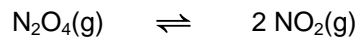


Example: The reaction below was studied at 298 K. Data are summarized below. Show that the reaction quotient has the same value at equilibrium for all three experiments.

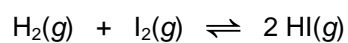


We use the symbol \rightleftharpoons when we are interested in the rates (i.e. kinetics) of a reversible reaction.

We use the symbol \rightleftharpoons when we are interested in a reversible reaction that has reached a state of dynamic equilibrium.

	[N ₂ O ₄]	[NO ₂]	Reaction Quotient
<u>Expt 1</u>	[N ₂ O ₄] _o = 0.0250 $\frac{\text{mol}}{\text{L}}$ [N ₂ O ₄] _{eq} = 0.0202 $\frac{\text{mol}}{\text{L}}$	[NO ₂] _o = 0 $\frac{\text{mol}}{\text{L}}$ [NO ₂] _{eq} = 0.00966 $\frac{\text{mol}}{\text{L}}$	
<u>Expt 2</u>	[N ₂ O ₄] _o = 0.0125 $\frac{\text{mol}}{\text{L}}$ [N ₂ O ₄] _{eq} = 0.0146 $\frac{\text{mol}}{\text{L}}$	[NO ₂] _o = 0.0125 $\frac{\text{mol}}{\text{L}}$ [NO ₂] _{eq} = 0.00823 $\frac{\text{mol}}{\text{L}}$	
<u>Expt 3</u>	[N ₂ O ₄] _o = 0.0 $\frac{\text{mol}}{\text{L}}$ [N ₂ O ₄] _{eq} = 0.00923 $\frac{\text{mol}}{\text{L}}$	[NO ₂] _o = 0.0250 $\frac{\text{mol}}{\text{L}}$ [NO ₂] _{eq} = 0.00654 $\frac{\text{mol}}{\text{L}}$	

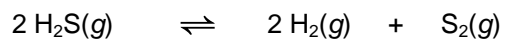
Example: The chemical equation describing the gas-phase reaction between H_2 and I_2 is shown below.



In an experiment, 1.0 mol H_2 and 1.0 mol I_2 are placed in a 5.0-L flask. At equilibrium, the concentration of I_2 is determined to be 0.044 mol L^{-1} .

- (a) What is K_c for the reaction?
- (b) If the reaction is carried out at the same temperature but with $[\text{H}_2]_0 = [\text{I}_2]_0 = [\text{HI}]_0 = 0.10 \text{ mol L}^{-1}$, then what are the equilibrium concentrations?
- (c) Repeat part (b) but with $[\text{H}_2]_0 = [\text{I}_2]_0 = 0.10 \text{ mol L}^{-1}$ and $[\text{HI}]_0 = 1.0 \text{ mol L}^{-1}$.

Example: For the reaction below, $K_c = 4.20 \times 10^{-6}$ at 830°C . What are the equilibrium concentrations when 0.0700 mol H_2S is placed in an empty 1.0-L vessel at 830°C ?



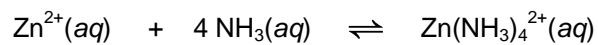
Check your assumptions!

If we use an approximation to simplify our calculations, we must always check to make sure that the approximation is justified. We'll use the 5% rule.

The 5% Rule

The approximation that $C - x \approx C$ is valid only if the value of x turns out to be no more than 5% of C .

Example: For the reaction below, $K_c = 7.8 \times 10^8$. What are the equilibrium concentrations when 1.00 mol each of $Zn(NO_3)_2$ and NH_3 are dissolved in water to make 1.0 L of solution?



In aqueous solution, some of the NH_3 reacts with water molecules to form NH_4^+ ions which cannot bind to Zn^{2+} . In principle, we should also take this reaction into account. However, only a small amount of NH_3 will be converted into NH_4^+ so we will not worry about this additional complication.

Method of Successive Approximations

In an earlier example, the answer was just barely acceptable according to the 5% rule. The approximation we made would have been unacceptable if the initial concentration of H_2S had been slightly smaller than 0.07 mol L^{-1} .

A useful technique that we can use for obtaining answers that are more accurate is the method of successive approximations. Let's see how this method could be used to obtain an accurate answer to the problem on page 7 but with $[\text{H}_2\text{S}]_0 = 0.0500 \text{ mol L}^{-1}$. The appropriate equilibrium expression to solve is

$$K_c = \frac{4x^3}{(0.0500 - 2x)^2}.$$

We can re-arrange this expression into the following form:

$$x^3 = \frac{(0.0500 - 2x)^2 K_c}{4} \Rightarrow x = \sqrt[3]{\frac{(0.0500 - 2x)^2 K_c}{4}}$$

We can use this re-arranged form to obtain answers that get successively closer to the correct answer.

First approximation.

$$2x \ll 0.0500 \Rightarrow x = \sqrt[3]{\frac{(0.0500)^2 K_c}{4}} = 1.38 \times 10^{-3}$$

Second approximation.

$$x \approx 1.38 \times 10^{-3} \Rightarrow x_{\text{new}} = \sqrt[3]{\frac{(0.0500 - 2 \cdot 1.38 \times 10^{-3})^2 K_c}{4}} = 1.33 \times 10^{-3}$$

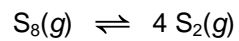
Third approximation.

$$x \approx 1.33 \times 10^{-3} \Rightarrow x_{\text{new}} = \sqrt[3]{\frac{(0.0500 - 2 \cdot 1.33 \times 10^{-3})^2 K_c}{4}} = 1.33 \times 10^{-3}$$

The answers from the second and third approximations are identical to three significant figures. If we needed a higher degree of precision, we would continue the process. We'll use a variation of this method to solve cubic equations that arise in some acid-base equilibrium problems.

An exercise for you: This method can also be used to solve quadratic equations without resorting to the use of the quadratic formula! Use this method to solve $1.7 \times 10^{-4} = x^2 / (0.01 - x)$. You should obtain the following results: $x_{1\text{st}} = 1.30 \times 10^{-3}$, $x_{2\text{nd}} = 1.22 \times 10^{-3}$, and $x_{3\text{rd}} = 1.22 \times 10^{-3}$.

Example: At elevated temperatures, $S_8(g)$ decomposes to $S_2(g)$:



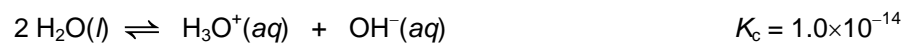
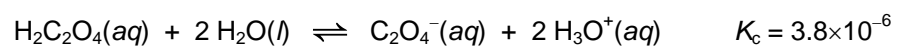
In an experiment, an empty flask is filled initially with $S_8(g)$ at 1.00 atm. At equilibrium, the total pressure in the flask is 3.25 atm. What are K_p and K_c for the reaction above, assuming that $T = 1325$ K throughout the entire experiment?

3.6 Manipulating reactions and equilibrium constants

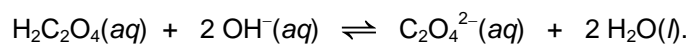
The mathematical expression we write down for Q and the value of K both depend on how we write the equation for the reaction. Here are some general rules to keep in mind.

If we ...	Then we must ...
reverse a reaction	
multiply a reaction by " n "	
add two reactions together	

Example: Consider the following reactions.



Use the information given above to calculate K_c for the reaction below.



Example: $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g)$, $\Delta H = 181 \text{ kJ (per mol N}_2)$

Given that $K_p = 4.03 \times 10^{-4}$ at 2000 K, what is K_p at 2200 K?