

College Chemistry

A Comprehensive Set of Imperfect Notes

The Open Education Initiative at CUNY



November 22, 2024 (12:25 Noon)

1 IA

1	H	Hydrogen
3	Li	Lithium
2	Be	Boron
5	Mg	Magnesium
11	Na	Sodium
19	K	Calcium
37	Rb	Rubidium
55	Cs	Cesium
87	Fr	Francium

Periodic Table of Chemical Elements

18 VIIA

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3	Li	Lithium															
2	Be	Boron															
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TO THE READER

The work of chemists is certainly challenging, but also exciting and rewarding. Chemists produce everything from plastics and paints to pharmaceuticals, foods, flavors, fragrances, detergents, and cosmetics. Chemistry students are well-prepared for medical, veterinarian, dentistry, optometry, or pharmacy school. This set of lecture notes was designed with a focus on the student—with a focus on you. It introduces the basic concepts of college chemistry in a way that a student of any level can hopefully understand. Some of the chapters included in this guide can be challenging. Success is not an accident. Only with hard work, patience, and perseverance, you will be able to achieve what you want.

Chemistry is not an easy subject. You may experience frustration due to the terminology or the math content. This guide is developed in chapters and sections to break down the very basics of chemistry concepts. One of the main goals here is to help you solve chemistry problems. Solving problems—not only chemistry problems but problems of any kind—is an extremely useful skill in life. Chemists approach the solving of problems in a very specific way. They use critical thinking and previous knowledge to find solutions based on the information presented. As you study this set of lectures, I encourage you to read the different sections of a chapter, highlight the main ideas, and find keywords that represent new concepts. Numerous examples are presented in the chapters with the full solution. A lot of examples are also presented without the worked solution, just including the answer. Plenty of end of the chapter problems is further included. After you read the content of a chapter you are highly encouraged to work on the end of the chapter problems. As with any skill, practice makes perfect.

There are numerous tools in this guide to help you focus on the most relevant content. For example, when the numerical problems get too complex, an *analyze the problem* box is included to help you identify what is given and what is asked in the problem.

This set of lectures resonates with the open textbook movement that is taking over CUNY as well as SUNY. Education is expensive and you as a student often rely on textbooks to learn. These valuable educational resources are often used for a very limited period and tossed or returned when a class has finished. The open textbook movement aims to alleviate the cost of education by relying on resources that are free for both the students and the educators. Still, these sources are imperfect and not as curated as textbooks, and this is the price to pay. I warn you this set of lectures is indeed imperfect, hence its title. Yet, it is the result of many hours of work—indeed months of work. Your role is key. I encourage you first to be understanding and patient, and then to contribute to the

development of this guide. With your input, we can make this guide a better educational resource. Mind that this guide was written by an educator and as such, it sometimes uses terms and a way of thinking that corresponds to the educators' point of view.

This set of lectures does not intend to replace any textbook. Indeed, there are many high-quality textbooks in the literature that I recommend. For College Chemistry:

- Chemical Principles: The Quest for Insight by Peter Atkins et al.
 - Chemistry: The Central Science by Theodore E. Brown et al.
 - Chemistry by Steven S. Zumdahl et al.
 - Chemistry: The Molecular Nature of Matter and Change by Martin Silberberg et al.
 - Chemistry by Raymond Chang et al.
 - Chemistry: Atoms First by OpenStax
- For GOB Chemistry:
- General, Organic, and Biological Chemistry: Structures of Life by Karen C. Timberlake et al.

With the help of the textbooks above you can certainly expand and complement the information presented in this guide.

This guide was fully coded in *LATeX* from the cover or the periodic table to the molecular orbital diagrams or the solid representations. Chemistry is a microscopic science not accessible to the naked eye. Visuals play a very important role in chemistry education. Visuals—in the form of images or diagrams—help make chemistry more apparent to the viewer. One of the weak points of many open education chemistry guides is the visuals. They tend to be simplistic with low quality. This guide extensively relies on images and diagrams and uses the *Tikz* software package and other open-source tools to freshly generate diagrams every time the book is compiled. All other images used here are open-source images.

I hope you enjoy this guide and more importantly, that it contributed to the success of your career.



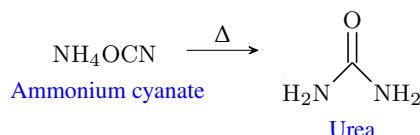
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Ch. 1. Organic Chemistry

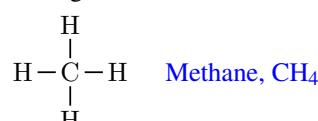
ORGANIC chemistry is a vast subject that studies the properties of carbon-based compounds, and organic compounds are chemicals based mostly on carbon as well as hydrogen. On one hand, organic chemistry plays a key role in the understanding of the functioning and composition of living cells. On the other hand, many products of industrial organic chemistry such as plastics, fuels, perfumes, or prescription drugs are an accepted part of our everyday lives. These types of compounds have common organic properties, from their smells to their powerful action. Key organic chemistry concepts are the naming of organic compounds and the properties of functional groups that give unique properties to molecules such as caffeine or even addictive drugs such as cocaine.

1.1 Organic and non-organic compounds

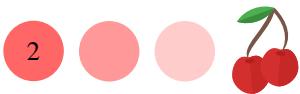
Organic compounds are chemicals mostly made of Carbon and Hydrogen, containing chains or rings of carbon atoms. Here a few examples of organic compounds: CH₄, C₂H₆, or C₆H₆. Differently, inorganic compounds contain elements other than Carbon and Hydrogen. Examples of inorganic compounds are: NaCl, CO₂, HCl, FeO or NaOH. Mind that carbonates (Na₂CO₃), carbon monoxide (CO) or carbon dioxide (CO₂) are not organic compounds. Originally the distinction between organic and inorganic compounds was made based on whether the chemical comes from a living system. Indeed organic compounds were thought of as synthesized only from living organisms. This belief was disregarded after Friedrich Wöhler was able to synthesize urea—a component of urine—from ammonium cyanate, an inorganic salt:



Alkanes are simple organic compounds made of Carbon and Hydrogen with all carbons connected using simple bonds—these are single lines representing the connections between atoms. The simplest alkane and the simplest organic compound is methane: CH₄, a fuel and the main constituent of natural gas.



Its structure is representative of organic compounds in general as it shows that each carbon atom in an organic molecule is connected to four different atoms.



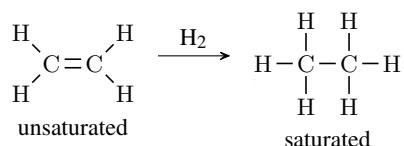
1.2 Alkanes

This first section will introduce organic chemistry, covering the simplest organic compounds: alkanes. Alkanes—also called hydrocarbons—are simply made of carbon and hydrogen with all C-C bonds being single bonds. First, you will be introduced to a few organic chemicals, and you will learn about a series of different organic formulas that can represent the same compound. Then, you will learn the basic naming rule of alkanes, which extends to other—more complex—organic chemicals. Hydrocarbons composed of single C-C bonds are called saturated hydrocarbons, whereas hydrocarbons containing multiple C-C bonds are described as being unsaturated. All carbons in a saturated hydrocarbon are bound to four atoms. You can produce saturated hydrocarbons by reacting an unsaturated hydrocarbon with hydrogen:

- ▼ Methane (CH_4) is used as a fuel for ovens, homes, water heaters.



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Molecular formula for alkanes The naming of alkanes results from the combination of a prefix and a suffix. On one hand, the suffix is always *ane*. On the other hand, the prefix depends on the number of carbons in the molecule. Table 1.1 shows a list of the different prefixes. For example, the alkane with a single carbon is called methane (CH_4). Other examples of alkanes are ethane which contains two carbons (C_2H_6) or propane with three carbons (C_3H_8). The molecular formula for an alkane with n carbon atoms is:

$$\text{C}_n\text{H}_{2n+2} \quad (1.1)$$

Hence, we have that the molecular formula for methane ($n = 1$) is CH_4 and the molecular formula for octane ($n = 8$) is C_8H_{18} . *Molecular formulas* represent only the molecular compositions, showing only the elements in the molecule.

Sample Problem 1

Write down the molecular formula for decane and pentane.

SOLUTION

Using Equation 1.1 we have that the molecular formula for decane ($n = 10$) would be: $C_{10}H_{22}$. Similarly, the molecular formula for pentane ($n = 5$) would be: C_5H_{12} .

► Answer: (decane) C₁₀H₂₂; (pentane) C₅H₁₂

STUDY CHECK

Name the alkane with formula C₇H₁₆ and give the molecular formula for nonane.

► Answer: heptane, C₉H₂₀.

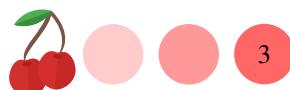
▼ The octane rating of gas is a standard measure of the performance of engine fuels, originally determined by mixing a gasoline made entirely of heptane and 2,2,4-trimethylpentane (a highly branched octane).



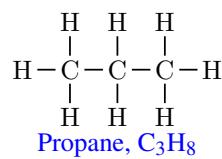
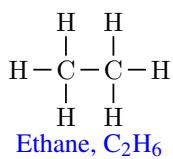
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Table 1.1 Prefixed for alkane naming

# Carbons	prefix	# Carbons	prefix
1	Meth	6	Hex
2	Eth	7	Hepta
3	Prop	8	Octa
4	But	9	Nona
5	Pent	10	Deca



Expanded structural formula for alkanes At this point, we have addressed the molecular formulas of three simple alkanes: methane (CH_4), ethane (C_2H_6), and propane (C_3H_8). However, these formulas do not inform about the molecular connections. The structure of ethane and propane is shown below:

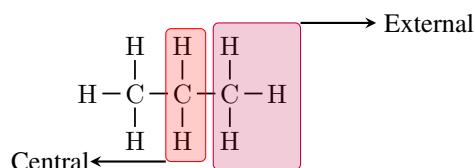


These structures show that each carbon connects to four different atoms, and each hydrogen connects to only one atom. The formulas presented above are called *expanded structural formulas* as all atoms and all bonds connecting these atoms are shown, representing the molecular structure.

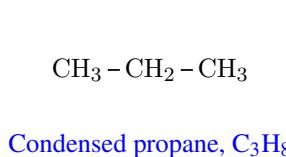
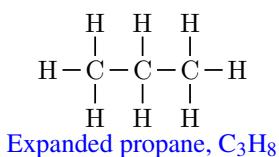
Table 1.2 Alkane names based on the number of carbons in the chain

Number of Carbons	Name	Condensed Structural formula	Molecular formula
1	Methane	CH_4	CH_4
2	Ethane	CH_3-CH_3	C_2H_6
3	Propane	$\text{CH}_3-\text{CH}_2-\text{CH}_3$	C_3H_8
4	Butane	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$	C_4H_{10}
5	Pentane	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	C_5H_{12}
6	Hexane	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	C_6H_{14}
7	Heptane	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	C_7H_{16}
8	Octane	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	C_8H_{18}
9	Nonane	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	C_9H_{20}

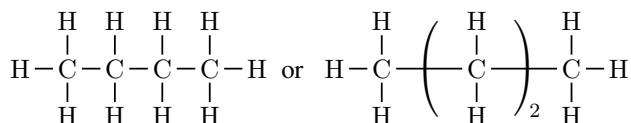
Condensed structural formula Let us analyze the formula of propane shown below. In this molecule, there are two different types of carbons: the end of the chain carbon, in the left and the right of the structure, and a central carbon. The external carbons are bound to three hydrogens (and one carbon), whereas the central carbons are bonded to two hydrogens (and two carbons).



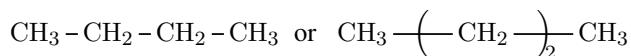
The extremes of the chain are indeed CH_3 units and the central carbon is a CH_2 unit. So, another way to represent propane would be:



This representation is called *condensed structural formula* or simple condensed structure, as the units of carbon and hydrogen are condensed into CH_2 and CH_3 units. Table ?? displays molecular formulas and condensed structures for different alkanes. For larger alkenes it is often convenient to use parenthesis to simplify the structure. For example, the expanded structure of butane can be written as:



Similarly, the condensed structure of butane can be written as:

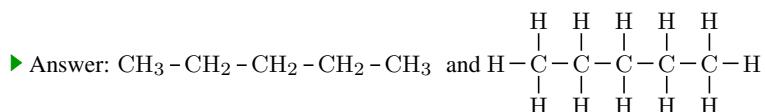


Sample Problem 2

Write down the condensed and expanded formulas for pentane.

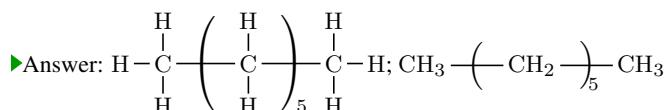
SOLUTION

Pentane has five carbons, hence its condensed formula will have two CH_3 units and three CH_2 units. On the other hand, the expanded formula for pentane should display all carbons and hydrogens:



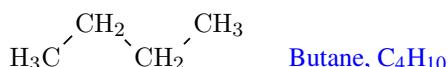
◆ STUDY CHECK

Write down the condensed and expanded formulas for heptane.



Skeletal structural formula Let us analyze the structure of butane again.

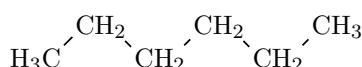
This molecule has four carbons in the form of a C-C chain such as C-C-C-C.



However, in reality, C-C chains with more than two carbons are not linear, and their structure resembles more a zig-zag rather than a line, since the tetrahedral C-C-C angle is 109.5° . So instead of representing butane as a line, it should be represented as:



This type of structural representation is called *skeletal structural formula* as you only represent the C-C skeleton of the molecule. Another example would be:



condensed formula of hexane



skeletal formula of hexane

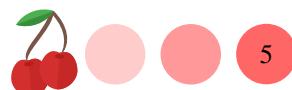
The ending of a skeletal formula represents a CH_3 , and the points in between represent CH_2 . Hydrocarbons in which carbon atoms form a long, continuous string are called straight-chain (e.g. butane) or unbranched hydrocarbons, in contrast to branched hydrocarbons (e.g. isobutane).



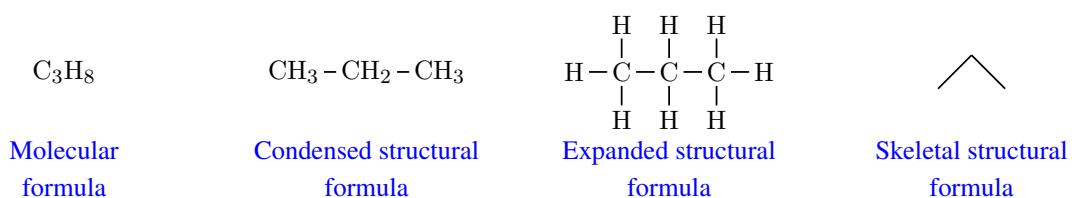
butane



isobutane



A review of the different structural formulas At this point, you have seen four different ways to represent organic molecules. Using propane as an example, here are all the formulas: We have that the *molecular formula* (e.g. C₃H₈ for propane) is mainly used to indicate the composition of the molecule in the form of Carbon and Hydrogen atoms. A second way to represent propane is using its *expanded structural formula*, that is by representing all atoms in the molecule and all atomic connections. A third molecular representation is the *condensed structural formula* that uses CH₃ and CH₂ units, only representing the C-C bonds. Finally, the *skeletal formula* is perhaps the most simplistic representation as only the C-C bonds are represented in the form of simple lines. It is important to understand that *all formulas are just different ways to represent the same molecule.*

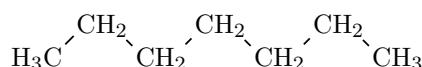


Sample Problem 3

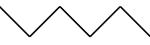
Write down the condensed and skeletal formulas for heptane.

SOLUTION

Heptane has seven carbons, hence its condensed formula will have two CH₃ units and five CH₂ units:



The skeletal formula for would be:

► Answer: 

❖ STUDY CHECK

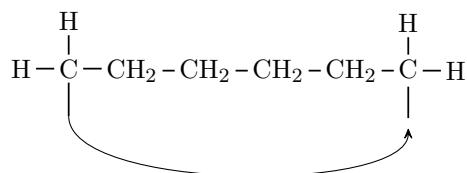
Draw the skeletal formula of decane.

► Answer: 

1.3 Cycloalkanes

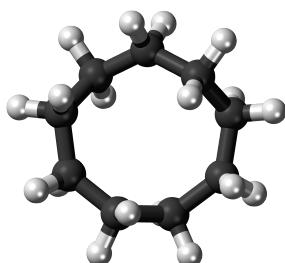
Alkanes are perfect examples of hydrocarbons, with C-C chains and all carbon atoms saturated with hydrogen. Cycloalkanes are simply alkanes with a cyclic structure. We will cover the molecular, condensed, and skeletal formulas for these chemicals.

Cyclic alkanes Consider the expanded structure of hexane. A cycloalkane results from removing the left and right hydrogen while connecting the molecule in the form of a cycle:

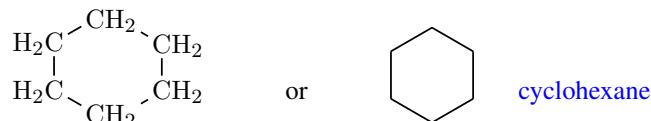


As the most stable structure for six lines is the hexagon, the resulting structure of cyclohexane would be:

▼3D representation of Cyclononane



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Naming cycloalkanes The naming of alkanes and cycloalkanes is very similar. You just need to add the cyclo prefix to the name. For example, the alkane with five carbons is called pentane, whereas the corresponding cycloalkane is called cyclopentane:



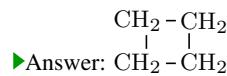
Sample Problem 4

Write down the condensed structure and name the following cycloalkane:



SOLUTION

The cycloalkane has four carbons and its name is cyclobutane. Its condensed structure is



◆ STUDY CHECK

Write down the condensed structure and name the following cycloalkane:



Molecular formulas for cycloalkanes The molecular formula for a general cycloalkane with n carbon atoms is:

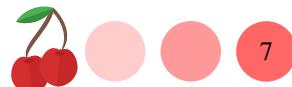
$$\text{C}_n\text{H}_{2n} \quad (1.2)$$

As an example, the formula for cyclobutane ($n = 4$) is C_4H_8 and the formula for cyclooctane ($n = 8$) is C_8H_{16} .

Sample Problem 5

Write down the molecular formula for cyclodecane and cyclopentane.

SOLUTION



Using Equation 1.2 we have that the molecular formula for cyclodecane ($n = 10$) would be: $C_{10}H_{20}$. Similarly, the molecular formula for cyclopentane ($n = 5$) would be:

►Answer: C_5H_{10} .

◆ STUDY CHECK

Name the alkane with formula C_7H_{14} and give the formula for cyclononane.

►Answer: cycloheptane, C_9H_{18} .

1.4 Alkanes with substituents

Oftentimes alkanes have other groups of atoms called substituents attached to the hydrocarbon chain. This section covers the naming of alkanes with substituents. Here is an example of an alkane and an alkane with a substituent:



Propane

Nitropropane

In the substituted molecule, a nitro group has replaced a hydrogen atom.

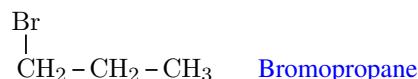
Substituents There are many different substituents—also called groups—that can be found attached to an alkane chain. Their names are indicated in Table ???. The easiest substituents are halogens; atoms of chlorine (Cl —), bromine (Br —) or iodine (I —) can replace hydrogen atoms in an alkane. The name of these substituents—chloro, bromo, and iodo—resembles the name of the corresponding atom. Other substituents can contain carbon, like a methyl (CH_3 —) or a ethyl (CH_3CH_2 —). There are even more complex substituents such as tert-butyl in which a central carbon atom is connected to three different methyl groups. The name of substituents (methyl) comes from the name of the alkane (methane) by replacing the *-ane* suffix with *-yl*.

Alkanes with a single substituent Let us consider the following example.

