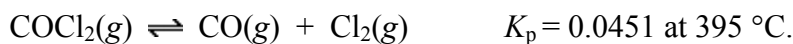
- 1 a. What is the difference between the stoichiometric coefficients of the products and reactants in the decomposition of dinitrogen tetroxide (eqn **2** in the Model)? Show your work.

$$\Delta n =$$

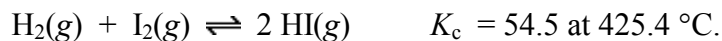
- b. What is the power to which RT is raised in eqn **2d**? Does eqn **2d** comply with eqn **1**?
2. When would K_c be equal to K_p for the same reaction? Explain your answer.

Exercises

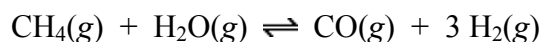
3. Calculate K_c for the decomposition of phosgene at 395 °C.



4. What is the value of K_p for formation of hydrogen iodide from its elements at 425.4 °C?



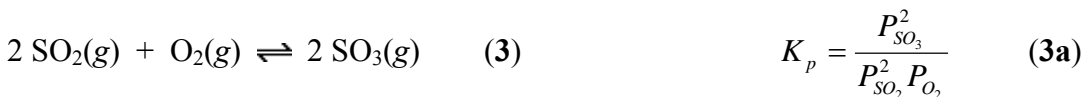
5. Hydrogen is industrially synthesized by reacting methane with steam at high temperatures.



The value of K_c for the above reaction is 0.0267 at 1133 K. What is K_p for this reaction at 1133 K?

The Model: Change of Stoichiometric Coefficients and the Effect on the value of K

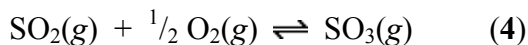
Stoichiometric coefficients are arbitrary. For example, the oxidation of sulfur dioxide to sulfur trioxide may be written as eqn 3. Corresponding to eqn 3, the law of mass action is shown as eqn 3a.



$$K_p = 0.0012 \text{ at } 1500 \text{ K.}$$

Key Questions

6. Alternatively, the reaction (eqn 3 in the Model) could be written as eqn 4.



- a. Complete the law of mass action for eqn 4. (The apostrophe on the K_p (together called “ K_p -prime”) simply tells the reader that this equilibrium constant applies to the same chemical system, but its value is different than the one without an apostrophe.)

$$K'_p =$$

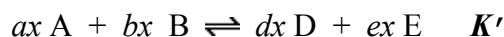
- b. Compare eqn 3a (in the Model) to eqn 4b (your answer to Question 6a). What must the value of x be in the following equation to make it true?

$$K'_p = (K_p)^x$$

- c. By what factor are the stoichiometric coefficients multiplied in going from eqn 3 to eqn 4 (both of which describe the oxidation of SO_2)? (Compare your answers to Questions 6b and 6c.)

7. Given the following generic reversible reaction: $a \text{A} + b \text{B} \rightleftharpoons d \text{D} + e \text{E} \quad K$

Suppose all of the stoichiometric coefficients are multiplied by a constant x :



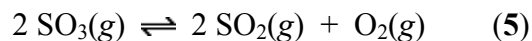
How is K' related to K ?

Exercise

8. What is the value of K'_p at 1500 K for eqn 4?

Key Questions

9. Instead of its formation, suppose we consider the decomposition of sulfur trioxide (eqn 5).



a. Finish the law of mass action for eqn 5.

$$K_p'' =$$

b. How does the law of mass action for eqn 5 (your answer to Question 9a) compare to the law of mass action for eqn 3 (eqn 3a in the Model)?

Exercises

10. a. What is the value of K_p'' for eqn 5 at 1500 K?

b. A mixture of SO_3 , SO_2 , and O_2 gases at 1500 K is found to have the following partial pressures at equilibrium: $P_{\text{SO}_3} = 0.013 \text{ atm}$ and $P_{\text{O}_2} = 0.788 \text{ atm}$. What is the partial pressure of SO_2 (in atm)?

11. The K_p for the decomposition of ammonia into its elements $\text{NH}_3(\text{g}) \rightleftharpoons \frac{3}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{N}_2(\text{g})$ is 111 at 427 °C. What is the value of K_p' for the following reaction at 427 °C?

