Equilibrium Calculations

Calculating values for equilibrium constants and/or equilibrium concentrations is of practical benefit to many applications. A mathematical strategy that uses initial concentrations, changes in concentrations, and equilibrium concentrations (and goes by the acronym ICE) is useful for performing equilibrium calculations.

17.1 Equilibrium Calculations

Learning Objectives

By the end of this section, you will be able to:

- Identify the changes in concentration or pressure that occur for chemical species in equilibrium systems
- Calculate equilibrium concentrations or pressures and equilibrium constants, using various algebraic approaches
- Explain how temperature affects the spontaneity of some proceses
- Relate standard free energy changes to equilibrium constants

Having covered the essential concepts of chemical equilibria in the preceding sections of this chapter, this final section will demonstrate the more practical aspect of using these concepts and appropriate mathematical strategies to perform various equilibrium calculations. These types of computations are essential to many areas of science and technology—for example, in the formulation and dosing of pharmaceutical products. After a drug is ingested or injected, it is typically involved in several chemical equilibria that affect its ultimate concentration in the body system of interest. Knowledge of the quantitative aspects of these equilibria is required to compute a dosage amount that will solicit the desired therapeutic effect.

Many of the useful equilibrium calculations that will be demonstrated here require terms representing changes in reactant and product concentrations. These terms are derived from the stoichiometry of the reaction, as illustrated by decomposition of ammonia:

$$2NH_3\,(g) \rightleftharpoons N_2\,(g) + 3H_2\,(g)$$

As shown earlier in this chapter, this equilibrium may be established within a sealed container that initially contains either NH_3 only, or a mixture of any two of the three chemical species involved in the equilibrium. Regardless of its initial

composition, a reaction mixture will show the same relationships between changes in the concentrations of the three species involved, as dictated by the reaction stoichiometry (see also the related content on expressing reaction rates in the chapter on kinetics). For example, if the nitrogen concentration increases by an amount x:

$$\Delta[N_2] = +x,$$

the corresponding changes in the other species concentrations are

$$\Delta[H_2] \quad = \quad \Delta[N_2](\tfrac{3 \text{ mol } H_2}{1 \text{ mol } N_2}) = +3x$$
$$\Delta[NH_3] \quad = \quad -\Delta[N_2](\tfrac{2 \text{ mol } NH_3}{1 \text{ mol } N_2}) = -2x,$$

where the negative sign indicates a decrease in concentration.

Video: Equilibrium Practice Problem 17.1.1

310

Video: Equilibrium Practice Problem 17.1.2
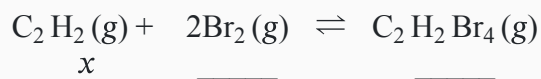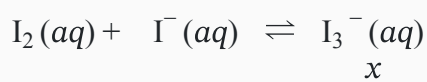

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EXAMPLE 17.1.3

Determining Relative Changes in Concentration

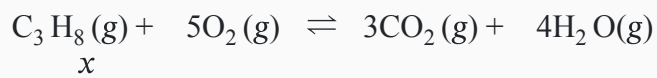Derive the missing terms representing concentration changes for each of the following reactions.

(a)

$$C_2H_2(g) + 2Br_2(g) \rightleftharpoons C_2H_2Br_4(g)$$
$$\quad x \qquad \underline{\quad} \qquad \underline{\quad}$$

(b)

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$
$$\underline{\quad} \quad \underline{\quad} \qquad x$$

(c)

$$C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)$$
$$\quad x \qquad \underline{\quad} \qquad \underline{\quad} \qquad \underline{\quad}$$

Solution

(a)

$$C_2H_2(g) + 2Br_2(g) \rightleftharpoons C_2H_2Br_4(g)$$
$$\quad x \qquad 2x \qquad -x$$

(b)

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$
$$\;-x \qquad -x \qquad x$$

(c)

$$C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)$$
$$\quad x \qquad 5x \qquad -3x \qquad -4x$$
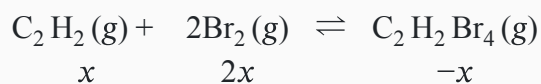
Check Your Learning

Complete the changes in concentrations for each of the following reactions:

(a)

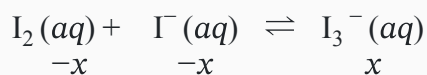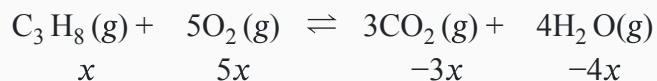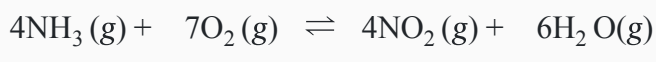$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$