The condensed formula for propane is



Now, this would be propane with a substituent:

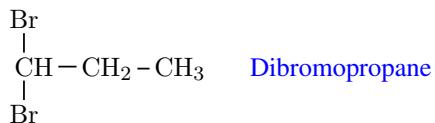


As you can see a bromine atom substitutes one of the hydrogen atoms of the second first of the molecule (starting from the left). The name simply results from the combination of the substituent group and the alkane name

**Table 1.3 Substituent name**

Substituents	name	Substituents	name		
CH ₃ —	Methyl	F —	Fluoro	CH ₂ = CH —	Vinyl
CH ₃ CH ₂ —	Ethyl	Cl —	Chloro	NO ₂ —	Nitro
CH ₃ CH ₂ CH ₂ —	Propyl	Br —	Bromo	NH ₂ —	Amino
CH ₃ CH ₂ CH ₂ CH ₂ —	Butyl	I —	Iodo	H ₃ C — — CH — CH ₂ CH ₃	sec-Butyl
$\begin{array}{c} \\ \text{H}_3\text{C} - \text{C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	t-butyl	$\begin{array}{c} \\ \text{H}_3\text{C} - \text{CH} - \text{CH}_3 \end{array}$	Isopropyl	CH ₃ CH ₂ CH ₂ —	Propyl

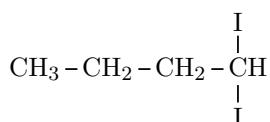
Alkanes with two or more equal substituents In the same way, as when you have a single bromo substituent attached to propane, you can also have two Br —. In this case, you need to use the prefix *di* to indicate there are two identical bromos. For example, the name of the following molecule would be:



Similarly, you should use the prefix *tri* and *tetra* for three equal substituents.

Sample Problem 6

Name the following hydrocarbon:



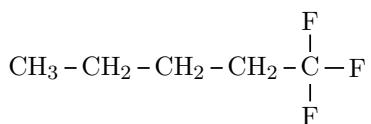
SOLUTION

The carbon chain has four carbons and hence the ending of the name would be: butane. Also there are two iodines (iodo substituents) attached to the carbon chain. As there are two of the same iodo atoms, we need to use the prefix *di*. The full name would be:

►Answer: Dioiodobutane.

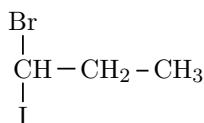
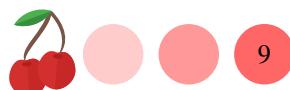
◆ STUDY CHECK

Name the following hydrocarbon:



►Answer: Trifluoropentane.

Alkanes with different substituents Now imagine you have two different halogens as substituents: Br — and I — like in next example



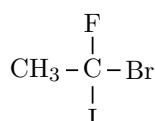
As both substituents have different names you cannot use the prefix *di*. Still, when you indicate the names of the substituents you need to order them alphabetically. So Bromo goes first in the name and Iodo after. You also need to separate the different substituents with a hyphen ('-'). The final name of the hydrocarbon above would be Bromo-Iodopropane.

Naming rules for alkanes Overall, the rules for naming alkanes are:

- 1 **Step one:** The number of carbon atoms in the chain will give the ending name of the molecule (e.g. four carbons would be butane).
- 2 **Step two:** Number the main chain starting at the end closest to the substituents so that the numbers for the substituents are small.
- 3 **Step three:** Name the substituents with their position and order them alphabetically (di, tri, etc. do not count in the alphabetic order).

Sample Problem 7

Name the following hydrocarbon:



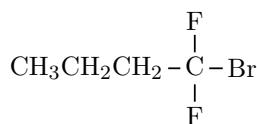
SOLUTION

The carbon chain has two carbons and hence the ending of the name would be: ethane. Also there are three different substituents: iodine (ido substituents), bromine (bromo substituents) and fluorine (fluoro substituents). We need to order them according to the *abc*, hence the order would be: bromo, then fluoro and finally iodo. The full name of the alkane would be:

►Answer: Bromo-Fluoro-Iodoethane.

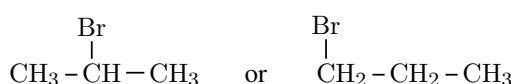
◆ STUDY CHECK

Name the following hydrocarbon:



►Answer: Bromodifluorobutane.

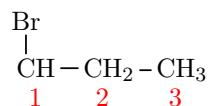
Numbering the chain Substituents are atoms or groups of atoms that replace hydrogens in alkane chains. You could envision attaching substituents at different points of the chain. For example:



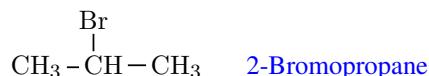
In the right example, Br is plugged into the left C atom, whereas in the left example, C is plugged into the middle carbon. Hence, it is important first, to learn how to number a hydrocarbon chain. Let us use propane—a molecule with three atoms—as an example. To



number the chain, you start by selecting the extreme that is the closest to the substituent using this carbon as number one. Next carbon would be carbon number two and so on until you arrive at carbon number three.

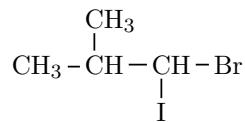


As the Br atom in the carbon number one, the name of the molecule would be 1-bromopropane or simply bromopropane. Differently, when the substituent is in a carbon different than one, you need to indicate that location. For example:



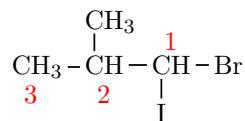
Sample Problem 8

Name the following hydrocarbon:



SOLUTION

First we find the ending of the name: as the molecule has three carbons in the main chain, the ending of the name would be: propane. Then we need to number the chain so that the number one carbon is the closest to the substituents:

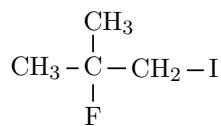


A methyl is connected to carbon two, and two halogens, a iodo and a bromo are connected to carbon number one. The substituents are: 2-methyl, 1-bromo, 1-iodo. If we order them: 1-bromo-1-iodo-2-methyl. And the final name would be:

►Answer: 1-bromo-1-iodo-2-methylpropane.

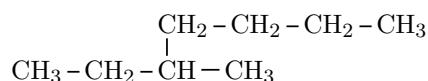
◆ STUDY CHECK

Name the following hydrocarbon:

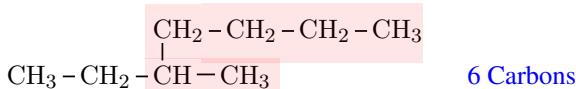
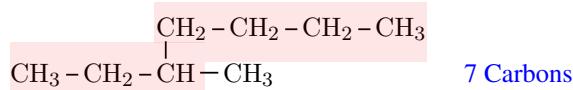
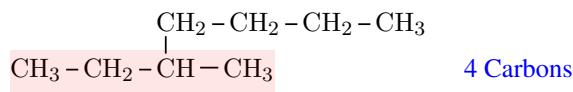


►Answer: 1-iodo-2-fluoro-2-methylpropane.

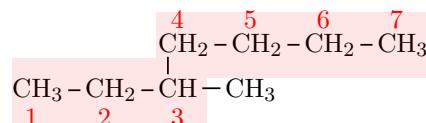
Finding the longest chain Alkanes are complex molecules often containing more than one hydrocarbon chain. Therefore, one can envision several ways to number the chain. However, the rule is to first locate the longest chain. Let us use the following hydrocarbon. How many chains can you find, and which is the longest chain?



The answer should be three chains. Let me highlight the three different possibilities and the number of atoms in each chain:



As the longest chain has seven carbons, the name of the molecule would be heptane. Still, you need to add the substituents to the name. Hence, after you locate the longest chain, you need to number the chain so that the substituents are located the closest to the carbon number one possible:



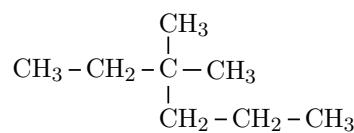
As there is a methyl in carbon number three the final name of the molecule would be:
3-methylheptane.

Naming rules for branched alkanes Overall, the rules to name branched alkanes are:

- 1 **Step one:** Look for the longest carbon-carbon chain that will give the ending name of the molecule (e.g. four carbons would be butane).
 - 2 **Step two:** Number the main chain starting at the end closest to the substituents so that the numbers for the substituents are small.
 - 3 **Step three:** Name the substituents with their position and order them alphabetically.

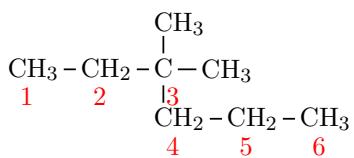
Sample Problem 9

Name the following hydrocarbon:



SOLUTION

First we locate the longest chain. We have five possible chains, and the longest one has six carbons. Hence the name of the hydrocarbon would be hexane. Now we need to number the carbons so that we start numbering the closest to the substituents the possible.

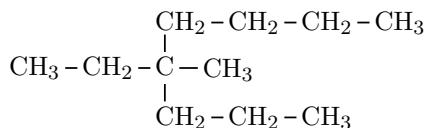


We have two methyl connected to carbon number three. Hence the final name will be:

►Answer: 3-dimethylhexane.

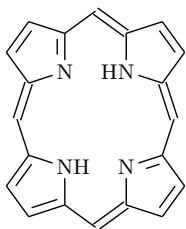
◆ STUDY CHECK

Name the following hydrocarbon:

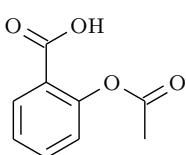


►Answer: 4-ethyl-4-methyloctane.

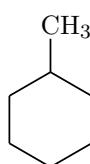
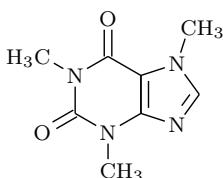
▼Porphyrin has several amine groups.



▼Aspirin contains an aromatic cycle, a carboxylic acid and a ester.

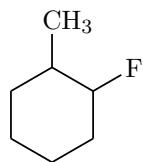


▼Caffeine contains amides and amines

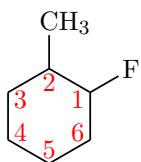
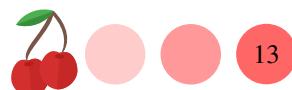


this is a cyclohexane connected to a methyl substituent. As there is only one substituent, there is no need to number the carbon chain. Hence the name would be simply methylcyclohexane.

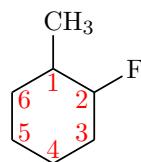
Cycloalkanes with two substituents Let us look at the following cycloalkane:



this is a cyclopentane connected to two different substituents: a methyl and a fluoro. In order to name this molecule, we need to number the carbons first, and there are two different ways to number the cyclopentane ring:



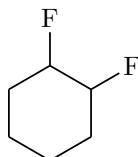
1-Fluoro-2-methylcyclohexane



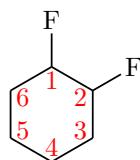
Fluoro-1-methylecyclohexane

we will choose the name that gives the lowest numbers: 1-Fluoro-2-methylcyclohexane.

Cycloalkanes with repeated substituents Let us look at the following cycloalkane, which has two repeated fluorine substituents:



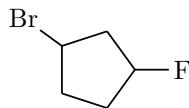
After numbering the chain:



The name would be: 1,2-difluorocyclohexane.

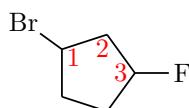
Sample Problem 10

Name the following hydrocarbon:



SOLUTION

The molecule is a cyclopentane with two substituents: fluoro and bromo. I will start numbering in bromo and continue until bromo. This way I will have small numbers and follow the abc rule:

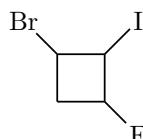


And the name of the molecule would be:

►Answer: 1-bromo-3-fluorocyclopentane.

◆ STUDY CHECK

Name the following hydrocarbon:



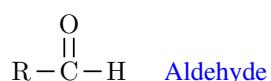
►Answer: 1-bromo-3-fluoro-2-bromocyclobutane.



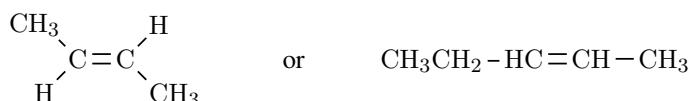
1.6 Molecular diversity

You have certainly taken painkillers for a headache or over-the-counter drugs to get over a cold. Maybe you drink coffee and perhaps you like tea. All these substances contain active organic molecules. These active molecules are hydrocarbon derivatives and differ from plain hydrocarbons, which are simply made of carbon and hydrogen. Active molecules contain functional groups such as alcohol, ethers, carboxylic acids, amines, amides, or aromatic groups. These groups of atoms have a specific function and give activity to the molecule. The goal of this section is simply to identify the different groups.

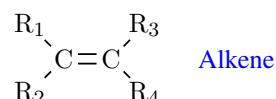
Multiple bonds Ketones and aldehydes both contain a C=O group. Still, these are two different groups, and ketones have a C=O group bounded to two different carbon atoms



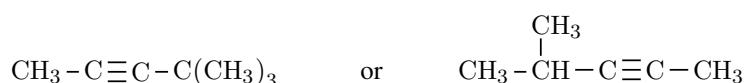
whereas aldehydes have the same C=O group but this time bound to a carbon and a hydrogen. Alkenes contain at least one double bond between carbons. An example would be:



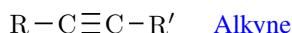
Double bonds are also called unsaturations. Hence, we say alkenes are unsaturated. Both extremes of an alkene chain can be connected to different hydrocarbons. We normally represent this as:



where R and R' represent any hydrocarbon chain. For Example R and R' can be CH₃— or CH₃CH₂—. Alkynes contain at least one triple bond between carbons. An example would be:

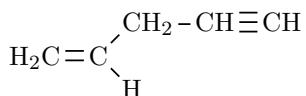


Again, we could use R and R' to represent any hydrocarbon chain:



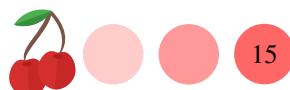
Sample Problem 11

Identify the alkene and alkyne groups in the molecule:



SOLUTION

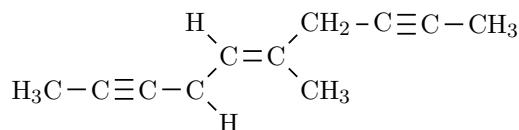
A double bond is carbon atoms sharing two pairs of electrons, whereas a triple bond is a pair of atoms sharing three pairs of electrons. They are represented with a double and triple line, respectively.



► Answer: (left) alkene; (right) alkyne

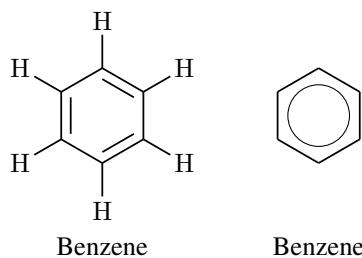
◆ STUDY CHECK

Identify the alkene and alkyne groups in the molecule:



► Answer: (center) alkene; (right, left) alkyne

Aromatic group Aromatic groups are based on benzene, a carcinogenic cyclohexane-like molecule with a series of alternating double bonds, which is often represented as a circle for simplicity:



Examples of molecules containing aromatic groups are:

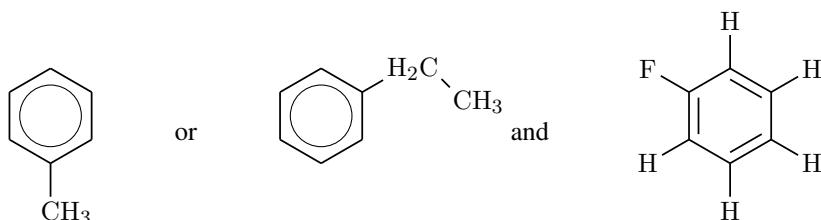


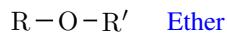
Table 1.4 Names of several functional groups

Functional group	Name	Functional group	Name	Functional group	Name
$\begin{array}{c} \text{R}_1 \\ \diagdown \\ \text{C} = \text{C} \\ \diagup \\ \text{R}_2 \end{array}$	Alkene	$\begin{array}{c} \text{O} \\ \\ \text{R} - \text{C} - \text{R}' \end{array}$	Ketone	$\text{R} - \text{OH}$	Alcohol
$\text{R} - \text{C} \equiv \text{C} - \text{R}'$	Alkyne	$\begin{array}{c} \text{O} \\ \\ \text{R} - \text{C} - \text{H} \end{array}$	Aldehyde	$\text{R} - \text{SH}$	Thiol
$\begin{array}{c} \text{O} \\ \\ \text{R} - \text{C} - \text{OH} \end{array}$	Carboxylic acid	$\begin{array}{c} \text{R}' \\ \\ \text{R} - \text{N} - \text{R}'' \end{array}$	Amine	$\text{R} - \text{O} - \text{R}'$	Ether
$\begin{array}{c} \text{O} \\ \\ \text{R} - \text{C} - \text{O} - \text{R}' \end{array}$	Ester	$\begin{array}{c} \text{O} \quad \text{R}'' \\ \quad \\ \text{R} - \text{C} - \text{N} - \text{R}' \end{array}$	Amide		Phenyl

Alcohol, ether and thiol group Alcohols contain an –OH group attached to a carbon.



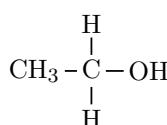
Whereas ethers have oxygen atoms attached to two carbon atoms:



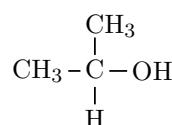
Examples of alcohols and ether are:



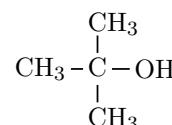
Alcohols can be classified as primary (one hydrocarbon fragment), secondary (two hydrocarbon fragments), and tertiary (three hydrocarbon fragments) alcohols, based on the number of hydrocarbon fragments connected to the carbon attached to the hydroxyl group.



Primary



Secondary



Tertiary

Thiols contain a –SH group attached to a carbon. They are equivalent to alcohols but based on sulfur:



Examples of thiols are:



Thiols are responsible for the characteristic smell of rotten eggs and burned hair.

Sample Problem 12

Classify the following molecules as alcohol or ether.



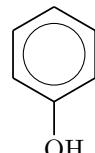
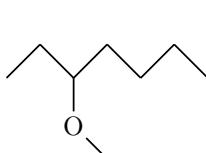
SOLUTION

The OH groups is an alcohol, and we find this group in the left molecule. Differently, the right molecule is an ether as it contains the R – O – R' group.

► Answer: (left) alcohol; (right) ether.

STUDY CHECK

Classify the following molecules as alcohol or ether.

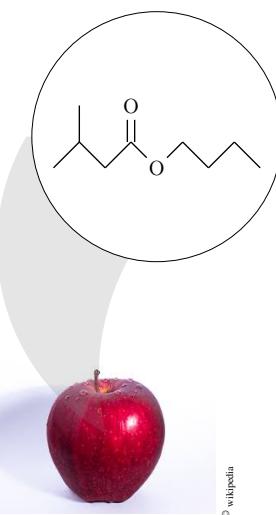


► Answer: (left) ether; (right) alcohol.

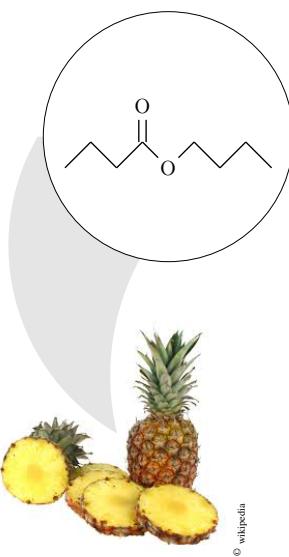
▼Acetone, the smallest ketone, is also known as nail polish remover.



▼Ethyl isovalerate is an ester that flavors apples.



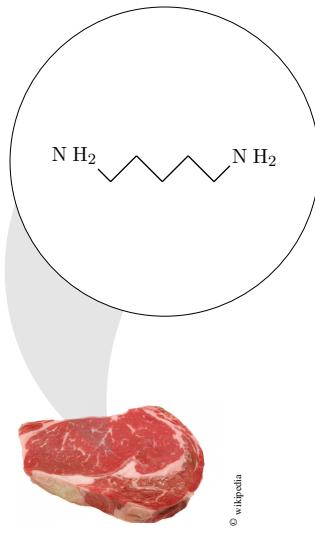
▼Butyl butyrate is an ester that flavors pineapple.



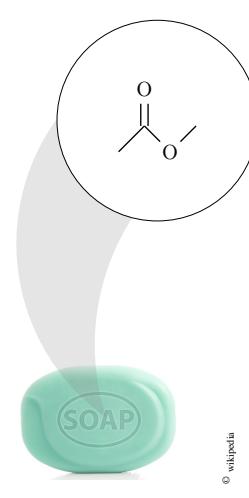
▼Diethyl ether was formerly used as a general anesthetic, until non-flammable drugs were developed.



▼Amines are responsible of the bad smell of decaying meat.



▼Esters are found in soaps



▼Vinegar contains acetic acid, the smallest carboxylic acid.

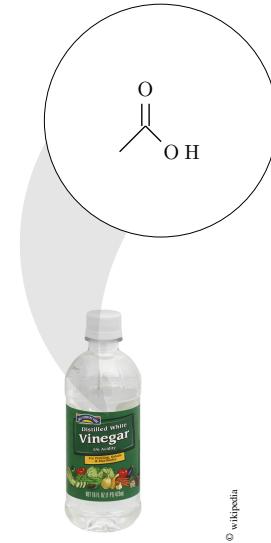
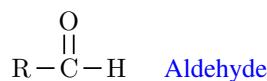
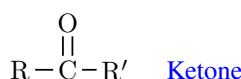


Figure 1.1 Some examples of functional groups with applications to real life.

Aldehydes and ketones Ketones and aldehydes both contain a $\text{C}=\text{O}$ group. Still, these are two different groups, and ketones have a $\text{C}=\text{O}$ group bounded to two different carbon atoms

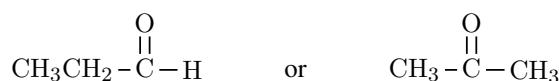


whereas aldehydes have the same $\text{C}=\text{O}$ group but this time bound to a carbon and a hydrogen.





Examples of aldehydes and ketones are:



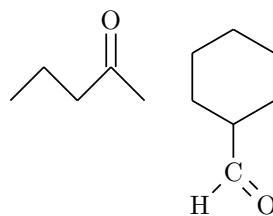
Aldehyde

Ether

Ketones are good solvents. For example, acetone is commonly found in nail polish removers for example. Aldehydes have strong smells. For example, vanillin is an aldehyde responsible for the vanilla smell. Cinnamaldehyde is responsible for the cinnamon odor.

Sample Problem 13

Classify the following molecules as an aldehyde or ketone



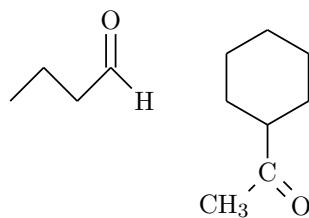
SOLUTION

The left molecule is a ketone as the carbonyl group ($\text{C}=\text{O}$) is connected to a CH_3 and a CH_2 . Differently, the right molecule is an aldehyde as the carbonyl group is connected to a cycloalkane but also to a hydrogen.

►Answer: (left) ketone; (right) aldehyde.

◆ STUDY CHECK

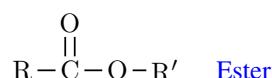
Classify the following molecules as an aldehyde or ketone



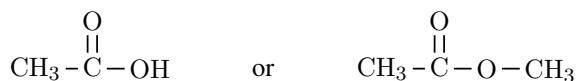
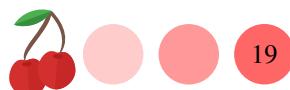
Carboxylic acids and esters Carboxylic acids contain a carbonyl group ($\text{C}=\text{O}$) connected to both a hydrocarbon chain and an alcohol group:



Esters have the same $\text{C}=\text{O}$ group but this time bounded to a carbon (R) and an ether group ($-\text{O}-\text{R}'$).



Examples of carboxylic acids and esters are:

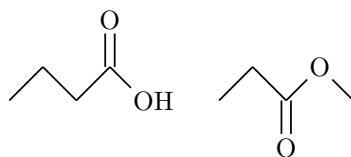


Carboxylic acid

Esters

Sample Problem 14

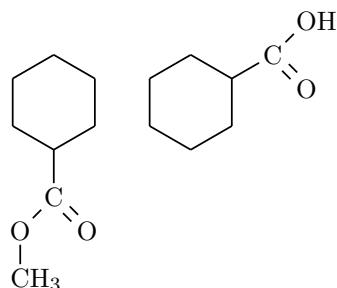
Classify the following molecules as an carboxylic acid or ester:

**SOLUTION**

The molecule in the left is a carboxylic acid as the carbonyl group ($\text{C}=\text{O}$) is connected to an alcohol $-\text{OH}$. Differently, the molecule in the right is a ester as the carbonyl group is connected to a $-\text{O}-\text{CH}_3$ group.

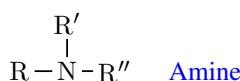
◆ STUDY CHECK

Classify the following molecules as an carboxylic acid or ester:

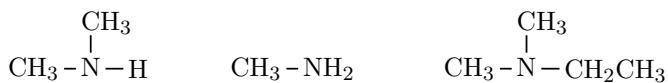


►Answer: (left) ester; (right) acid.

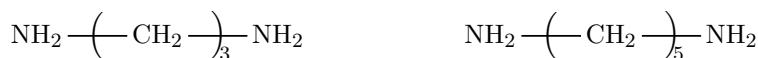
Amines and amides Amines and amides are groups containing nitrogen. Amines are derivative of ammonia (NH_3) with one or more of the hydrogen atoms being replaced by a hydrocarbon



Examples of amines are:



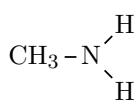
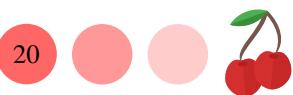
Amines have very strong and unpleasant odors—fishy like—often associated with the smell of decaying flesh:



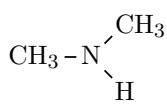
putrescine

cadaverine

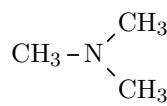
Similar to alcohols, amines can be classified as primary (one hydrocarbon fragment), secondary (two hydrocarbon fragments), and tertiary (three hydrocarbon fragments) amines, based on the number of hydrocarbon fragments connected to the nitrogen atom:



Primary

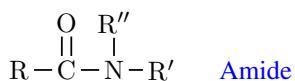


Secondary

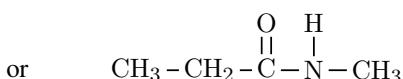
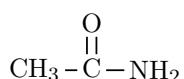


Tertiary

Amides, on the other hand, contain a carbonyl group ($\text{C}=\text{O}$) connected to an amine group (—N—)



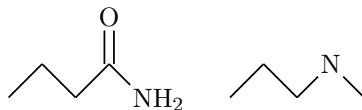
Examples of amides are:



Amides are primarily used in the pharmaceutical industry as drugs, including pain killers like morphine and Demerol, anesthetics like Novocain, and are also found in many important structural materials like nylon.

Sample Problem 15

Classify the following molecules as an amide or amine:



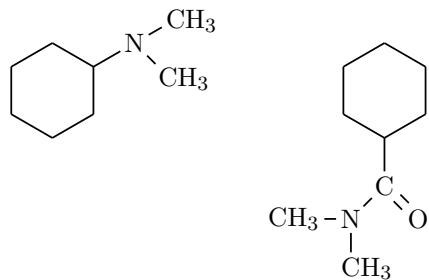
SOLUTION

The molecule in the left is a amide as the carbonyl group ($\text{C}=\text{O}$) is connected to a nitrogen atom. Differently, the molecule in the right is an amine as the nitrogen group is not connected to any carbonyl group.

►Answer: (left) amide; (right) amine.

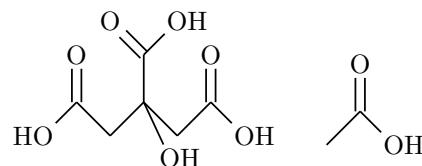
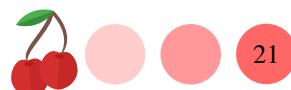
◆ STUDY CHECK

Classify the following molecules as an amide or amine:



►Answer: (left) amine; (right) amide.

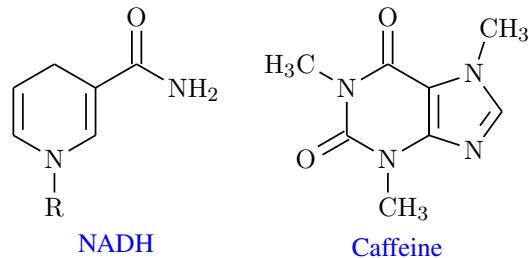
Identifying organic acids and bases Acid organic molecules, in general, contain one or more carboxylic acid groups. An example would be vinegar and citric acid, the acid found in citrus.



Citric acid

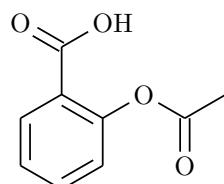
Acetic Acid

Bases contain one or more amine groups. Examples of bases are NADH, a coenzyme found in all living cells, or caffeine, a base found in coffee.

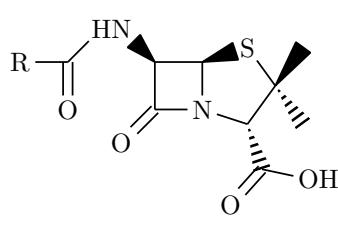


Sample Problem 16

Classify the following molecules as an acid or base:



Aspirin



Penicillin

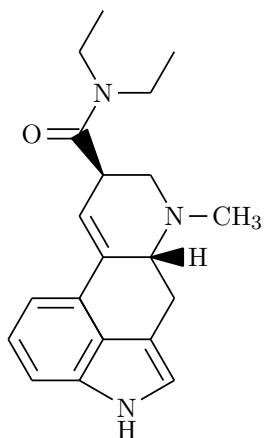
SOLUTION

Aspirin contains an acid group and hence it will be acidic. Penicillin contains both acidic and amine groups and hence will be both acidic and basic.

►Answer: (left) acid; (right) both.

◆ STUDY CHECK

Classify the following molecules as an carboxylic acid or base:



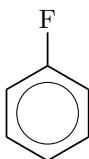
LDS

► Answer: base

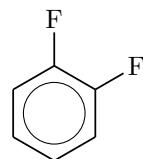
1.7 Aromatic hydrocarbons

Aromatic compounds are unsaturated hydrocarbons with increased stability and unique chemical properties. Benzene represents the simplest of all aromatic compounds. In this molecule, all carbon atoms are equivalent. A combination of the localized electron model and hybrid orbitals predicts this equivalency. The localized electron model supports this equivalence through two equivalent resonant structures. The orbitals model describes each carbon using three sp^2 orbitals that form three σ bonds (one C-H and two C-C bonds), while a remaining $2p$ atomic orbital creates a π delocalized orbital. The circle inside benzene's ring represents a combination of all delocalized π orbitals. This electronic delocalization gives benzene unique chemical properties. This section will address the reactivity and nomenclature of aromatic hydrocarbons.

Nomenclature The standard nomenclature for benzene derivatives resembles the ones for substituted alkanes. For benzenes with more than one substituent, we follow the *abc* ordering rule and we use numbers to indicate the location of each substituent. See examples below:

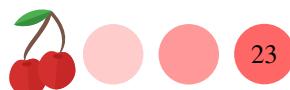


Fluorobenzene

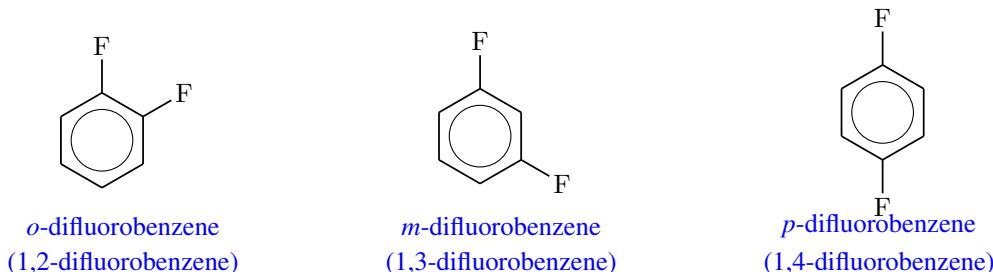


1,2-difluorobenzene

There is an alternative, but extensively used, nomenclature that uses the prefixes *ortho*, *meta*, and *para* to describe the location of double-substituted benzene. *Ortho o-* is used when the substituents are adjacents (1,2 location), whereas *meta m-* is used when there is a carbon in between the two substituents (1,3 location). *Para p-* is used when there

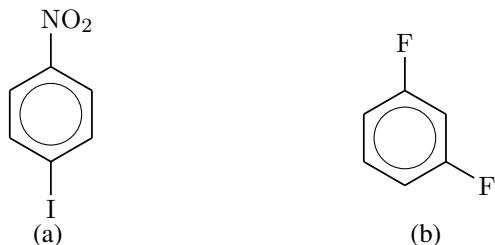


are two carbons in between the two substituents (1,4 location). Below you can see this alternative nomenclature in use:



Sample Problem 17

Name or formulate the following aromatic compounds:



SOLUTION

(a) This chemical is *p*-iodonitrobenzene also called 1,4-iodonitrobenzene. (b) This chemical is *m*-difluorobenzene also called 1,3-difluorobenzene.

►Answer: (a) *p*-iodonitrobenzene; (b) *m*-difluorobenzene (1,3-difluorobenzene).

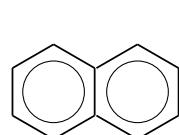
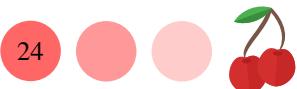
◆ STUDY CHECK

Name or formulate the following aromatic compounds:

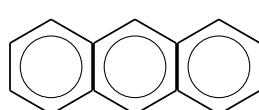


►Answer: (a) ethylbenzene; (b) *o*-fluoroiodobenzene (1,2-fluoroiodobenzene).

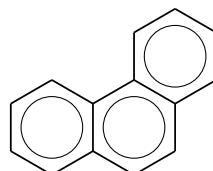
Complex aromatic systems Benzene rings can fuse forming complex aromatic rings as shown below. Naphthalene was used for the manufacturing of mothballs, whereas anthracene is used for the production of dyes. Phenanthrene is a precursor of synthetic drugs. 3,4-benzpyrene is an active carcinogen found in smoke and smog.



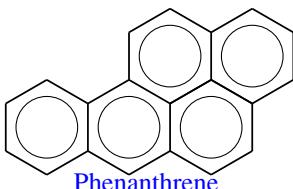
Naphthalene



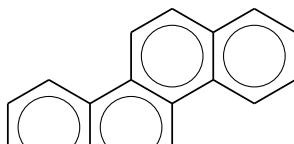
Anthacene



Phenanthrene

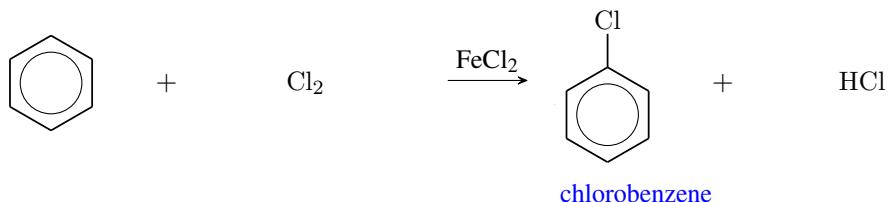


Phenanthrene

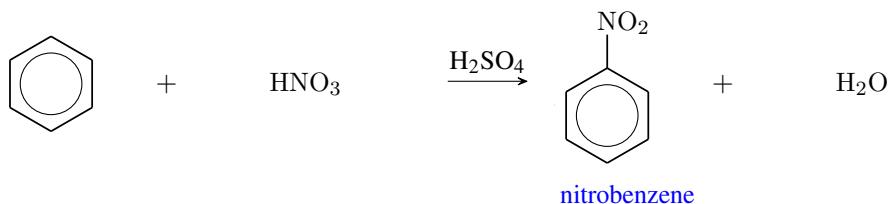


Chrysene

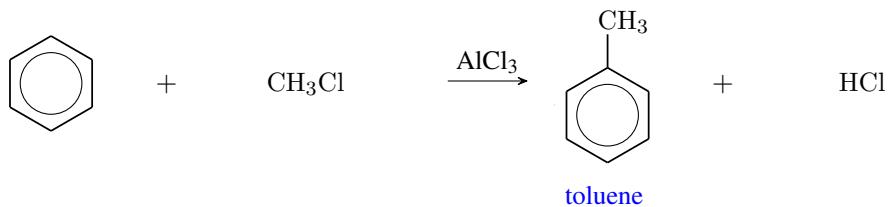
Reactivity Aromatic hydrocarbons undergo *substitution reactions* in which hydrogen atoms are replaced by other atoms. For example, chlorine replaces a hydrogen atom in benzene, hence producing chlorobenzene, when iron(II) chloride is used as a catalyst:



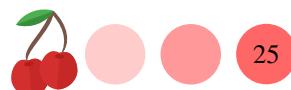
Also, benzene reacts with nitric acid in the presence of sulfuric acid producing nitrobenzene.



Finally, chloromethane reacts with benzene to produce toluene (methylbenzene).

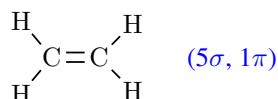


The reactivity of aromatic compounds is very different than that of unsaturated hydrocarbons which undergo *addition reactions* in which external atoms add to double bonds.



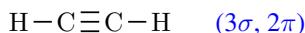
Alkenes and alkynes are hydrocarbons with multiple C-C bonds, particularly double and triple bonds. They result from removing hydrogens from the hydrocarbon's structure. This section addresses the naming and structure of these important chemicals.

Bonding Alkenes contain at least one double bond. Ethylene is the smallest of all alkenes with just two carbon atoms. Let us analyze its structure and bonding:



Every carbon center in the double bond has three sp^2 orbitals and two empty $2p$ orbitals. The three sp^2 orbitals combine, giving three σ bonds. Two of these are used to bond carbon atoms with two hydrogens, whereas the remaining bond is used in the C-C double bond. One of the empty $2p$ orbitals forms a π orbital in the double bond. Therefore, for every double bond, we have a σ and a π orbitals.

Alkynes contain at least one triple bond. Ethylene, also called acetylene, is the smallest of all alkynes with just two carbon atoms. Let us analyze its structure and bonding:



The triple bond in acetylene can be understood as a σ bond with two π bonds between the carbon atoms. σ and π bonds have very different mobility. π bonds are rigid, as the p orbitals involved in the bond need to be lined up parallel to the three σ bonds (see Figure 1.2). Differently, σ bonds are mobile and as such, free rotation is possible. Therefore, double and triple bonds are rigid, whereas single bonds are mobile.

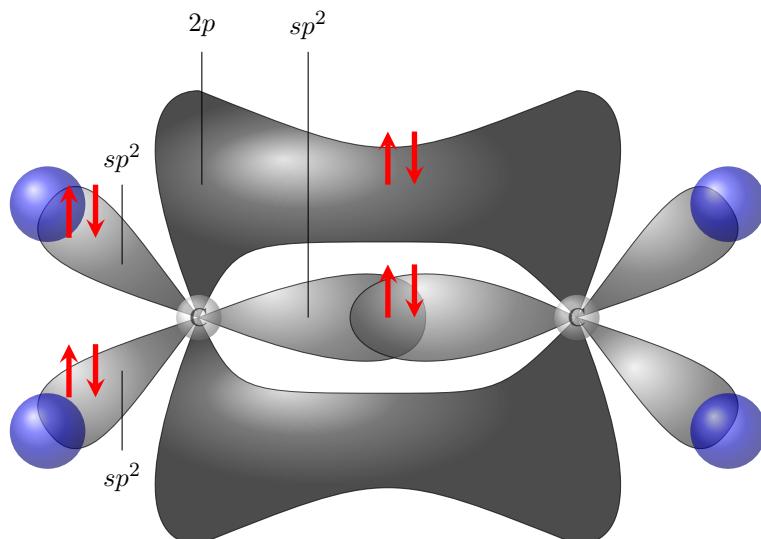
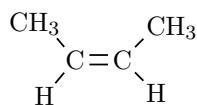


Figure 1.2 Bonding of ethylene in which three sp^2 hybrid orbitals and one $2p$ orbital populated with paired electrons. The orbitals of C (H) are represented with grey (blue) shading.

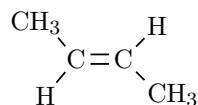
Stereoisomerism As the carbon atoms bonded through a double bond have restricted rotation, their mobility is limited, which enables cis-trans stereoisomerism. Remember isomers are molecules with the same molecular formula but different properties. In particular, stereoisomers are molecules with the same molecular formula but different spatial arrangements of the bonds. Let us address the two possible isomers of butene: cis-butene and trans-butene. Cis isomers have the same substituents located on the same



side of the double bond, whereas trans isomers have the same substituents placed on opposite sides of the double bond.



cis-butene



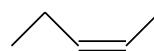
trans-butene

Alkynes do not present cis-trans stereoisomerism as every carbon atom in the triple bond is only bonded to a single substituent.

Nomenclature For the case of alkenes, its nomenclature is similar to that of alkanes, but switching the *-ane* ending into *-ene*. For example, the smallest alkene CH_2CH_2 is called ethene (its common name is ethylene). When the molecule has more than three carbons, one needs to specify the location of the double bond with a number as the lowest-numbered carbon atom involved in the double bond. For example, 1-pentene and 2-pentene are represented below.