_____ x _____

(b)

$$C_4H_8\,(g) \rightleftharpoons 2C_2H_4\,(g)$$

_____ $-2x$

(c)

$$4NH_3\,(g) + 7O_2\,(g) \rightleftharpoons 4NO_2\,(g) + 6H_2O(g)$$

_____ _____ _____ _____
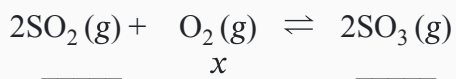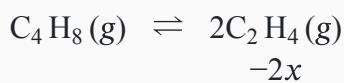
∨ Answer

(a) $2x$, x, $-2x$; (b) x, $-2x$; (c) $4x$, $7x$, $-4x$, $-6x$ or $-4x$, $-7x$, $4x$, $6x$

17.2 Calculation of an Equilibrium Constant

The equilibrium constant for a reaction is calculated from the equilibrium concentrations (or pressures) of its reactants and products. If these concentrations are known, the calculation simply involves their substitution into the K expression. A slightly more challenging example is provided next, in which the reaction stoichiometry is used to derive equilibrium concentrations from the information provided. The basic strategy of this computation is helpful for many types of equilibrium computations and relies on the use of terms for the reactant and product concentrations *initially* present, for how they *change* as the reaction proceeds, and for what they are when the system reaches *equilibrium*. The acronym ICE is commonly used to refer to this mathematical approach, and the concentrations terms are usually gathered in a tabular format called an ICE table.

EXAMPLE 17.2.1

Calculation of an Equilibrium Constant

Iodine molecules react reversibly with iodide ions to produce triiodide ions.

$$I_2\,(aq) + I^-\,(aq) \rightleftharpoons I_3^-\,(aq)$$
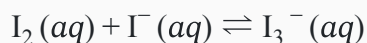
If a solution with the concentrations of I_2 and I^- both equal to 1.000

$\times$

10^{-3} M before reaction gives an equilibrium concentration of I_2 of 6.61

$\times$

10^{-4} M, what is the equilibrium constant for the reaction?

Solution

To calculate the equilibrium constants, equilibrium concentrations are needed for all the reactants and products:

$$K_C = \frac{[I_3^-]}{[I_2][I^-]}$$

Provided are the initial concentrations of the reactants and the equilibrium concentration of the product. Use this information to derive terms for the equilibrium concentrations of the reactants, presenting all the information in an ICE table.

	I_2	+	I^-	$\rightleftharpoons$	I_3^-
Initial concentration (*M*)	1.000×10^{-3}		1.000×10^{-3}		0
Change (*M*)	$-x$		$-x$		$+x$
Equilibrium concentration (*M*)	$1.000 \times 10^{-3} - x$		$1.000 \times 10^{-3} - x$		x

At equilibrium the concentration of I_2 is 6.61

$\times$

10^{-4} M so that

$$1.000 \times 10^{-3} - x = 6.61 \times 10^{-4}$$

$$x = 1.000 \times 10^{-3} - 6.61 \times 10^{-4}$$

$$= 3.39 \times 10^{-4} \ M$$

The ICE table may now be updated with numerical values for all its concentrations:

|	I_2 + I^- ⇌		I_3^-
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	-3.39×10^{-4}	-3.39×10^{-4}	$+3.39 \times 10^{-4}$
Equilibrium concentration (*M*)	6.61×10^{-4}	6.61×10^{-4}	3.39×10^{-4}

Finally, substitute the equilibrium concentrations into the *K* expression and solve:

$$K_c = \frac{[I_3^-]}{[I_2][I^-]}$$

$$= \frac{3.39 \times 10^{-4} \ M}{(6.61 \times 10^{-4} \ M)(6.61 \times 10^{-4} \ M)} = 776$$

Check Your Learning

Ethanol and acetic acid react and form water and ethyl acetate, the solvent responsible for the odor of some nail polish removers.

$$C_2H_5OH + CH_3CO_2H \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$
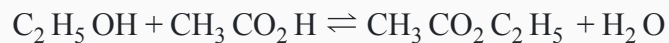
When 1 mol each of C_2H_5OH and CH_3CO_2H are allowed to react in 1 L of the solvent dioxane, equilibrium is established when

$\frac{1}{3}$

mol of each of the reactants remains. Calculate the equilibrium constant for the reaction. (Note: Water is a solute in this reaction.)

17.3 Calculation of a Missing Equilibrium Concentration

When the equilibrium constant and all but one equilibrium concentration are provided, the other equilibrium concentration(s) may be calculated. A computation of this sort is illustrated in the next example exercise.

EXAMPLE 17.3.1

Calculation of a Missing Equilibrium Concentration

Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the K_c for the reaction,

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO(g),$$

is 4.1×10^{-4}. Calculate the equilibrium concentration of NO(g) in air at 1 atm pressure and 2000 °C. The equilibrium concentrations of N_2 and O_2 at this pressure and temperature are 0.036 M and 0.0089 M, respectively.

Solution

Substitute the provided quantities into the equilibrium constant expression and solve for [NO]:

$$K_c = \frac{[NO]^2}{[N_2]\,[O_2]}$$

$$[NO]^2 = K_c\,[N_2]\,[O_2]$$

$$[NO] = \sqrt{K_c\,[N_2]\,[O_2]}$$

$$= \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)}$$

$$= \sqrt{1.31 \times 10^{-7}}$$

$$= 3.6 \times 10^{-4}$$

Thus [NO] is 3.6×10^{-4} mol/L at equilibrium under these conditions.

To confirm this result, it may be used along with the provided equilibrium concentrations to calculate a value for K:

$$\begin{aligned}
K_c &= \frac{[NO]^2}{[N_2]\,[O_2]} \\
&= \frac{(3.6 \times 10^{-4})^2}{(0.036)(0.0089)} \\
&= 4.0 \times 10^{-4}
\end{aligned}$$

This result is consistent with the provided value for *K* within nominal uncertainty, differing by just 1 in the least significant digit's place.

Check Your Learning

The equilibrium constant K_c for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is 6.00×10^{-2}. Calculate the equilibrium concentration of ammonia if the equilibrium concentrations of nitrogen and hydrogen are 4.26 *M* and 2.09 *M*, respectively.

⌄ Answer

1.53 mol/L

17.4 Calculation of Equilibrium Concentrations from Initial Concentrations

Perhaps the most challenging type of equilibrium calculation can be one in which equilibrium concentrations are derived from initial concentrations and an equilibrium constant. For these calculations, a four-step approach is typically useful:

1. Identify the direction in which the reaction will proceed to reach equilibrium.
2. Develop an ICE table.
3. Calculate the concentration changes and, subsequently, the equilibrium concentrations.
4. Confirm the calculated equilibrium concentrations.

The last two example exercises of this chapter demonstrate the application of this strategy.

EXAMPLE 17.4.1

Calculation of Equilibrium Concentrations

Under certain conditions, the equilibrium constant K_c for the decomposition of $PCl_5(g)$ into $PCl_3(g)$ and $Cl_2(g)$ is 0.0211. What are the equilibrium concentrations of PCl_5, PCl_3, and Cl_2 in a mixture that initially contained only PCl_5 at a concentration of 1.00 M?

Solution

Use the stepwise process described earlier.

1. Step 1.

   Determine the direction the reaction proceeds.

   The balanced equation for the decomposition of PCl_5 is

   $$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

   Because only the reactant is present initially $Q_c = 0$ and the reaction will proceed to the right.

2. Step 2.

   Develop an ICE table.

	PCl_5 $\rightleftharpoons$	PCl_3	+	Cl_2
Initial concentration (*M*)	1.00	0		0
Change (*M*)	$-x$	$+x$		$+x$
Equilibrium concentration (*M*)	$1.00 - x$	x		x

3. Step 3.

   Solve for the change and the equilibrium concentrations.

   Substituting the equilibrium concentrations into the equilibrium constant equation gives

   $$K_c = \frac{[PCl_3\,][Cl_2\,]}{[PCl_5\,]} = 0.0211$$

   $$= \frac{(x)(x)}{(1.00 - x)}$$

   $$0.0211 = \frac{(x)(x)}{(1.00 - x)}$$

   $$0.0211(1.00 - x) = x^2$$

   $$x^2 + 0.0211x - 0.0211 = 0$$

   Appendix B shows an equation of the form $ax^2 + bx + c = 0$ can be rearranged to solve for x:

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

In this case, $a = 1$, $b = 0.0211$, and $c = -0.0211$. Substituting the appropriate values for a, b, and c yields:

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0211)}}{2(1)}$$

$$= \frac{-0.0211 \pm \sqrt{(4.45 \times 10^{-4}) + (8.44 \times 10^{-2})}}{2}$$

$$= \frac{-0.0211 \pm 0.291}{2}$$

The two roots of the quadratic are, therefore,

$$x = \frac{-0.0211 + 0.291}{2} = 0.135$$

and

$$x = \frac{-0.0211 - 0.291}{2} = -0.156$$

For this scenario, only the positive root is physically meaningful (concentrations are either zero or positive), and so $x = 0.135$ M.

The equilibrium concentrations are

$$[PCl_5] = 1.00 - 0.135 = 0.87 \ M$$

$$[PCl_3] = x = 0.135 \ M$$

$$[Cl_2] = x = 0.135 \ M$$

4. Step 4.
Confirm the calculated equilibrium concentrations.

Substitution into the expression for K_c (to check the calculation) gives

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

The equilibrium constant calculated from the equilibrium concentrations is equal to the value of K_c given in the problem (when rounded to the proper number of significant figures).