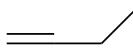


1-pentene

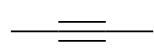


2-pentene

The nomenclature of alkynes involves the use of *-yne* and for example $\text{HC}\equiv\text{CHCH}_2\text{CH}_3$ is called 1-butyne and $\text{HC}\equiv\text{CHCH}(\text{CH}_3)_2$ is called 3-methyl-1-butyne.



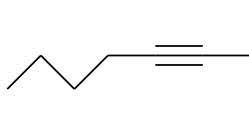
1-butyne



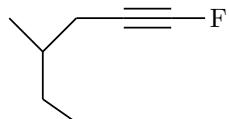
2-butyne

Sample Problem 18

Name or formulate the following organic compounds:



(a)

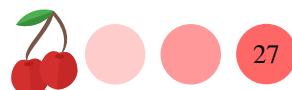


(b)

SOLUTION

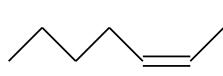
(a) This alkyne has seven carbons, and its triple bond is located on carbon number two. Hence its name would be: 2-heptyne; (b) This alkyne has six carbons, with a fluorine and the triple bond on carbon number one, and a methyl group on carbon number four. Hence, its name is 1-fluoro-4-methyl-1-hexyne

►Answer: (a) 2-heptyne; (b) 1-fluoro-4-methyl-1-hexyne.

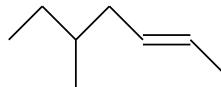


◆ STUDY CHECK

Name or formulate the following organic compounds:



(a)



(b)

►Answer: (a) *cis*-2-heptene; (b) 5-methyl-*trans*-2-heptene.

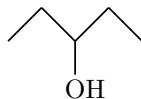
1.9 Naming of hydrocarbon derivatives

Hydrocarbon derivatives are organic molecules with a hydrocarbon base and extra functional groups. Examples are alcohols, ketones, aldehydes, or carboxylic acids. All those contain a hydrocarbon skeleton with some functional group. This section covers the naming rules for these chemicals.

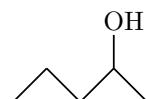
Alcohols Alcohols are systematically named from the parent hydrocarbon by replacing the *-e* (methane) ending with an *-ol* ending (methanol). A number should indicate the location of the alcohol group for alcohols with more than one carbon. For example, CH₃OH is called methanol and CH₃CH₂CH₂OH is called 1-propanol. Examples of five-carbon alcohols are:



pentanol

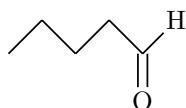


3-pentanol

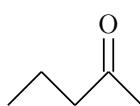


2-pentanol

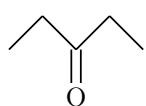
Ketones and aldehydes Aldehydes are systematically named from the parent hydrocarbon by replacing the *-e* (methane) ending with the *-al* ending (methanal). For example, CH₃COH is called ethanal. Ketones are systematically named from the parent hydrocarbon by replacing the *-e* (propane) ending with the *-one* ending (propanone). A number should indicate the location of the carboxyl group. For example, CH₃COCH₂CH₃ is called 2-butanone. Examples of aldehydes and ketones are:



pentanal



2-pentanone

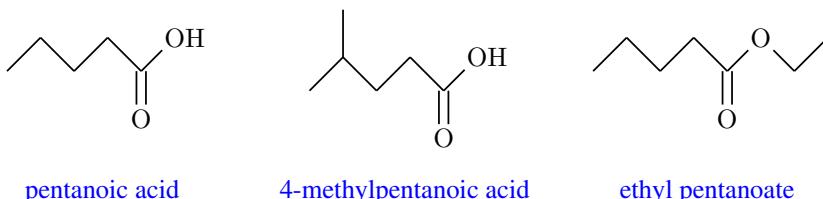


3-pentanone

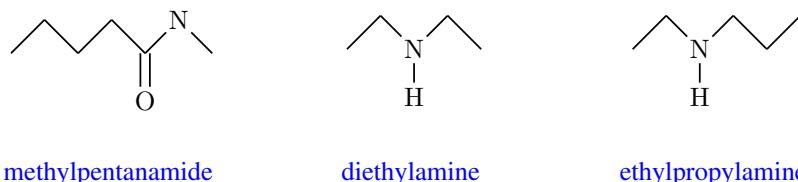
Carboxylic acids and esters Carboxylic acids are systematically named from the parent hydrocarbon by replacing the *-e* (methane) ending with an *-oic* ending and ending the name with the word acid (methanoic or formic acid). For example, CH₃COOH is called ethanoic (acetic) acid.



Esters, which result from the combination of an alcohol and a carboxylic acid, are systematically named from the parent hydrocarbon by replacing the *-ol* (methane) ending of the alcohol part with an *-yl* ending and the *-oic* ending the acid with an *-oate* ending, with a space between both words. For example, the ester resulting from the combination of methanol (CH_3OH) and methanoic acid (CH_3COOH) is called methylmethanoate ($\text{CH}_3\text{COOCH}_3$). Esters have also common names. As (CH_3COOH) is also called acetic acid, the corresponding ester from the combination with methanol can be called methyl acetate. Examples of carboxylic acids and esters are:

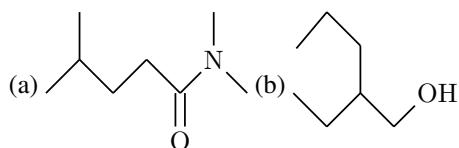


Amines and amides Amines are named used the name *amino* for the functional group and for example CH_3NH_2 is called aminomethane. Common name of amines end with the word *amine*. For example, CH_3NH_2 is commonly called methylamine and $(\text{CH}_3)_2\text{NH}$ is called dimethylamine. Amides, which result from the combination of an amine and a carboxylic acid, are systematically named from the parent hydrocarbon by replacing the *-amine* (methylamine) ending of the amine part with an *-yl* ending and the *-oic* ending the acid with an *-amide* ending, without space between both words. For example, the amide resulting from the combination of methylamine (CH_3NH_2) and methanoic acid (CH_3COOH) is called methylmethanamide ($\text{CH}_3\text{CONH}_2\text{CH}_3$). Examples of amines and amides are:



Sample Problem 19

Name the following hydrocarbon derivatives:



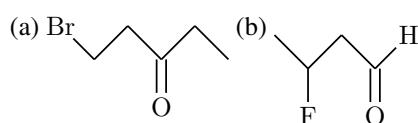
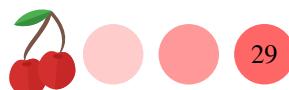
SOLUTION

(a) This amide results from combining dimethylamine and 4-methylpentanoic acid. Hence, the amide is called: dimethyl-4-methylpentanamide; (b) This is an alcohol with five carbons on its longest hydrocarbon chain. It has an ethyl substituent in carbon number two. Hence its name is 4-ethylpentanol.

►Answer: (a) dimethyl-4-methylpentanamide; (b) 4-ethylpentanol

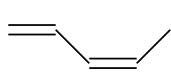
◆ STUDY CHECK

Name the following hydrocarbon derivatives:

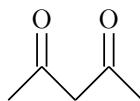


►Answer: (a) 1-bromo-3-pentanone; (b) 3-fluorobutanal

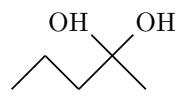
Double functional groups You must use the *di* prefix before the *ol* ending if a chemical has two alcohol groups, while preserving the *-ane* ending. For example, a pentane hydrocarbon with two alcohol groups on carbon 2 would be named 2,2-pentanediol. The same rule applies for other functional groups and even double or triple bonds:



cis-2,4-pentadiene



2,4-pentanedione

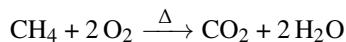


2,2-pentanediol

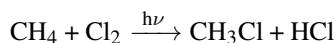
1.10 Reactivity of organic compounds

This section addressed some of the reactions undergone by organic compounds. For example, carboxylic acids can also react with alcohols producing esters, which are indeed organic salts, commonly known as soaps or gels. In this chapter, reducing or oxidation conditions will be represented as $\xrightarrow{\text{[reduc]}}$ and $\xrightarrow{\text{[ox]}}$, respectively, as many reagents can carry out oxidations or reductions.

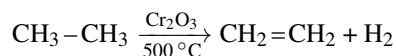
Hydrocarbons Alkanes are almost inert materials under normal conditions. They do not react with acids, bases, or oxidizing agents. This is because of the C-C and C-H strength. As such, alkanes are used in the manufacturing industry to produce plastics and lubricants. At high temperatures (Δ), they can undergo *combustion reactions* with oxygen.



Alkanes can also react with halogens undergoing *substitution reactions*, in which one or more hydrogen atoms of the alkane are replaced with a halogen. In this reaction, ultraviolet light $h\nu$ is needed to break down the halogen (e.g. Cl_2) producing very reactive halogen radical (e.g. Cl^\bullet): an atom with an unpaired electron.

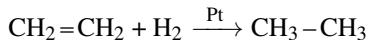


Halogenated alkanes have many uses. For example, $\text{CF}_x\text{Cl}_{4-x}$ are chlorofluorocarbons or freons. These chemicals were historically used in air conditioning systems and can present a threat to the ozone layer. Alkanes can also undergo *dehydrogenation reaction* producing alkenes as hydrogen atoms are removed by a reducing agent at high temperature:

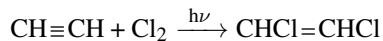




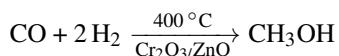
Alkenes and alkynes undergo *addition reactions* as hydrogen, or halogens can add to the multiple bonds, replacing a π bond with a σ bond. Alkenes can hydrogenate at normal temperature with the use of a Ni or Pt catalyst.



This reaction is involved in the manufacturing of solid shortenings from liquid, unsaturated fats. Similarly, halogens can add to a triple bond:



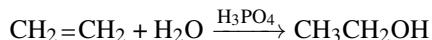
Alcohols There are a few relevant alcohols, both simple and complex alcohols. The simplest alcohol is called methanol, CH_3OH . It was originally called wood alcohol as it can be produced by heating wood in the absence of air. It is produced from the hydrogenation of carbon monoxide catalyzed by supported chromium(III) oxide:



Another important alcohol is ethanol $\text{CH}_3\text{CH}_2\text{OH}$, which is produced in the fermentation of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) catalyzed by yeast

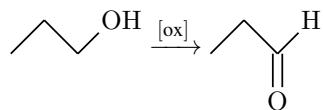


This reaction only proceeds until the alcohol concentration is 13%. After that point, yeast can not survive the high alcohol level and distilling is necessary to produce high-alcohol beverages. Ethanol (rubbing alcohol) can also be produced by means of the hydration of ethane catalyzed by phosphoric acid:

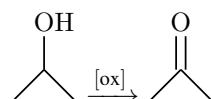


Finally, 1,2-ethanediol known as ethylene glycol is a toxic chemical used as car antifreeze.

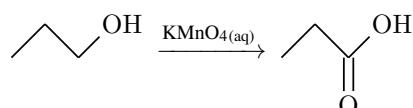
Aldehydes and ketones Ketones and aldehydes are products of the partial oxidation of complex alcohols with mild oxidants (e.g. Pyridinium chlorochromate (PCC), Dess-Martin periodinane (DMP), Swern oxidation reagent). In particular, primary alcohols produce aldehydes



and secondary alcohols produce ketones:

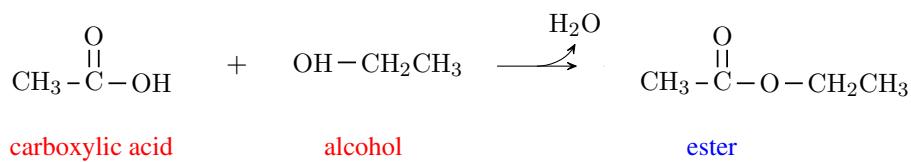


Carboxylic acids and esters Carboxylic acids are produced from the total oxidation of primary alcohols. One can use a strong oxidant such as potassium permanganate to carry out the oxidation:

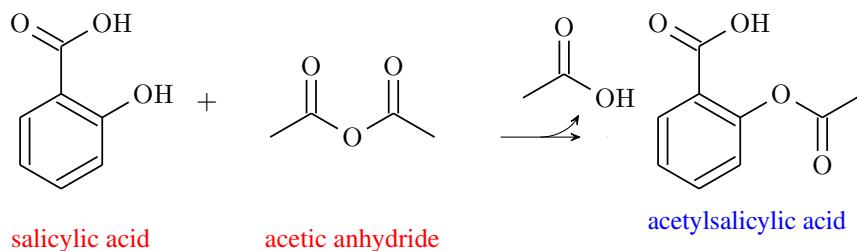




Carboxylic acids also react with alcohols to produce esters, for example:

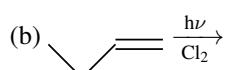


The synthesis of acetylsalicylic acid is a very important reaction between an acid and an alcohol as acetylsalicylic acid is also known as aspirin. Aspirin is currently the most widely used drug worldwide, being one of the most important pharmacological achievements of the twentieth century. Unfortunately, the acidic nature of acetylsalicylic acid makes it damaging for the stomach, where it is absorbed.



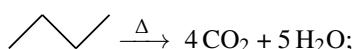
Sample Problem 20

Predict the product of the following reactions:

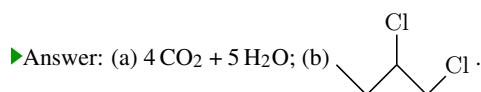
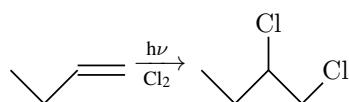


SOLUTION

(a) This is the combustion of butane reaction and the products are:

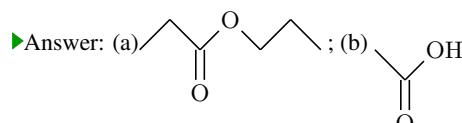
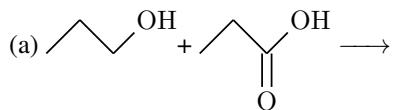


(b) This is the chlorination of butene that produces 1,2-dichlorobutane:



❖ STUDY CHECK

Predict the product of the following reactions:





CHAPTER 1

ALKANES

1.1 Classify the following chemicals in organic and inorganic. Give a rationale for your classification (a) KCl (b) C₂H₂ (c) C₄H₁₀ (d) FeO_(s) (e) C₆H₁₂ (f) PH₃ (g) H₂O

1.2 Working in groups, select an everyday-life object (e.g a spoon) and guess whether the materials that made this object are mostly organic or inorganic (e.g mostly inorganic). Without revealing your answer, present the material you selected to another team member and ask him or her to give you his or her point of view regarding whether the materials that made this object are mostly organic or inorganic.

1.3 Indicate the molecular formula of the following organic compounds: (a) ethane (b) butane

1.4 Indicate the molecular formula of the following organic compounds: (a) methane (b) decane

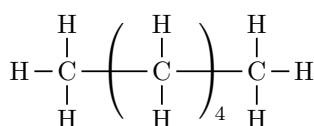
1.5 Name the following alkanes: (a) C₃H₈ (b) C₈H₁₈

1.6 Name the following alkanes: (a) C₅H₁₂ (b) C₉H₂₀

1.7 Write down the condensed formula of the following alkanes: (a) hexane (b) propane

1.8 Write down the expanded formula of the following alkanes: (a) pentane (b) decane

1.9 Write down the molecular formula for the chemical below:



1.10 Write down the molecular formula for the chemical below:



1.11 Write down the molecular formula for the chemical below:



1.12 Write down the expanded formula for the following chemical:

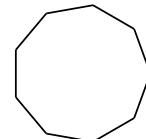


CYCLOALKANES

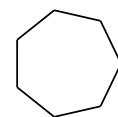
1.13 Indicate the molecular formula of the following cycloalkanes: (a) cyclobutane (b) cyclopentane

1.14 Indicate the molecular formula of the following cycloalkanes: (a) cyclopropane (b) cyclohexane

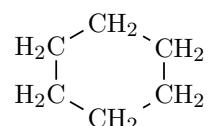
1.15 Name the following cycloalkane:



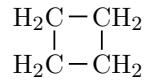
1.16 Name the following cycloalkane:



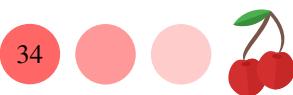
1.17 Name the following compound:



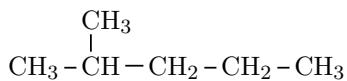
1.18 Name the following compound:



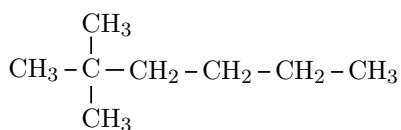
ALKANES WITH SUBSTITUENTS



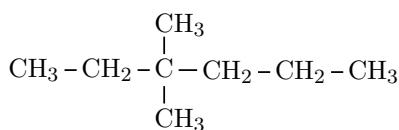
1.19 Name the following compound:



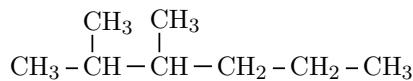
1.20 Name the following compound:



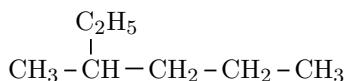
1.21 Name the following compound:



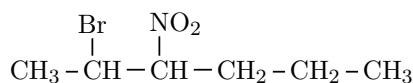
1.22 Give the name for the following compound:



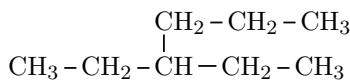
1.23 Give the name for the following compound:



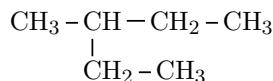
1.24 Give the name for the following compound:



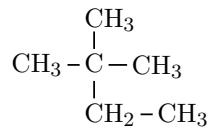
1.25 Give the name for the following compound:



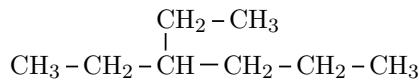
1.26 Give the name for the following compound:



1.27 Give the name for the following compound:

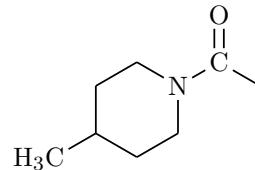


1.28 Give the name for the following compound:

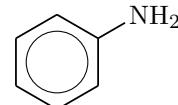


FUNCTIONAL GROUPS

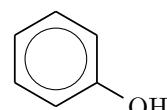
1.29 Identify the functional groups in the following molecule and give the molecular formula:



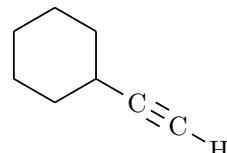
1.30 Identify the functional groups in the following molecule and give the molecular formula:



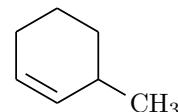
1.31 Identify the functional groups in the following molecule and give the molecular formula:



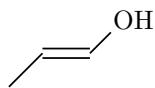
1.32 Identify the functional groups in the following molecule and give the molecular formula:



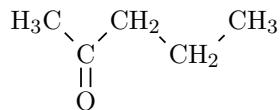
1.33 Identify the functional groups in the following molecule and give the molecular formula:



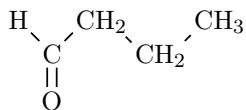
1.34 Identify the functional groups in the following molecule:



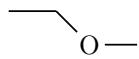
1.35 Identify the functional groups in the following molecule:



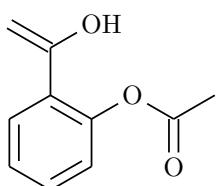
1.36 Identify the functional groups in the following molecule:



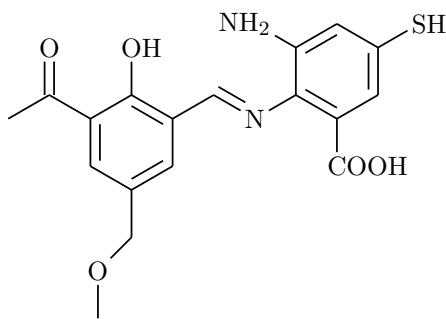
1.37 Identify the functional groups in the following molecule and give the molecular formula:



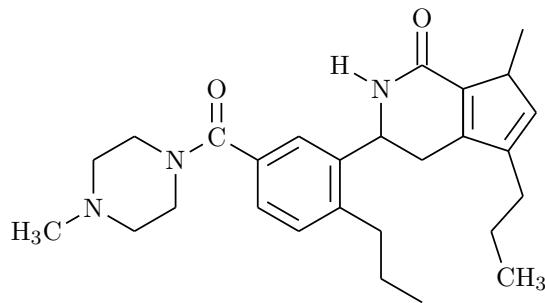
1.38 Identify the functional groups in the following molecule and give the molecular formula:



1.39 Identify the functional groups in the following molecule:

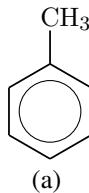


1.40 Identify the functional groups in the following molecule:

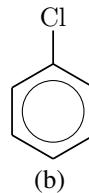


AROMATIC HYDROCARBONS

1.41 Name or formulate the following aromatic derivatives:

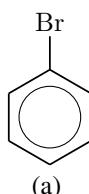


(a)

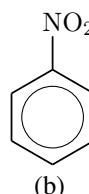


(b)

1.42 Name or formulate the following aromatic derivatives:



(a)

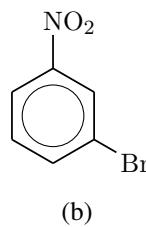


(b)

1.43 Name or formulate the following aromatic derivatives, using both the standard and the orto, meta and para nomenclature:

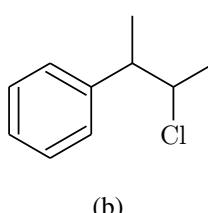


(a)

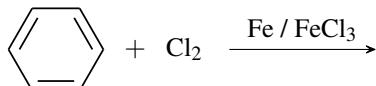


(b)

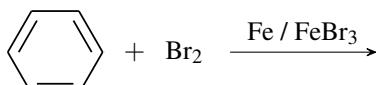
1.44 Name or formulate the following aromatic derivatives, using both the standard and the orto, meta and para nomenclature:



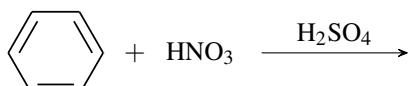
1.45 Predict the product of the following reactions:



1.46 Predict the product of the following reactions:



1.47 Predict the product of the following reactions:

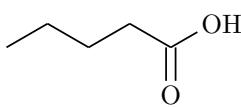


1.48 Predict the product of the following reactions:

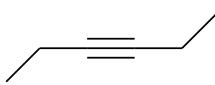


ALKENES AND ALKYNES

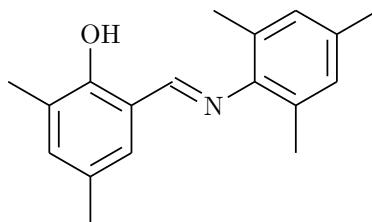
1.49 Indicate the number of σ and π bonds present in the following structure:



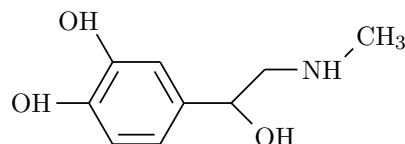
1.50 Indicate the number of σ and π bonds present in the following structure:



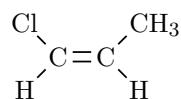
1.51 Indicate the number of σ and π bonds present in the following structure:



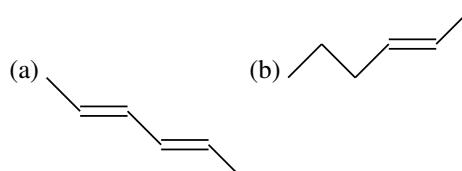
1.52 Indicate the number of σ and π bonds present in the following structure:



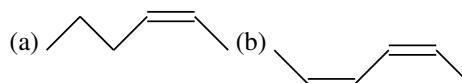
1.53 In the following pair of geometric isomers, indicate which is the cis and the trans isomer and name both.



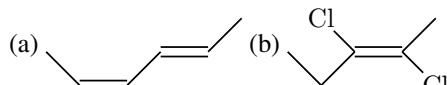
1.54 Name or formulate the following chemicals:



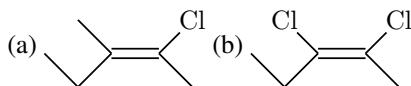
1.55 Name or formulate the following chemicals:



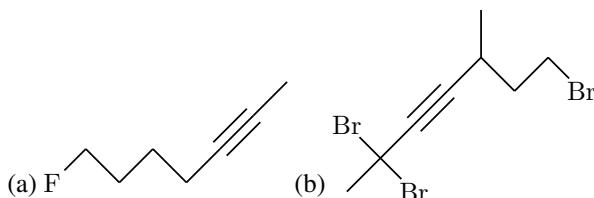
1.56 Name or formulate the following chemicals:



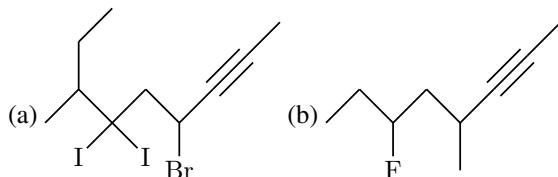
1.57 Name or formulate the following chemicals:



1.58 Name or formulate the following chemicals:

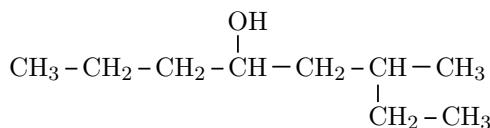


1.59 Name or formulate the following chemicals:

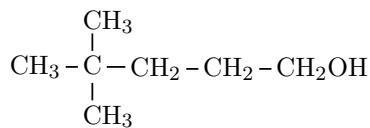


NAMING OF HYDROCARBON DERIVATIVES

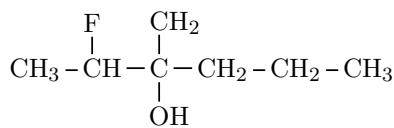
1.60 Name or formulate the following alcohol and label it as primary, secondary or tertiary:



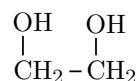
1.61 Name or formulate the following alcohol and label it as primary, secondary or tertiary:



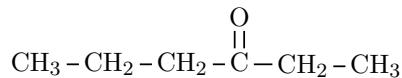
1.62 Name or formulate the following alcohol and label it as primary, secondary or tertiary:



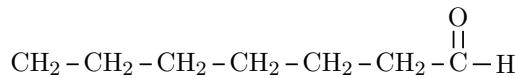
1.63 Name or formulate the following alcohol and label it as primary, secondary or tertiary:



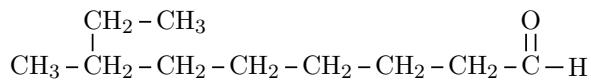
1.64 Name or formulate the following compound:



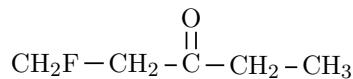
1.65 Name or formulate the following compound:



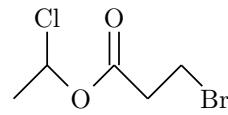
1.66 Name or formulate the following compound:



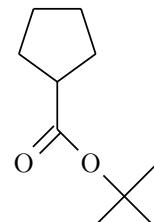
1.67 Name or formulate the following compound:



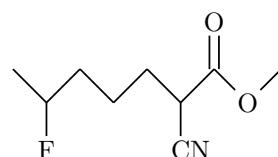
1.68 Name or formulate the following compound:



1.69 Name or formulate the following compound:

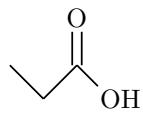


1.70 Name or formulate the following compound:

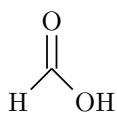




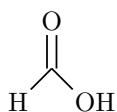
1.71 Name or formulate the following compound:



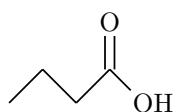
1.72 Name or formulate the following compound:



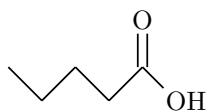
1.73 Name or formulate the following compound:



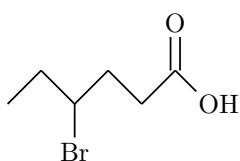
1.74 Name or formulate the following compound:



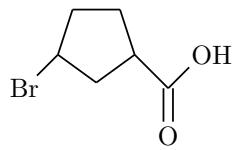
1.75 Name or formulate the following compound:



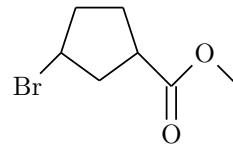
1.76 Name or formulate the following compound:



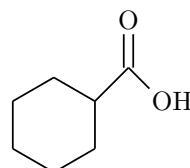
1.77 Name or formulate the following compound:



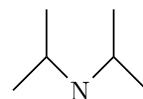
1.78 Name or formulate the following compound:



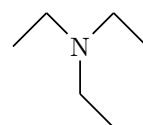
1.79 Name or formulate the following compound:



1.80 Name or formulate the following compound:



1.81 Name or formulate the following compound:



1.82 Name or formulate the following compound:



1.83 Name or formulate the following compound:





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Ch. 2. Physical properties of solutions

SOLUTIONS are homogeneous mixtures of a solvent and one or more solutes. In your everyday life, you will encounter numerous liquid-based mixtures, from recovery drinks to fancy champagne or plain milk. However, solutions are not just liquid-based as you can also find solid solutions such as an alloy, and even gas solutions such as the air. This chapter will cover the physical properties of solutions—boiling, freezing, and melting—and in particular, we will gain insight into the impact of the solute on the physical properties of the solvent. The chapter will also address the meaning of different concentration units and the relationship between them, as well as the properties of colloids—a special type of unstable mixture.

2.1 Solutions and colloids

A solution is a homogeneous mixture of a solvent and one or more solutes. Homogeneous means that a solution consists of only one visible phase (e.g. wine) in contrast to heterogeneous which means that a mixture would be composed of two or more distinct phases (e.g. a chocolate chip cookie).

Solutions in terms of phase and solubility One can find gas, liquid, or solid solutions depending on the final phase of the resulting solutions. For example, brass is a solid solution of copper and zinc and the air is a gaseous solution of oxygen, nitrogen, and other components. Solutions can be classified in terms of solubility. The solubility of a given solute in a solvent is the maximum amount of solute one can dissolve in a volume of solvent. Solutions can be saturated when they contain the maximum amount of solute one can fit, unsaturated when they contain less than the maximum amount of solute one can fit, or supersaturated when they contain more than a saturated solution. Supersaturated solutions tend to be unstable and the solute tends to eventually precipitate. Table 2.1 reports different types of solutions with examples.

Table 2.1 Types of solutions

Solute	Solvent	Solution state	Example
Gas	Gas	Gas	Air
Gas	Liquid	Liquid	Club soda
Gas	Solid	Solid	H ₂ in Pd
Liquid	Liquid	Liquid	Acetone in water
Liquid	Solid	Solid	Easy light charcoal
Solid	Liquid	Liquid	Saltwater
Solid	Solid	Solid	Brass



Table 2.1 reports different types of solutions with examples.

Solutions In solutions, the solute particles are dispersed evenly throughout the solvent giving homogeneous mixtures. As such, in a solution such as seawater, the solute cannot be visually distinguished from the solvent. The mixture appears transparent even when it may have a certain color. The solute particles are so small that they can go through filters and membranes.

Suspensions Suspensions are heterogeneous mixtures. The particles of a suspension are so large that they can often be visually seen and they can be trapped using filters and membranes. Because of its weight, suspended particles tend to segregate and settle out on the bottom of suspensions. Examples of suspensions are antacid mixtures or liquid penicillin (see Figure 2.1).

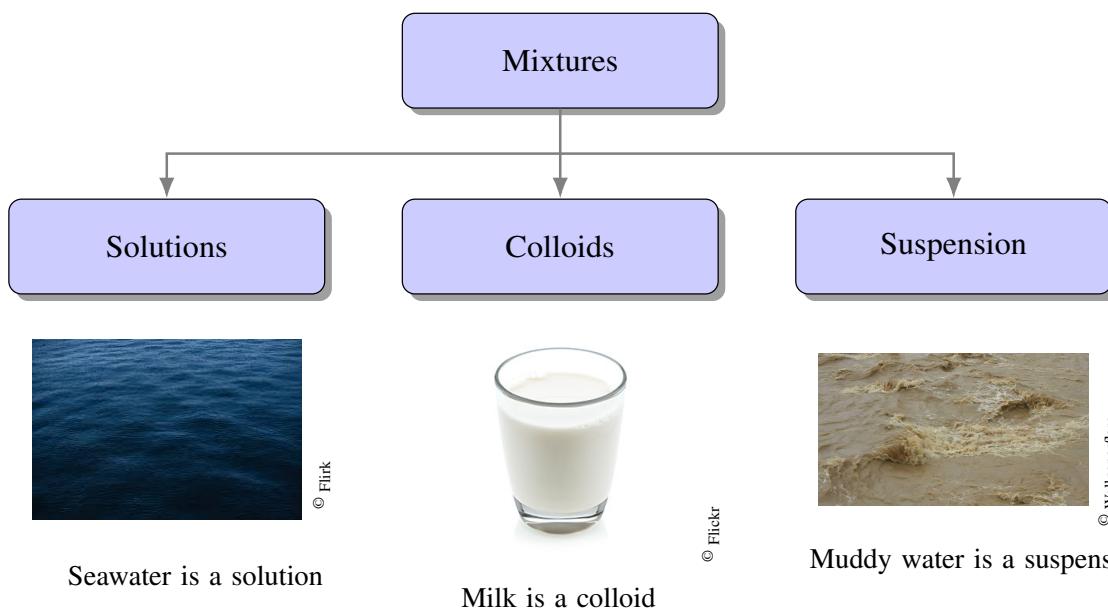
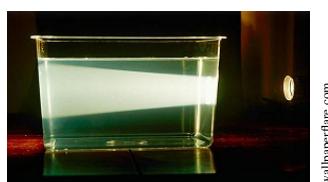


Figure 2.1 Classification of the mixtures

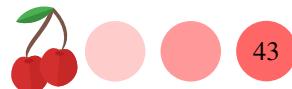
▼The Tyndall effect of a liquid



▼The Tyndall effect of a gas



Colloids We have that solutions are homogeneous mixtures in the form of only one visible phase. If we add an ionic solute to a solvent, the solute particles would break down into ions and these ions would be solvated by the solvent molecules. As such, the solute in solution exists in a different state than the solid solute. We also have that a heterogeneous mixture would result from mixing sand and water. The particles of sand will suspend on the liquid but eventually, they will deposit on the bottom of the container. Between homogeneous and heterogeneous mixtures we have colloids or *colloidal dispersions*. Colloids are special types of homogeneous mixtures. Colloids are suspensions of two components that are indeed immiscible in a non-homogeneous way. Think for example of milk, which is a colloid containing small particles of fat and protein suspended in a liquid. The particles of fat are called the dispersed phase and the liquid matrix is called the dispersing medium. The suspended particles of a colloid are larger than the particles of a normal homogeneous solution. Also, and perhaps more importantly, the particles of a colloid can be separated and for example, by adding a few drops of lemon to a glass of milk you will be able to separate both the fat and the liquid. In contrast, solutions are made of inseparable components and the only way to separate the solvent and solute in a solution is by boiling it. Colloids are named depending on the nature of the dispersed and dispersant phases: aerosols (e.g. fog), foams (e.g. whipped cream), emulsions (e.g. mayonnaise), sols (e.g. milk of magnesia), and gels (e.g. jelly) are just a few examples of different types of colloids. How to differentiate a solution and a colloid? The Tyndall effect exposes the differences between solutions and



colloids. A focused beam of light can easily pass through a solution as the particles of the solute are smaller than the light wavelength. Differently, when a colloid is exposed to the same light it will be scattered by the dispersed phase of the colloid which has a larger size. Therefore, you will be able to see the beam passing through the colloid. An example of the Tyndall effect is the scattering of light from the car headlights on a foggy day. Many factors stabilize a colloid, allowing two very different phases to coexist. In particular, electrostatic repulsions are known to play a key role in colloidal stability, hence avoiding coagulation. Colloidal particles are electrically neutral. Still, when applying an electrical field experiment demonstrates that all particles migrate towards the same electrode. Hence, all particles seem to have the same electrical charge. How can these particles coexist together? Experiments indicate that colloidal particles can be surrounded by several layers of electrically charged particles. These layers can impede coagulation. For example, colloidal particles can surround themselves with a layer of positive particles, and at the same time, this positive layer surrounds with another layer of negative charges. This series of external layers of charged particles exert repulsion among colloidal particles avoiding coagulation. Colloids can be destructed in a process called *coagulation*, which can be accomplished either by heating or by adding an electrolyte. On one hand, heating increases the average speed of colloidal particles which helps coagulation. On the other hand, adding electrolytes impacts the charged, protective layer that stabilizes colloidal particles, hence inducing coagulation (e.g. think what happens when you add lemon juice to a glass of milk). An example of colloid coagulation happens when a river reaches the salty ocean depositing. Sea electrolytes help produce clay particles. Similarly, electrostatic precipitators improve the air quality of industrialized cities by removing soot from smoke. Table 2.2 reports all different types of colloids one can encounter with examples for each of them.

Table 2.2 Types of colloids

Dispersing medium	Dispersed medium	name	Example
Gas	Liquid	Aerosol	Fog
Gas	Solid	Aerosol	Smoke
Liquid	Gas	Foam	Whipped cream
Liquid	Liquid	Emulsion	Mayonnaise
Liquid	Solid	Sol	Milk of magnesia
Solid	Gas	Foam	Styrofoam
Solid	Liquid	Gel	jelly
Solid	Solid	Solid sol	alloys

2.2 Units of concentration

There are numerous units to express concentration. Here, we will cover molarity, molality, percent of the mass, and mole fraction. We will also review the concept of density under a new light. More importantly, we will also learn how to interchange different concentration units.

The concept of solution Mind that solution results of adding a solute to a solvent.

$$\text{solution} = \text{solvent} + \text{solute} \quad (2.1)$$



Molarity, M Molarity, M, is defined as the moles of solute divided by the liters of solution. In this chapter, it is critical to specify the nature of the moles and the volume, as one can think of moles of solute or moles of solvent, as well as liters of solution or liters of solvent.

$$M = \frac{\text{moles of solute}}{\text{liters of solution}} \quad (2.2)$$

For example, if we mix 0.4 moles of NaCl and we fill the beaker until we reach a 100mL (0.1L) mark, the molarity of the solution will be 4M.

Mole fraction, χ The mole fraction of a solute is the ratio of the moles of solute over the moles of solution—that is moles of solute plus the moles of solvent.

$$\chi = \frac{\text{moles of solute}}{\text{moles of solute} + \text{moles of solvent}} \quad (2.3)$$

For example, if we mix 0.4 moles of NaCl and 0.6 moles of water, the mole fraction of solute will be 0.4. We can define a similar mole fraction of solvent and both, the mole fraction of solvent and solute should add up to 1.

Percent by mass, $\%_m$ The percent by mass (or percent by weight) of a solute is the ratio of the grams of solute over the grams of solution—that is grams of solute plus the grams of solvent—multiplied by 100.

$$\%_m = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100 \quad (2.4)$$

There is an equivalent concentration measure to the solute percent by mass but based on volume called the solute percent by volume. $\%_v$ is calculated as the ratio of the solute volume and the solution volume in percent form. This percentage is useful when the solute and solvent are both liquids and can be measured in terms of volume. For example, if we mix 5 grams of NaCl and 100 grams of water, the percent by mass of solute will be 5%. We can define a similar percent by mass of solvent and both, the percent by mass of solvent and solute should add up to 100.

Molality, m The molality of a solution is the number of moles of solute per kilogram of solvent.

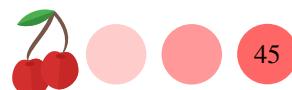
$$m = \frac{\text{moles of solute}}{\text{kg of solvent}} \quad (2.5)$$

For example, if we mix 5 grams of NaCl and 100 grams (0.1 kg) of water, the molality of the solution will be 50m. The properties of molarity and molality are different. In particular, molarity (M) depends on temperature. As the volume of a liquid slightly increases with temperature, molarity decreases with temperature. Differently, molality (m) is temperature-independent.

Density of a solution, d The density of a solution—often expressed in g/mL—is the ratio of the grams of solution and the mL of solution.

$$d = \frac{\text{grams of solution}}{\text{mL of solution}} \quad (2.6)$$

Density is used to convert the mass of solution into the volume of solution, or the opposite. In the case of pure water, the density of water is 1g/mL that is the mass in grams of water equals its volume in mL.



Normality of a solution, N Normality is another way to express concentration. This unit is normally used for acid, bases, oxidizing, or reducing agents. *Normality* is defined as the number of equivalents per liter of solution and is related to molarity

$$N = n_{eq} \cdot M$$

where M is molarity and n_{eq} is the number of equivalents. Still, the definition of an equivalent changes based on the species in solution. In an acid-base reagent, the number of equivalents is the number of protons or hydroxyls an acid or base can produce. For example, for H_2SO_4 n_{eq} is 2 and for H_3PO_4 n_{eq} is 3. Therefore, a 1M solution of H_2SO_4 will be 2 normal. For redox reactions, the equivalent is defined as the quantity of redox agents that can exchange one mole of electrons. For example, permanganate exchanges $5e^-$ during redox reaction based in the reaction below: $MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$ therefore 1M solution of $KMnO_4$ will be 5 normal. When dealing with normality, historically one speaks about the *equivalent mass* or equivalent weight of a reagent, defined as the molar mass divided by the number of equivalents.