Check Your Learning

Acetic acid, CH_3CO_2H, reacts with ethanol, C_2H_5OH, to form water and ethyl acetate, $CH_3CO_2C_2H_5$.

$$CH_3\,CO_2\,H + C_2\,H_5\,OH \rightleftharpoons CH_3\,CO_2\,C_2\,H_5 + H_2\,O$$
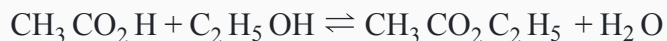
The equilibrium constant for this reaction with dioxane as a solvent is 4.0. What are the equilibrium concentrations for a mixture that is initially 0.15 M in CH_3CO_2H, 0.15 M in C_2H_5OH, 0.40 M in $CH_3CO_2C_2H_5$, and 0.40 M in H_2O?

⌄ Answer

$[CH_3CO_2H]$ = 0.18 M, $[C_2H_5OH]$ = 0.18 M, $[CH_3CO_2C_2H_5]$ = 0.37 M, $[H_2O]$ = 0.37 M

Check Your Learning

A 1.00-L flask is filled with 1.00 moles of H_2 and 2.00 moles of I_2. The value of the equilibrium constant for the reaction of hydrogen and iodine reacting to form hydrogen iodide is 50.5 under the given conditions. What are the equilibrium concentrations of H_2, I_2, and HI in moles/L?
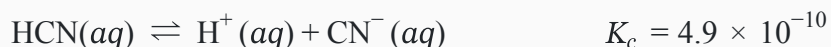
$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI(g)$$
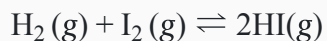
⌄ Answer

$[H_2]$ = 0.06 M, $[I_2]$ = 1.06 M, $[HI]$ = 1.88 M

EXAMPLE 17.4.2

Calculation of Equilibrium Concentrations Using an Algebra-Simplifying Assumption

What are the concentrations at equilibrium of a 0.15 M solution of HCN?

$$\mathrm{HCN}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{CN}^-(aq) \qquad K_c = 4.9 \times 10^{-10}$$

Solution

Using "x" to represent the concentration of each product at equilibrium gives this ICE table.

	HCN(aq) $\rightleftharpoons$ H$^+$(aq) + CN$^-$(aq)		
Initial concentration (M)	0.15	0	0
Change (M)	−x	+x	+x
Equilibrium concentration (M)	0.15 − x	x	x

Substitute the equilibrium concentration terms into the K_c expression

$$K_c = \frac{(x)(x)}{0.15 - x}$$

Rearrange to the quadratic form and solve for x

$$x^2 + 4.9 \times 10^{-10} - 7.35 \times 10^{-11} = 0$$

$$x = 8.56 \times 10^{-6}\ M\ (3\ \text{sig. figs.}) = 8.6 \times 10^{-6}\ M\ (2\ \text{sig. figs.})$$

Thus [H$^+$] = [CN$^-$] = x = 8.6×10^{-6} M and [HCN] = 0.15 − x = 0.15 M.

Note in this case that the change in concentration is significantly less than the initial concentration (a consequence of the small K), and so the initial concentration experiences a negligible change:

$$\text{if } x \ll 0.15\ \text{M, then } (0.15 - x) \approx 0.15$$

This approximation allows for a more expedient mathematical approach to the calculation that avoids the need to solve for the roots of a quadratic equation:

$$K_c = \frac{(x)(x)}{0.15 - x} \approx \frac{x^2}{0.15}$$

$$4.9 \times 10^{-10} = \frac{x^2}{0.15}$$

$$x^2 = (0.15)(4.9 \times 10^{-10}) = 7.4 \times 10^{-11}$$

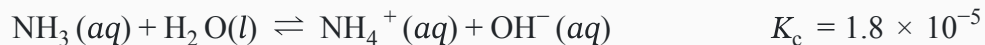$$x = \sqrt{7.4 \times 10^{-11}} = 8.6 \times 10^{-6} \ M$$

The value of x calculated is, indeed, much less than the initial concentration

$$8.6 \times 10^{-6} \ll 0.15$$

and so the approximation was justified. If this simplified approach were to yield a value for x that did *not* justify the approximation, the calculation would need to be repeated without making the approximation.

Check Your Learning

What are the equilibrium concentrations in a 0.25 M NH$_3$ solution?

$$\text{NH}_3\,(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4{}^+(aq) + \text{OH}^-(aq) \qquad\qquad K_c = 1.8 \times 10^{-5}$$

✓ Answer

$$[\text{OH}^-] = [\text{NH}_4{}^+] = 0.0021 \ M;$$

$[\text{NH}_3] = 0.25 \ M$

17.4.3 Practice Problem

[Watch on YouTube](#)

Files

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Previous Citation(s)

Flowers, P., et al. (2019). Chemistry: Atoms First 2e. https://openstax.org/details/books/chemistry-atoms-first-2e (13.4)

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