Sample Problem 21

A solution is prepared by mixing 1g of NaCl (MW=59g/mol) in 100g of water to give a final volume of 120mL. Calculate: (a) The percent by mass of solute (b) The mole fraction of solute (c) The molarity of the solution (d) The molality of the solution (e) The density of the solution

SOLUTION

In this example it is convenient to recall all the parameters we have in terms of solute, solvent and solution. Regarding the solute, we have the mass of solute ($m_{solute} = 1g$), and the moles of solute ($n_{solute} = 1g \times \frac{1\text{ mol of NaCl}}{59\text{ g of NaCl}} = 0.017\text{ moles}$). Regarding the solvent, we have the mass of solvent ($m_{solvent} = 100\text{ g} = 0.1\text{ kg}$), the moles of water ($n_{solvent} = 100\text{ g} \times \frac{1\text{ mol of H}_2\text{O}}{18\text{ g of H}_2\text{O}} = 5.6\text{ moles}$), and the volume of solvent ($v_{solvent} = 100\text{ mL}$). Mind that in the case of water, very normally, its mass in grams equals to its volume in mL. In terms of solution, we can compute the mass of solution ($m_{solution} = 1 + 100 = 101\text{ g}$), the moles of solution ($n_{solution} = 0.017 + 5.6 = 5.617\text{ moles}$), and the volume of solution ($v_{solution} = 120\text{ mL} = 0.12\text{ L}$). Now, we are ready to compute all concentration units of the solution. The percent by mass of solute is the ratio between the mass of solute and the mass of solution times 100:

$$\%_m = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100 = \frac{1\text{ g of solute}}{101\text{ g of solution}} \times 100 = 0.99\%$$

The mole fraction is the ration between the moles of solute and moles of solution:

$$\chi = \frac{\text{moles of solute}}{\text{moles of solute} + \text{moles of solvent}} = \frac{0.017\text{ moles of solute}}{5.617\text{ moles of solution}} = 3.02 \times 10^{-3}$$

The molarity of the solution is the ration between the moles of solute and the liters of solution:

$$M = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{5.617\text{ moles of solute}}{0.12\text{ L of solution}} = 46.8\text{ M}$$

The molality is the ration between the moles of solute and the kg of solvent:

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}} = \frac{0.017\text{ moles of solute}}{0.1\text{ kg of solvent}} = 0.17\text{ m}$$

Finally, density of the solution is the ration of the grams of solution and the volume of solution:

$$d = \frac{\text{grams of solution}}{\text{mL of solution}} = \frac{101\text{ g of solution}}{120\text{ mL of solution}} = 0.84\text{ g/mL}$$



❖ STUDY CHECK

A solution is prepared by mixing 1g of glucose (MW=180g/mol) in 50g of water to give a final volume of 100mL. Calculate: (a) The percent by mass of solute (b) The mole fraction of solute (c) The molarity of the solution (d) The molality of the solution (e) The density of the solution

►Answer: (a) 1.96% (b) 2×10^{-3} (c) 0.05M (d) 0.11m (e) 0.51g/mL

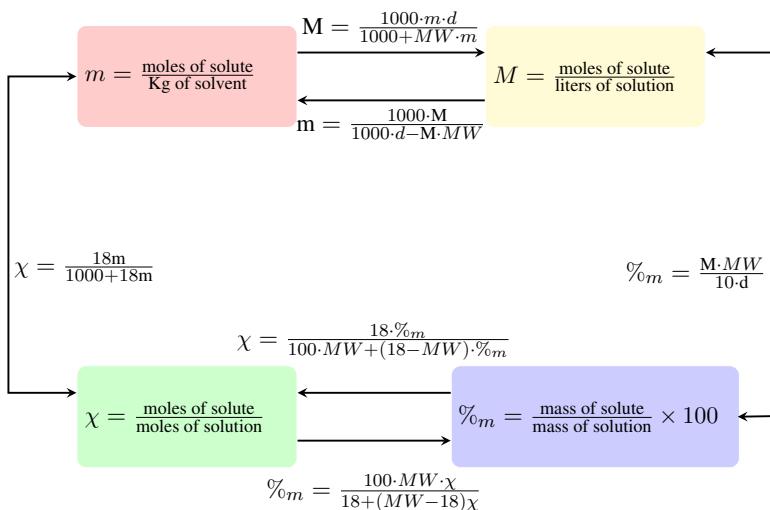


Figure 2.3 Diagram displaying the set of formulas used to relate, from left to right, molality with molarity, mass percent of solute, and mole fraction. In some of these formulas, the solution density d (in g/mL) is needed as well as the molar mass of the solute (MW). The solvent in all these equations is assumed to be water and hence the 18 value in some of the formulas.

2.3 Relating units of concentration

When you prepare a solution you normally weigh a given amount of solute and add some volume of solvent. That will give you a given concentration that you can compute in terms of for example molarity. Often, you encounter a solution already prepared, for example, a 2M solution and you need to know a different type of concentration unit, such as its molality. That is why relating concentration units is important. In the next sections, we will cover how the different concentration units are related. Figure displays all formulas used to relate different units of concentration.

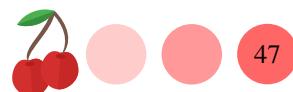
Relating molarity and molality, $M \longleftrightarrow m$ We can use the following formula to relate Molarity and molality

$$m = \frac{1000 \cdot M}{1000 \cdot d - M \cdot MW} \quad \text{or} \quad M = \frac{1000 \cdot m \cdot d}{1000 + MW \cdot m} \quad (2.7)$$

where:

M is the molarity of the solution

m is the molality of the solution



d is the density of the solution

MW is the molecular weight of the solute

Mind that this formula only works for water as a solvent and uses 1g/mL as the density of water.

Relating molarity and the percent by mass of solute, $M \longleftrightarrow \%_m$

We can use the following formula to relate Molarity and percent by mass of solute

$$M = \frac{\%_m \cdot d \cdot 10}{MW} \quad \text{or} \quad \%_m = \frac{M \cdot MW}{10 \cdot d} \quad (2.8)$$

where:

M is the molarity of the solution

$\%_m$ is the percent by mass of solute

d is the density of the solution

MW is the molecular weight of the solute

Relating percent by mass and mole fraction of solute, $\chi \longleftrightarrow \%_m$

We can use the following formula to relate Molarity and percent by mass of solute

$$\chi = \frac{18 \cdot \%_m}{100 \cdot MW + (18 - MW) \cdot \%_m} \quad \text{or} \quad \%_m = \frac{100 \cdot MW \cdot \chi}{18 + (MW - 18)\chi} \quad (2.9)$$

where:

χ is the solute mole fraction

$\%_m$ is the solute percent by mass

MW is the molecular weight of the solute

18 is the molar weight of water

Mind that this formula only works for water as a solvent. If using a different solvent you just need to update the 18 value and use the molar weight of the new solvent instead.

Sample Problem 22

A 2M NaCl (MW=59g/mol) solution has a density of 1.2g/mL. Calculate:

- (a) The molality of the solution
- (b) The mass percent of solute
- (c) The mole fraction of solute

SOLUTION

We will first convert molarity into molality using density and the molar mass of the solute.

$$m = \frac{1000 \cdot M}{1000 \cdot d - M \cdot MW} = \frac{1000 \cdot 2}{1000 \cdot 1.2 - 2 \cdot 59} = 1.84m$$

We will then convert molality into mass percent:

$$\%_m = \frac{M \cdot MW}{10 \cdot d} = \frac{2 \cdot 59}{10 \cdot 1.2} = 9.83\%$$

We will finally convert the mass percent of solute into mole fraction:

$$\chi = \frac{18 \cdot \%_m}{100 \cdot MW + (18 - MW) \cdot \%_m} = \frac{18 \cdot 9.83\%}{100 \cdot 59 + (18 - 59) \cdot 9.83\%} = 0.03$$

❖ STUDY CHECK

For a 0.11m glucose (MW=180g/mol) solution with density 0.51g/mL, calculate:



- (a) The percent by mass of solute (b) The mole fraction of solute (c) The molarity of the solution

►Answer: (a) 1.76% (b) 1.78×10^{-3} (c) 0.05M

Compute molecular masses from molality and molarity In numerous applications, one needs to compute the molecular weight of a solute using a given molality or molarity. It is useful to remember that the molality of a solution is related to the moles of solute and the kilograms of solvent, in contrast to the molarity of a solution that depends on the liters of solution. When we prepare a solution we normally know the mass of the solute used and the mass of the solvent or the volume of the solution. We can compute the molar mass of the solute using:

$$MW = \frac{\text{g of solute}}{\text{m} \cdot \text{kg of solvent}} \quad \text{or} \quad MW = \frac{\text{g of solute}}{\text{M} \cdot \text{L of solution}} \quad (2.10)$$

where:

MW is the molar mass of the solute

g of solute is the mass of solute

kg of solvent is the mass of solvent

L of solution is the volume of solution

m is the molality of the solution

Sample Problem 23

We prepare a solution by weighting 5g of solute and adding 10g of solvent in order to prepare a 0.1m solution. Calculate the molar mass of the solute.

SOLUTION

In this example, we are given molality ($m=0.1$), the mass of solute ($m_{\text{solute}}=5\text{g}$) and the mass of solvent ($m_{\text{solvent}}=0.01\text{kg}$). In order to calculate the molar mass of a solute by means of molality we have that:

$$MW = \frac{\text{g of solute}}{\text{m} \cdot \text{kg of solvent}} = \frac{5}{0.1 \cdot 0.01} = 5000\text{g/mol}$$

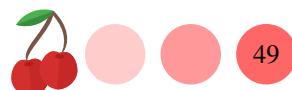
◆ STUDY CHECK

We prepare a solution by weighting 10g of solute and adding liquid until 100mL of solution in order to prepare a 2M solution. Calculate the molar mass of the solute.

►Answer: 50g/mol

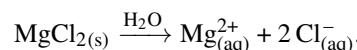
2.4 Solutions of electrolytes and effective solute particles

Chemicals can be classified based on their electrolyte character in strong electrolytes and non-electrolytes. Non-electrolytes do not dissociate in solution so each non-electrolyte molecule becomes a solute particle. Differently, strong electrolytes dissociate in solution

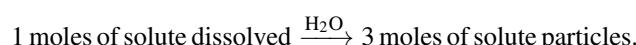


so that each strong electrolyte molecule gives more than one solute particle. This section covers the concept of effective solute particles and the idea of Van't Hoff factor i that relates the amount of moles of solute dissolved and the moles of solute particles.

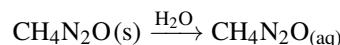
Strong electrolytes Strong electrolytes completely dissociate in water. Hence, in a solution of a strong electrolyte, you will mostly contain ions. Strong electrolytes are typically ionic compounds such as MgCl₂ or NaCl (table salt). We represent the dissociation of a strong electrolyte with a single arrow, meaning that the reaction proceeds to completion. For the example below, in the solution, we will only have ions (Mg²⁺_(aq) + 2 Cl⁻_(aq)) and not magnesium chloride molecules (MgCl_{2(s)}):



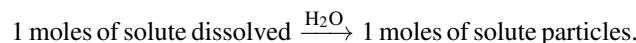
For this electrolyte, in terms of solute dissolved and solute particles, we have that one mole of solute dissolved will give three moles of solute particles:



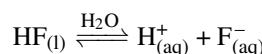
Nonelectrolytes and weak electrolytes Nonelectrolytes do not dissociate in water. Hence a solution of a nonelectrolyte will mostly contain molecules of that electrolyte and not ions. Examples of nonelectrolytes are carbon-based chemicals such as methanol, ethanol, urea, or sucrose. The dissociation of urea for example CH₄N₂O proceeds as:



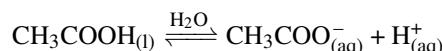
For this electrolyte, in terms of solute dissolved and solute particles, we have that one mole of solute dissolved gives one mole of solute particle:



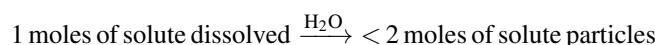
Weak electrolytes partially dissociate in water, and on paper, this is indicated using a chemical reaction with a double arrow. Hence in a solution of a weak electrolyte, you will have both ions as well as molecules of the electrolyte. Examples of weak electrolytes are hydrofluoric acid, water, ammonia, or acetic acid. The dissociation of hydrofluoric acid (HF) proceeds as:



Acetic acid (CH₃COOH) is an important weak electrolyte and its dissociation proceeds somehow in a peculiar way:



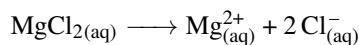
For this electrolyte, in terms of solute dissolved and solute particles, we have that one mole of solute dissolved will give less than two moles of solute particles:



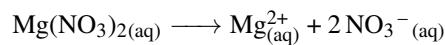
Breaking down electrolytes into ions Electrolytes—in particular strong electrolytes—dissociate producing ions. This way, a solution of for example NaCl does not contain NaCl molecules but Na⁺_(aq) cations and Cl⁻_(aq) anions. Hence it is important



to correctly break down electrolytes into ions. To do this, you need to revert the combination of ions that produce a given chemical while making sure the charges are balanced. For example, let us break magnesium chloride $MgCl_{2(aq)}$ into ions. This is a strong electrolyte formed by magnesium cations and chloride anions. The valence of magnesium is +II and the valence of chlorine is -I. The $MgCl_2$ formula also tells us we have one magnesium and two chlorines. The overall process is:



Another example is magnesium nitrate $Mg(NO_3)_2$. This strong electrolyte—as this is an ionic salt—is made of lithium with valence +I and nitrate with valence -I. The formula indicates we have one $Mg_{(aq)}^{2+}$ and two $NO_3^-_{(aq)}$. Hence:



Sample Problem 24

Break down the following chemicals into ions, if possible:

Chemical	Particles in solution
$K_2CrO_4(aq)$	
$Ba(NO_3)_2(aq)$	
$BaCrO_4(s)$	
$KNO_3(aq)$	

SOLUTION

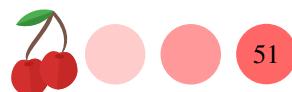
We can only break down into ions ionic compounds and oxosalts that are not solid. From the list of chemicals in the example, we will not be able to break down $BaCrO_4(s)$ into ions as it is a solid. From the other chemicals, $K_2CrO_4(aq)$ is named potassium chromate and contains $2K_{(aq)}^+$ and $CrO_4^{2-}_{(aq)}$ ions. Barium nitrate— $Ba(NO_3)_2(aq)$ —will produce $Ba_{(aq)}^{2+}$ and $2NO_3^-_{(aq)}$. Finally, potassium nitrate— $KNO_3(aq)$ —will produce $K_{(aq)}^+$ and $NO_3^-_{(aq)}$. In the table:

Chemical	Particles in solution
$K_2CrO_4(aq)$	$2K_{(aq)}^+ + CrO_4^{2-}_{(aq)}$
$Ba(NO_3)_2(aq)$	$Ba_{(aq)}^{2+} + 2NO_3^-_{(aq)}$
$BaCrO_4(s)$	$BaCrO_4(s)$
$KNO_3(aq)$	$K_{(aq)}^+ + NO_3^-_{(aq)}$

❖ STUDY CHECK

Break down the following chemicals into ions, if possible: $H_2O(l)$, $NH_3(l)$, $AgNO_3(aq)$.

►Answer: $H_2O(l)$, $NH_3(l)$, $Ag_{(aq)}^+$, $NO_3^-_{(aq)}$.

**Table 2.3 Expected and observed Van't Hoff factors for different concentrations.**

Solute	i^{Observed}			i^{Expected}	$i^{\text{Observed}} / i^{\text{Expected}} * 100$		
	0.1m	0.01m	0.001m		0.1m	0.01m	0.001m
C ₆ H ₁₂ O ₆	1.00	1.00	1.00	1.00	100%	100%	100%
NaCl	1.87	1.94	1.97	2.00	93.5%	97.0%	98.5%
K ₂ SO ₄	2.32	2.70	2.84	3.00	77.3%	90.0%	64.6%
MgSO ₄	1.21	1.53	1.82	2.00	60.5%	76.5%	91.0%

Table 2.3 reports observed and expected i values for different salts and different concentrations.

Van't Hoff factor i This factor for a given electrolyte is related the number of dissolved particles and the number of solute particles:

$$i = \frac{\text{moles of solute particles}}{\text{moles of dissolved particles}} \quad (2.11)$$

For example, all non-electrolytes produce only a single solute particle, as they do not break down in solution and therefore for all non-electrolytes i is 1. Differently, the i values for a strong electrolyte depend on the salt stoichiometry. For example, for NaCl i is two, as one mole of salt produces two moles of ions, and for CaCl₂ i is 3, as one mole of calcium fluoride produces three moles of ions, overall. It is important to notice the research has found that the Van't Hoff factor indeed depends on the concentration of the salt and for large concentrations the expected i value not always correspond to the observed value, due to the formation of ion pairs, pairs of ions that associate on solution reducing the effective ion concentration.

At low concentrations, the effect of ion pairs is less pronounced and the expected value tends to resemble the observed value: $i^{\text{Expected}} \approx i^{\text{Observed}}$. The Van't Hoff factor is reported for strong electrolytes. A property called percent dissociation of an electrolyte, α , is helpful to describe the dissociation of weak electrolytes. Strong electrolytes dissociate completely and hence the effective concentration of ions is the same as the nominal concentration of solute particles. Weak electrolytes, on the other hand, do not completely dissociate in solution and the effective concentration of solute particles tends to be smaller than the nominal concentration. We have that:

$$\alpha = \frac{c^{\text{effective}}}{c^{\text{Nominal}}} \times 100 \quad (2.12)$$

Percent dissociation is zero for nonelectrolytes as no ions are produced and hence the effective ion concentration is null. Finally, percent dissociation for strong electrolytes is 100% as the nominal and effective ion concentrations are the same. Note that the percent dissociation can change with concentration. Table 2.3 reports observed and expected i values for different salts and different concentrations.

Sample Problem 25

A solution that is 0.02M in HF has a effective ion concentration of 0.015M. Calculate the percent dissociation of the electrolyte.

SOLUTION

The percent dissociation, α , is the ration between the effective ion concentration (the amount of ions in solution) and the nominal concentration (the amount of



▼ Streets are salted to reduce the freezing point of ice



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▼ A solution of ethyleneglycol is used as antifreeze in cars



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▼ Any salt would reduce the intensity of a perfume



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▼ Salting fish kills bacteria by removing water inside its cells



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▼ Adding salt to boiling water increases the boiling point of water



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solute added to the solution). We have that the nominal concentration is 0.02M and the effective concentration is 0.015M. As usual for weak electrolytes, the effective concentration is lower than the nominal one as some molecules did not dissociate. We can calculate the percent dissociation:

$$\alpha = \frac{c^{\text{effective}}}{c^{\text{Nominal}}} \times 100 = \frac{0.015}{0.02} \times 100 = 75\%$$

The results indicate that only the 75% of the solute dissociate in solution.

◆ STUDY CHECK

The percent dissociation of a 0.1M weak electrolyte is 40%. Calculate the effective concentration of the electrolyte.

► Answer: 0.04M

2.5 Colligative properties

Colligative properties of solutions are properties that depend on the concentration of solute but not on the nature of this solute. In the following, we will elaborate more on the idea of colligative properties. Indeed, there are four colligative properties of the solutions: the freezing point decrease, the boiling point increase, the osmotic pressure, and the vapor pressure. Mind that these are all properties of solutions and not of pure substances. Figure 2.3 displays the effect of the solute concentration on the phase diagram of water.

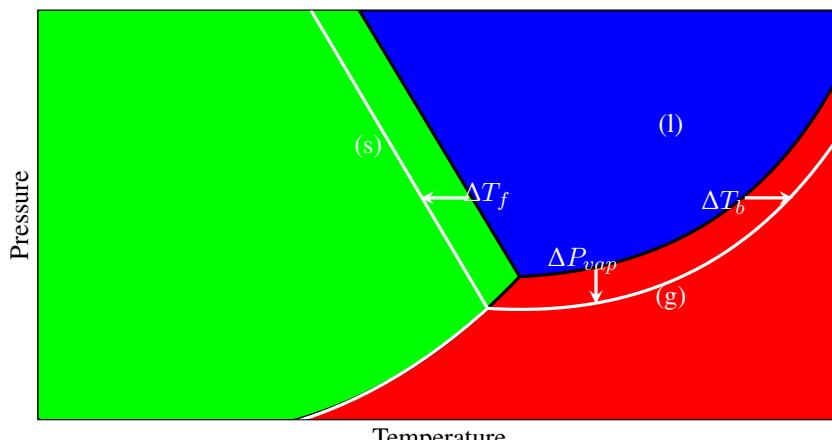


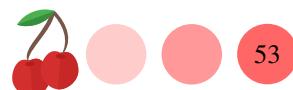
Figure 2.3 Effect of the solute concentration on the phase diagram of water

Boiling point elevation Solutions are made of a solute dissolved in a solvent.

Pure solvents have a specific boiling point. When we made a solution, the solution boils at a different temperature than the pure solvent, and in particular, a solution boils at a higher temperature than the solvent. This effect is called the boiling point elevation of a solution in comparison with the pure solvent. The boiling point elevation does not depend on the nature of the solute and only depends on the molality (m) of the solution using the following formula:

$$T_b^{\text{solution}} = T_b^{\text{solvent}} + k_b \cdot i \cdot m \quad \text{or} \quad \Delta T_b = k_b \cdot i \cdot m \quad (2.13)$$

where:



T_b^{solution} is the boiling point of the solution

T_b^{solvent} is the boiling point of the pure solvent

k_b is called molal boiling point elevation constant in units of $^{\circ}\text{C}/m$

m is the molality of the solution

i is van't Hoff factor of the solute

ΔT_b is the boiling point increase, that is $T_b^{\text{solution}} - T_b^{\text{solvent}}$

$i \cdot m$ is the effective concentration of solute particles

Mind that $i \cdot m$ represents the effective solute-particle concentration in the solution. For the case of NaCl i is 2 as every NaCl unit dissociates producing 2 ions or two solute-particles. The value of k_b depends on the solvent and in general boiling point increases tend to be modest. For example, a water-based solution containing NaCl boils at a higher temperature than pure water which boils at 100°C . A 1m NaCl solution boils at 101.04°C which is one degree higher than pure water. The boiling point elevation formula establishes a linear relationship between the boiling point of a solution and molality in which the slope of the relationship is positive and gives the value of k_b , the x variable is m and the y variable is T_b^{solution} . In other words, by plotting T_b^{solution} vs. m we should obtain a straight line with a slope that equals to k_b and an intercept equals to T_b^{solvent} .

Freezing point depression A pure solvent freezes at a specific temperature and for example, water freezes at 0°C . Solutions freeze at a lower temperature than the pure solvent. We call this effect the freezing point depression. This decrease in the freezing point depends only on the molality of the solution and not on the solute. The freezing point depression—or decrease—is given by the formula:

$$T_f^{\text{solution}} = T_f^{\text{solvent}} - k_f \cdot i \cdot m \quad \text{or} \quad \Delta T_f = -k_f \cdot i \cdot m \quad (2.14)$$

where:

T_f^{solution} is the freezing point of the solution

T_f^{solvent} is the freezing point of the pure solvent

k_f is called molal freezing point depression constant in units of $^{\circ}\text{C}/m$

m is the molality of the solution

i is van't Hoff factor of the solute

ΔT_f , a negative value, is the freezing point depression, that is

$T_f^{\text{solution}} - T_f^{\text{solvent}}$

$i \cdot m$ is the effective concentration of solute particles

Mind that $i \cdot m$ represents the effective solute-particle concentration in the solution. For the case of NaCl i is 2 as every NaCl unit dissociates producing 2 ions, or 2 solute particles. For example, pure water freezes at 0°C but a 1m NaCl solution freezes at -3.72°C , which is almost four degrees lower than pure water. The freezing point depression formula establishes a linear relationship between the freezing point of a solution and molality in which the slope of the relationship is negative and gives the value of k_f , the x variable is m and the y variable is T_f^{solution} . In other words, by plotting T_f^{solution} vs. m we should obtain a straight line with a slope in absolute value that equals k_f and an intercept equals T_f^{solvent} . Table 2.4 reports values for the boiling-point elevation and freezing-point depression for various solvents.

**Table 2.4 Boiling-point elevation and freezing-point depression for various solvents**

Solvent	T_b^{solvent} (°C)	k_b (°C/m)	T_f^{solvent} (°C)	k_f (°C/m)
Acetic acid	117.9	3.07	16.6	3.90
Benzene	80.1	2.53	5.5	4.90
Carbon disulfide	46.2	2.34	-111.5	3.83
Carbon tetrachloride	76.5	5.03	-23	30
Chloroform	61.7	3.63	-63.5	4.70
Diethyl ether	34.5	2.02	-116.2	1.79
Ethanol	78.5	1.22	-117.3	1.99
Water	100	0.512	0	1.86
Cyclohexane	80.7	2.79	6.5	20.1

Table 2.4 reports values for the boiling-point elevation and freezing-point depression for various solvents.

Sample Problem 26

For a solution of 5 g of I₂ (MW=254g/mol) in 100 g of benzene, C₆H₆: (a) Calculate its molality (b) Given that benzene boiling point is 80°C, and that $k_b = 2.53$ °C/m, calculate the boiling point and the boiling point elevation of the solution. (c) Given that benzene freezing point is 5°C, and that $k_f = 5.10$ °C/m, calculate the freezing point and the freezing point depression of the solution.

SOLUTION

In order to calculate the molality of the solution, we need the moles of solute ($5\text{g} \times \frac{1\text{mol}}{254\text{g}} = 0.019\text{moles}$) and the kilograms of solvent (100g=0.1kg). We have that molality is

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}} = \frac{0.019}{0.1} = 0.19m$$

With the molality, we can calculate the freezing and boiling point of the solution. Mind that the pure solvent freezes at 5°C and boils at 80°C. The solution will freeze at a lower temperature and will boil at a higher temperature—that is, it will experience a freezing depression and boiling elevation. We will calculate first the freezing point (and freezing point depression):

$$T_f^{\text{solution}} = T_f^{\text{solvent}} - k_f \cdot i \cdot m = 5 - 5.10 \cdot 1 \cdot 0.19 = 4.031^\circ\text{C}$$

In other words the freezing depression will be

$$\Delta T_f = -k_f \cdot i \cdot m = -5.10 \cdot 1 \cdot 0.19 = -0.969^\circ\text{C}$$

We will now calculate the boiling point elevation:

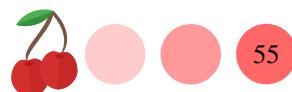
$$T_b^{\text{solution}} = T_b^{\text{solvent}} + k_b \cdot i \cdot m = 80 + 2.53 \cdot 1 \cdot 0.19 = 80.48^\circ\text{C}$$

In other words the boiling elevation will be

$$\Delta T_b = k_b \cdot i \cdot m = 2.53 \cdot 1 \cdot 0.19 = 0.4807^\circ\text{C}$$

◆ STUDY CHECK

For a solution of 5 g of NaCl (MW=58g/mol) in 100 g of acetic acid, CH₃COOH:



(a) Calculate its molality (b) Given that the boiling point of acetic acid is 118°C, and that $k_b = 3.08 \text{ } ^\circ\text{C}/\text{m}$, calculate the boiling point and the boiling point elevation of the solution. (c) Given that the freezing point of acetic acid is 17°C, and that $k_f = 3.59 \text{ } ^\circ\text{C}/\text{m}$, calculate the freezing point and the freezing point depression of the solution.

►Answer: (a) 0.86m (b) 123.3°C ; 5.29°C (c) 10.82°C ; -6.17°C

Vapor-pressure lowering Every liquid exerts a certain vapor pressure that depends on temperature. The molecules on the surface of the liquid are less tied than the molecules of the interior part of the liquid called the bulk. As such, they can escape producing what we call the vapor pressure of the liquid. Solutions exert lower vapor pressure than pure solvents. The vapor-pressure lowering is a colligative property that depends on the solute mole fraction:

$$P_{vap}^{\text{solution}} = P_{vap}^{\text{solvent}} - \chi \cdot P_{vap}^{\text{solvent}} \quad \text{or} \quad \Delta P_{vap}^{\text{solution}} = -\chi \cdot P_{vap}^{\text{solvent}} \quad (2.15)$$

where:

$P_{vap}^{\text{solution}}$ is the vapor pressure of the solution

P_{vap}^{solvent} is the vapor pressure of the pure solvent

χ is the solute mole fraction

$\Delta P_{vap}^{\text{solution}}$, a negative value, is the vapor-pressure lowering, that is,
 $P_{vap}^{\text{solution}} - P_{vap}^{\text{solvent}}$

For example, the vapor pressure of water at 25°C is 0.03 atm. If we make a solution with a 0.5 solute mole fraction by adding table salt to the water, the vapor pressure of this solution would be 0.015 atm. In other words, the vapor pressure is lower than the one from pure water. Equation 2.15 is called Raoult's Law. Raoult's Law establishes a linear relationship between the vapor pressure of a solution and the mole fraction in which the slope of the relationship gives the vapor pressure of the pure solvent, the x variable is $1 - \chi$ and the y variable is $P_{vap}^{\text{solution}}$. Simply put, by plotting $P_{vap}^{\text{solution}}$ vs. $1 - \chi$ we obtain a straight line with a slope equals to P_{vap}^{solvent} .

Sample Problem 27

Given that the vapor pressure of water at 25°C is 0.03 atm, calculate the vapor pressure and the vapor pressure lowering of a 20% of mass NaCl (MW=59g/mol) solution at that temperature.

SOLUTION

In order to calculate the vapor pressure of a solution or the vapor-pressure lowering of a solution we need to calculate the mole fraction of the solute. We can calculate χ by means of the solution of the solute mass percent:

$$\chi = \frac{18 \cdot \%_m}{100 \cdot MW + (18 - MW) \cdot \%_m} = \frac{18 \cdot 20}{100 \cdot 59 + (18 - 59) \cdot 20} = 0.07$$

Now, with the mole fraction of the solute and given that the vapor pressure of the solvent is 0.03atm, we can compute first the vapor pressure of the solution

$$P_{vap}^{\text{solution}} = (1 - \chi) \cdot P_{vap}^{\text{solvent}} = (1 - 0.07) \cdot 0.03 = 0.028 \text{ atm}$$



and then the vapor-pressure lowering

$$\Delta P_{vap}^{\text{solution}} = -2.1 \times 10^{-3} \text{ atm}$$

❖ STUDY CHECK

For a 3m I₂ (MW=254g/mol) solution in cyclohexane (MW=84g/mol) at 279K given given that the vapor pressure of cyclohexane at that temperature is 5.164kPa and the solution density is 1.3g/mL: (a) calculate the solute mole fraction. (b) calculate the vapor-pressure lowering in kPa.

►Answer: (a) $\chi = 0.24$ (b) $\Delta P_{vap} = -1.23 \text{ kPa}$

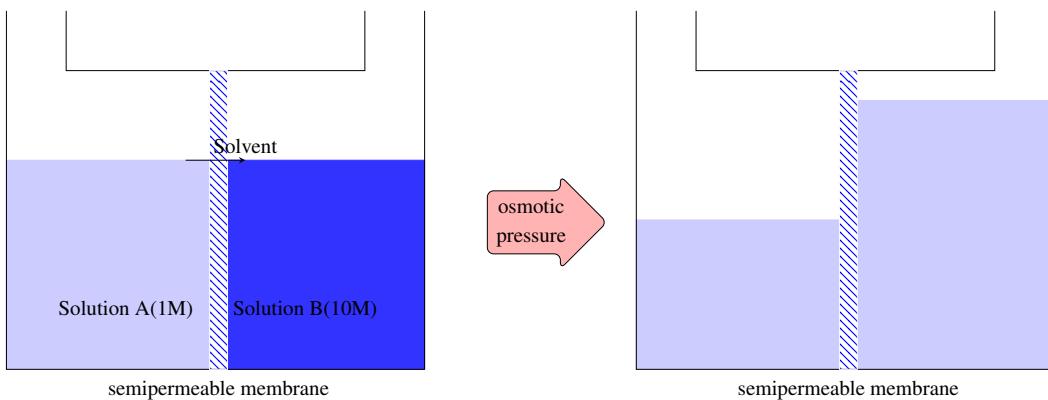


Figure 2.4 In the left diagram, we put in contact two solutions with different concentrations by means of a semipermeable membrane. The left solution is more diluted than the right solution. The difference in osmotic pressure between the membrane creates a water flow that goes from the more diluted to the more concentrated solution that minimizes the pressure gradient. As a result the liquid level changes.

Osmotic pressure of a solution The pressure of gas results from the movement of the gas particles as they hit the walls of their container. The higher the hitting frequency the higher pressure. More specifically, the pressure of a gas depends on the force exerted by the gas molecules per unit of container area. Solutions can also exhibit pressure as solute molecules also hit the walls of their container. This pressure is called osmotic pressure, Π . The higher the molarity, that is the number of moles per liter in the solution, the higher the osmotic pressure of a solution:

$$\boxed{\pi = i \cdot M \cdot RT} \quad (2.16)$$

where:

π is the osmotic pressure of the solution in atm

M is the molarity of the solution

R is the constant of the gases: 0.082 atm·L/(mol· K) (62.363577 torr·L/(mol· K))

T is the temperature of the solution in K

i is van't Hoff factor of the solute

$i \cdot M$ is the effective concentration of solute particles

The osmotic pressure of solutions is responsible for an effect called *osmosis*. First, let us talk about what is a semipermeable membrane. These are a type of membranes that allow the passing of solvent molecules without allowing the passing of solute molecules. We could set up an experiment in which we separate two solutions of



different concentrations by a semipermeable membrane and we will certainly see that the level of liquid in the most concentrated solution will rise, whereas the level of liquid in the most dilute will reduce. This effect results from the travel of water molecules from the less to the more concentrated solution equilibrating the osmotic pressure at the semipermeable membrane. Solute diffusion normally occurs against the concentration gradient. Solute diffuses from more to less concentrated solution. The more concentrated solution is referred to as the hypertonic solution, whereas the less concentrated solution is referred to as the hypotonic solution. Differently, solvent diffusion occurs following the concentration gradient (Low M → High M). On one hand, osmosis can be prevented by applying external pressure to the most concentrated solution. The minimum pressure that stops the osmosis is the osmotic pressure of the solution. On the other hand, osmotic pressure is regularly employed to experimentally obtain molar masses of soluble solutes. This colligative property is particularly useful on top of the others as small molarities cause relatively large osmotic pressures. Figure 2.4 displays how differences in osmotic pressure between the membrane create a water flow that goes from the more diluted to the more concentrated solution that minimizes the pressure gradient.

Sample Problem 28

Calculate the osmotic pressure in torr of a 0.0125M KCl solution at 25°C.

SOLUTION

We have that the osmotic pressure of a solution is the pressure needed to stop the osmotic flow of water when the solution is placed in contact with pure solvent by means of semipermeable membrane. It depends on the number of ions in solution—KCl produces two ions and therefore $i=2$, molarity, and on temperature. Employing the value of the R constant in torr (62.363577 torr·L/(mol· K)) we have:

$$\Pi = i \cdot M \cdot R \cdot T = 2 \cdot 0.0125 \cdot 62.363577 \cdot 298 = 465 \text{ torr}$$

This result indicates that we would have to apply a 465 torr pressure to the solution in order to stop the osmotic flow of water.

❖ STUDY CHECK

Calculate the osmotic pressure in torr of a 0.0345M K₂CO₃ solution at 25°C.

►Answer: 1923 torr

Colligative properties review As you can see from the equations previously presented here, the vapor-pressure lowering, the freezing-point depression, the boiling-point elevation, and the osmotic pressure are all controlled by the concentration of the solute particles, in terms of molality, molarity, or mole fraction and they are unaffected by the nature of the solute. As such, a 1m NaCl solution will experience the same boiling-point increase as a 1m KCl solution, even if the solute is different. Colligative properties are associated with the nature of the solvent and the concentration of solute but not the nature of the solute. Furthermore, these formulas work well for very diluted solutions. We call these solutions, in general, ideal solutions.

2.6 Application of colligative properties



Graphical method to calculate colligative constants The formulas for the different colligative properties represent linear relationships. Therefore using plotting, we can calculate some of the colligative constants. The next example explains how to obtain colligative constants using a graphical method. To obtain any colligative constants, the plot involved in the calculation should represent a good-quality linear trend, and the statistic tool used to assess the goodness of a linear plot is called linear correlation or linear regression. Linear regression uses a linear correlation coefficient, r^2 , to assess the quality of the fit. Good linear plots, in general, are characterized by values of linear correlation coefficient between 0.99 and 1. Differently, r^2 values lower than 0.99 in general do not result from a truly linear relationship. No accurate colligative constants should be calculated from a set of data characterized by a poor linear correlation coefficient. Is important to keep in mind:

$$\begin{array}{ll} 0.99 \leq r^2 \leq 1.00 & \text{(Good linear regression)} \\ r^2 < 0.99 & \text{(Poor linear regression)} \end{array} \quad (2.17)$$

You can fit a linear regression to a set of experimental data either using a graphic calculator or using specialized [internet websites](#).

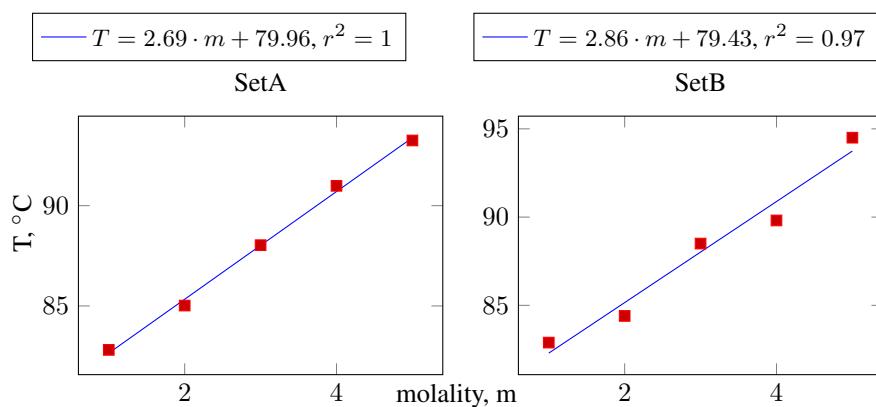
Sample Problem 29

The following two sets of data report the change in boiling point of a solution. Assess the data to calculate the boiling elevation constant, and if possible, calculate colligative constant and the boiling point of the pure solvent.

Set A		Set B	
T(°C)	m	T(°C)	m
82.81	1	82.89	1
85.02	2	84.4	2
88.03	3	88.5	3
90.99	4	89.81	4
93.25	5	94.5	5

SOLUTION

In order to ensure that the data is good enough to calculate the boiling elevation constant we need to assess the quality of the linear regression. By means of two regression analysis displayed below, we have that for Data set A, r^2 is larger than 0.99 and hence this data set fits well a linear regression. On the other hand, the Data set B is not good enough in order to calculate the boiling point elevation constant as r^2 is lower than 0.99. In another words, the Data set B does not represent a real linear relationship between boiling temperature and molality. Therefore, we will use Data set A in order to calculate the boiling elevation constant. From the slope of the line we will calculate $k_b=2.69\text{°C/m}$ and from the intersect we will calculate the boiling point of the pure solvent $T_b^{\text{solvent}} = 79.96\text{°C}$.



◆ STUDY CHECK

The following two sets of data report the change in boiling point of a solution. Assess the quality of the data to calculate graphically the boiling elevation constant, and if possible, calculate colligative constant and the boiling point of the pure solvent.

Set A		Set B	
T(°C)	m	T(°C)	m
17.02	1	17.21	1
15.21	2	14.42	2
11.10	3	11.63	3
7.65	4	8.84	4
6.05	5	6.05	5

► Answer: Data set B, $k_f = 2.79^\circ\text{C}$, $T_f^{\text{solvent}} = 20^\circ\text{C}$

Use of colligative properties to calculate α Colligative measurements can be used to calculate the percent dissociation (α) of an electrolyte. The idea is to compare the nominal concentration based on the preparation of the electrolyte solution and the effective concentration of ions and molecules in the solution obtained using the colligative measurements. Remember these measurements directly depend on the total number of particles in the solution: ions and molecules. However, in a weak electrolyte, the nominal concentration used to prepare the solution is not the same as the effective concentration of ions and molecules. This is because the concentration of ions and molecules in solution as weak electrolytes break down based on the degree of dissociation and, at the same time, the number of ions produced depends on the Van't Hoff factor i . The following equation gives the effective concentration of solute particles in the solution for a weak electrolyte in terms of the Van't Hoff factor and the nominal concentration:

$$c^{\text{effective}} = c^{\text{Nominal}} \cdot (1 + (i - 1) \frac{\alpha}{100})$$

For example, imagine we prepare a 0.1M (c^{Nominal}) solution of a weak electrolyte with a 98% degree of dissociation (α) and the electrolyte dissociates into two different ions ($i=2$). The number of solute particles in the solution, that is the effective concentration of particles, will be 0.198M. As you can see this number is larger than 0.1M as it accounts not only for molecules (0.002M) but also for ions (0.196M). The following



example demonstrates how to compute an electrolyte's degree of dissociation using osmotic pressure measurements.

Sample Problem 30

A solution of 0.07M HF—a weak electrolyte—has a osmotic pressure of 2atm at 298K. Calculate: (a) The nominal solute concentration. (b) The effective ion concentration. (c) The percent dissociation of the acid.

SOLUTION

(a) The nominal solute concentration is 0.07M. (b) The osmotic pressure depends on molarity and temperature. We know the temperature, R is 0.082atmL/Kmol, and the vale of the osmotic pressure. With this information we can calculate the effective concentration of particles in solution:

$$i \cdot M = \frac{\pi}{RT} = \frac{2}{0.082 \cdot 298} = 0.08M$$

This value accounts for the overall concentration of solute particles in the form of molecules and ions. (c) The osmotic pressure is related to the effective molarity and given that we know the nominal solute concentration, we can calculate the degree of dissociation of the acid:

$$c^{\text{effective}} = c^{\text{Nominal}} \cdot (1 + (i - 1) \frac{\alpha}{100})$$

Plugging the given values we have:

$$0.08 = 0.07 \cdot (1 + (2 - 1) \frac{\alpha}{100})$$

We can solve for α :

$$\alpha = 100 \cdot (0.08 / 0.07 - 1) = 14.28\%$$

This results indicated that 14% of the electrolyte dissociates forming $H^+ + F^-$, whereas 86% stays in the form of HF.

❖ STUDY CHECK

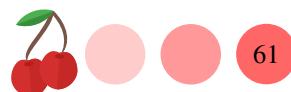
We prepare a 0.1M solution of a weak electrolyte with $i=3$. Given that the degree of dissociation of the electrolyte is 95%, calculate the osmotic pressure of the solution at 298K.

►Answer: 7.09atm

Use of colligative properties to calculate MW Colligative properties measurements are also useful to calculate molar masses of solutes as most of these properties are related to concentration and concentration is related to the molar mass of the solute. The method is based on carrying any colligative measurement, for example, the boiling point elevation, the freezing point depression, or the osmotic pressure, and with these measurements computing the corresponding concentration, molarity or molarity. Once we have the concentration we can use Equation 2.10 to compute the molar mass of the solute. We will work on an example:

Sample Problem 31

We prepare a solution by adding 1g of solute—a non-electrolyte—into 100mL of water. The solution experience a freezing point depression of $2.1^\circ C$. Given



than the freezing depression constant of water is $0.512^{\circ}\text{C}/\text{m}$, calculate the molar mass of the solute.

SOLUTION

We will first calculate the molality of the solution by means of the freezing point depression.

$$\Delta T_f = -i \cdot k_f \cdot m$$

We will use the freezing point depression ($\Delta T_f = -2.1^{\circ}\text{C}$), Van't Hoff's factor ($i=1$) and the freezing point depression constant ($k_f = 0.512^{\circ}\text{C}/\text{m}$):

$$-2.1 = -1 \cdot 0.512 \cdot m$$

we have that the molality of the solution is $m = 4.10\text{m}$. Now that we have the molality we will calculate the molar mass of the solute using the information provided regarding the solution preparation: mass of solute ($m_{\text{solute}} = 1\text{g}$) and volume of water ($m_{\text{solvent}} = 0.1\text{kg}$), taking into account that the density of water is 1g/mL . We have that the molar mass of the solute is:

$$MW = \frac{\text{g of solute}}{\text{m} \cdot \text{kg of solvent}} = \frac{1}{4.10 \cdot 0.1} = 2.44\text{g/mol}$$

◆ STUDY CHECK

We prepare a solution by adding 5g of solute—a non-electrolyte—into 50mL of water. The solution experience a boiling point elevation of 5.3°C . Given the boiling elevation constant of water, $1.86^{\circ}\text{C}/\text{m}$, calculate the molar mass of the solute. Mind the density of water is 1g/mL .

►Answer: 35.09g/mol

Osmosis The solute concentration impacts the movement of water in and out of the animal and vegetal cells. This important process is called osmosis. Osmosis occurs when two solutions of different concentrations—a more concentrated and a more diluted solution—are connected using a semipermeable membrane, that is a membrane that only allows the movement of small water molecules. Osmosis refers to the flow of water through a semipermeable membrane, from the most diluted to the most concentrated solution. The flow follows a gradient of osmotic pressure from the most diluted solution with lower osmotic pressure to the most concentrated with a larger osmotic pressure. Water molecules flow to reduce the concentration of the most concentrated solution and hence to minimize the difference in concentration across the semipermeable membrane. Due to the flow of liquid, the liquid level of the most concentrated side rises and the level of the most diluted side decreases.

In a process called *reverse osmosis*, external pressure is applied to a concentrated solution in contact with a container with pure solvent, to force the reverse flow of water against the concentration gradient. This way solutions drie up while solvent transfers out of it. This principle is applied in desalination plants that obtain pure water from salty water. Still, the pressure applied is so much that this process is not economically feasible in most parts of the world.

Dialysis Dialysis is a process that resembles osmosis in which a semipermeable membrane—referred to as the dialyzing membrane—is used to separate water and small molecules from larger molecules such as proteins. This process indeed occurs in most

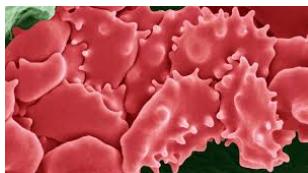


▼ Normal red cells



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▼ Shriveled red cell



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▼ Dialysis is based on the principles of osmosis



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plant and animal cells, with the difference that these membranes allow the pass not only of the solvent but also of small solutes and ions. This process is also used in artificial kidney machines that purify blood with the help of a cellophane membrane. In this process, a dialyzing solution with the same composition as blood but without any waste product is used to clean up blood. Hence, a movement of waste molecules from the solution cleanses blood.

Osmolarity The molarity of a solution is directly related to the number of moles of solute molecules in the solution. However, the osmotic pressure of a solution depends on the number of moles of ions and not the number of moles of solute molecules. The osmolarity (Osm) is defined as the number of osmoles per liter of solution, being the number of osmoles the number of moles times the number of particles on solution i :

$$Osm = i \cdot M \quad (2.18)$$

where:

M is the molarity

i is the number of ions produced per mole of solute

For example, the osmolarity of a 2M NaCl solution would be 4Osm as NaCl contains two ions ($i = 2$).

Isotonic, hypotonic and hypertonic solutions The cells in biological systems contain semipermeable membranes. *Isotonic solutions*—the prefix iso means the same—exert the same osmotic pressure as biological fluids such as blood. In hospitals, most intravenous solutions are made of isotonic solutions. Examples of isotonic solutions are a 1M NaCl solution or a 2M glucose ($C_6H_{12}O_6$) solution. Both have the same osmolarity of 2 Osm. If we place a red blood cell in an isotonic solution it will not experience any changes in its shape as the osmotic pressure inside and outside would be the same. The osmotic pressure of blood at $25^\circ C$ is $\Pi=7.70\text{atm}$. *Hypotonic solutions*—the prefix hypo means lower than—have a lower osmolarity than biological fluids. As such, if we place a red blood cell in a hypotonic solution it will swell and burst as water from the outside will flow inside the cell to compensate for the higher osmotic pressure. This phenomenon is called hemolysis. Differently, *hypertonic solutions*—the prefix hyper means higher than—have a higher osmolarity than biological solutions. A red blood cell placed in such a solution will shrink as water will flow out of the cell into the solution to compensate for the higher osmotic pressure outside the cell. This phenomenon is called crenation. Crenation is regularly used in the food industry to preserve food. By treating food with a solution hypertonic to bacteria one can kill these types of germs. This is why salt is used to protect meat and sugar to preserve fruits.

2.7 Ideal and real solutions

We have considered the impact of a solute on the vapor pressure of a liquid assuming that the solute with null vapor pressure. How about mixing two liquids? In this case, both liquids with different vapor pressures will contribute to the overall vapor pressure of the mixture using an expression equivalent to Raoul's law:

$$P_{vap}^{\text{solution}} = \chi_A \cdot P_{vap,A} + \chi_B \cdot P_{vap,B} \quad (2.19)$$

where:

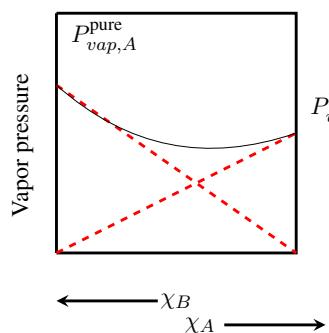
$P_{vap}^{\text{solution}}$ is the vapor pressure of the mixture

$P_{vap,A}$, $P_{vap,B}$ is the vapor pressure of the pure solvent A and B

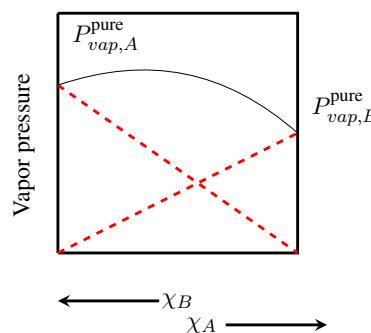
χ_A , χ_B is the mole fraction of A and B

Ideal mixtures will follow Equation 2.19. In other words, when the vapor pressure of the mixtures results from adding the vapor pressure of both liquids the mixture will be ideal. For some mixtures, the overall vapor pressure is lower or higher than the pressure resulting from adding the vapor pressure of both liquids. These mixtures are called real mixtures. We can encounter positive or negative deviations from the ideal behavior. When the interaction between the two liquids is exothermic and hence favorable ($\Delta H_{sol} < 0$), the resulting vapor pressure of the mixture will be lower than the resulting combined vapor pressure and the mixture will experience negative deviations from ideality (e.g. water and acetone). When the interaction between the two liquids is endothermic ($\Delta H_{sol} > 0$) and hence energetically unfavorable, the resulting vapor pressure of the mixture will be higher than the resulting combined vapor pressure and the mixture will experience positive deviations from ideality (e.g. hexane and ethanol). Mixtures of very similar liquids (e.g. benzene and toluene) with very small enthalpy of solution ($\Delta H_{sol} \simeq 0$) tend to behave as ideal mixtures, without deviating from Raoult's law.

Favorable solute-solvent interaction



Unfavorable solute-solvent interaction



Ideal mixture

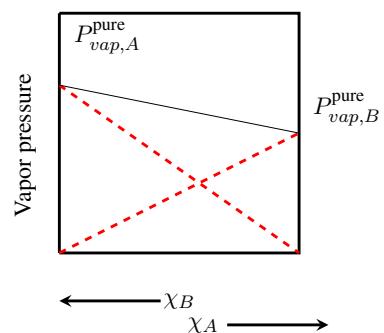


Figure 2.5 Different patterns for the vapor pressure of mixtures of two liquids. When the interaction is favorable, the resulting vapor pressure is lower than combined the pressure of both components. Differently, when the interaction is unfavorable, the resulting vapor pressure is higher than combined the pressure of both components. Finally, the vapor pressure of an ideal mixture is the result of combining the vapor pressure of both components.

2.8 Factors affecting the solubility of solids and gases

In this section, we will address the impact of temperature on the solubility of solids and gases on liquids and the impact of pressure on the solubility of gases on liquids. Figure 2.6 displays solubility vs. temperature plots for gases and solids in water.

Impact of the molecular structure on solubility The solubility of a solute into a solvent is intimately related to how the molecules of both compounds interact with each other. Polar solutes will tend to dissolve in polar solvents whereas nonpolar solutes will be more soluble in nonpolar solvents. Still, polarity only does not explain why a polar solute is more soluble in some polar solvents than others, and ultimately is the interaction between molecules and the energy associated with this interaction that determines solubility.

Impact of temperature on solubility The solubility of a solute in a solvent is the maximum amount of solute that one can dissolve in a solvent at a given



temperature. Solubility is affected by the state of matter of the solute—solids dissolve differently than gases—and by temperature. The nature of the temperature impact depends on the nature and state of matter of the solute (see Figure 2.6). The temperature has a strong impact on the solubility of solids. On one hand, temperature speeds up the dissolution process so that solids dissolve more rapidly at higher temperatures. On the other hand, the amount of solid that can be dissolved in a solvent can increase or decrease with temperature, depending on the nature of the solid. The solubility of sugar increases with temperature. That means the higher temperature the more solute one can dissolve. However, solid solutes like $\text{Ce}_2(\text{SO}_4)_3$ or Li_2SO_4 follow the opposite trend with lower solubility at higher temperatures. The change of solubility with temperature is more homogeneous for gases. We have that the solubility of gas solutes normally decreases with temperature (at least for low temperatures), that is, the higher the temperature the less amount of gas will be dissolved in a liquid. If you warm up a can of soda it goes flat as the gas comes out of the liquid—we call this desorption. Solubility changes with temperature have numerous applications in everyday life. For example, the decrease of gas solubility with temperature is responsible for the formation of boiler scale that occurs at the walls of kettles and industrial boilers. When increasing temperature, the solubility of carbon dioxide decreases, and this gas is released from water. To compensate for this effect, more carbon dioxide is absorbed in water leading to the formation of bicarbonate ions that can react with calcium leading to solid calcium carbonate, the boiler scale. Another example is thermal pollution. When water is used in cooling systems and returned to the rivers, it can be returned with higher temperatures. As the solubility of gases decreases with temperature, warm water floats on top of cold water and impedes access to oxygen.

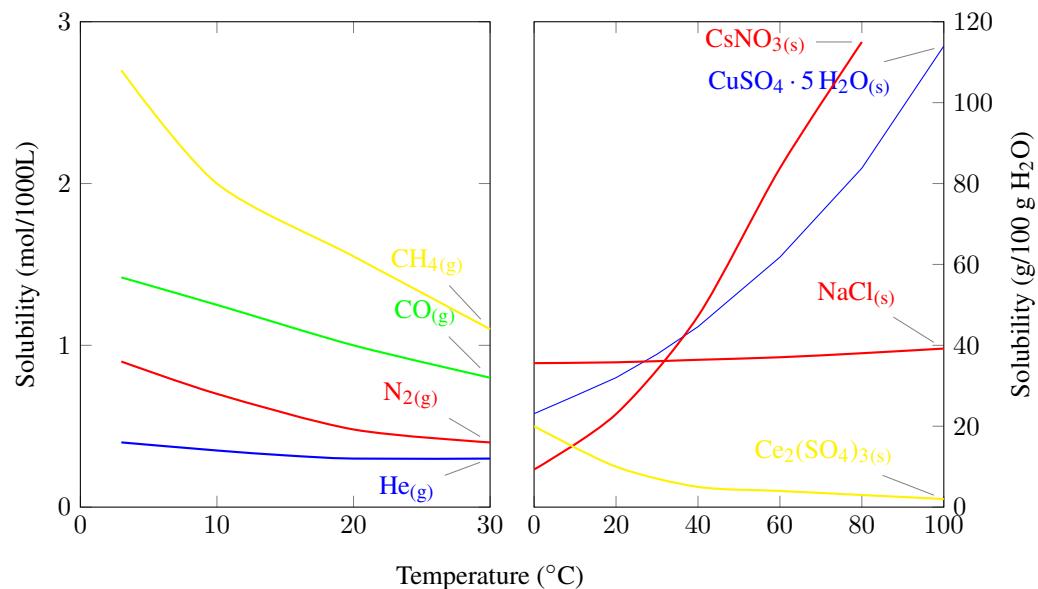


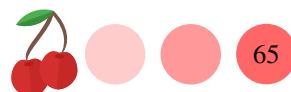
Figure 2.6 Solubility vs. Temperature plots for gases and solids in water.

Impact of pressure on the solubility of gases on liquids

Pressure does not impact the solubility of solids or liquids in a liquid solvent. However, gas pressure impacts the solubility of a gas solute on a liquid at a fixed temperature. In particular, the higher pressure the higher solubility. The law that related gas solubility with pressure is called Henry's law:

$$s = k \cdot P \quad (2.20)$$

where:



s is the solubility of a gas in a liquid solvent in M units

k is Henry's law constant with units of M/atm

P is the gas pressure in atm

Henry's law constant is characteristic of a solution at a fixed temperature. This law is obeyed for very diluted solutions of gases that do not dissociate or react with water (e.g. O₂ in water). For example, HCl_g does not follow this law as it can dissociate in water. An everyday life application of Henry's law is the production of carbonated beverages. These beverages are produced in contact with a liquid with an atmosphere of CO₂ of typical pressures of 5 atm. When you open a can container, the CO₂ in the drink comes out of the liquid in the form of bubbles to equilibrate the high gas pressure on the liquid and the low gas pressure in the atmosphere.

Sample Problem 32

For the dissolution of CO₂ in water, Henry's constant is 3.4×10^{-2} M/atm.

Calculate: (a) the CO₂ pressure needed to achieve a gas concentration of 0.04M.

(b) If we open a carbonated can until it goes flat and given that the partial pressure of CO₂ in the air is 4×10^{-4} atm at 25°C, calculate the final gas concentration in the drink.

SOLUTION

(a) We will apply Henry's law given that we know solubility and Henry's constant:

$$s = k \cdot P \quad 0.04 = 3.4 \times 10^{-2} \cdot P$$

Solving for the pressure we have: 1.17atm. (b) We will also apply Henry's law, this time knowing the partial pressure of CO₂ and again Henry's constant:

$$s = k \cdot P \quad s = 3.4 \times 10^{-2} \cdot 4 \times 10^{-4}$$

The solubility is 1.36×10^{-5} M.

❖ STUDY CHECK

Calculate the solubility of nitrogen in water after exposing water to a 5 atm nitrogen pressure, given that Henry's constant is 6.1×10^{-4} M/atm.

►Answer: 3.05×10^{-3} M

★★★★★ NEW FEATURE!

Table 2.5 Enthalpy of solution in KJ/mol for several compounds*

Compound	ΔH^{sol}	Compound	ΔH^{sol}	Compound	ΔH^{sol}	Compound	ΔH^{sol}
HF _(g)	-61.50	HCl _(g)	-74.84	(CH ₃) ₃ NHCl _(s)	+1.46	N(CH ₃) ₄ Cl _(s)	+4.08
HClO _{4(l)}	-88.76	HClO ₄ · H ₂ O _(s)	-32.95	N(CH ₃) ₄ Br _(s)	+24.27	N(CH ₃) ₄ I _(s)	+42.07
HBr _(g)	-85.14	HI _(g)	-81.67	AgClO _{4(s)}	+7.36	AgNO _{2(s)}	+36.94
HIO _{3(s)}	+8.79	HNO _{3(l)}	-33.28	AgNO _{3(s)}	+22.59	LiOH _(s)	-23.56
HCOOH _(l)	-0.86	CH ₃ COOH _(l)	-1.51	LiOH · H ₂ O _(s)	-6.69	LiF _(s)	+4.73
NH _{3(g)}	-30.50	NH ₄ Cl _(s)	+14.78	LiCl _(s)	-37.03	LiCl · H ₂ O _(s)	-19.08
NH ₄ ClO _{4(s)}	+33.47	NH ₄ Br _(s)	+16.78	LiClO _{4(s)}	-26.55	LiClO ₄ · 3 H ₂ O _(s)	+32.61
NH ₄ I _(s)	+13.72	NH ₄ IO _{3(s)}	+31.80	LiBr _(s)	-48.83	LiBr · H ₂ O _(s)	-23.26
NH ₄ NO _{2(s)}	+19.25	NH ₄ NO _{3(s)}	+25.69	NH ₄ CNS _(s)	+22.59	CH ₃ NH ₃ Cl _(s)	+5.77
NH ₄ C ₂ H ₃ O _{2(s)}	-2.38	NH ₄ CN _(s)	+17.57				

* Parker, V. B., Thermal Properties of Uni-Univalent Electrolytes

Natl. Stand. Ref. Data Series - Natl. Bur. Stand.(U.S.), No.2, 1965.

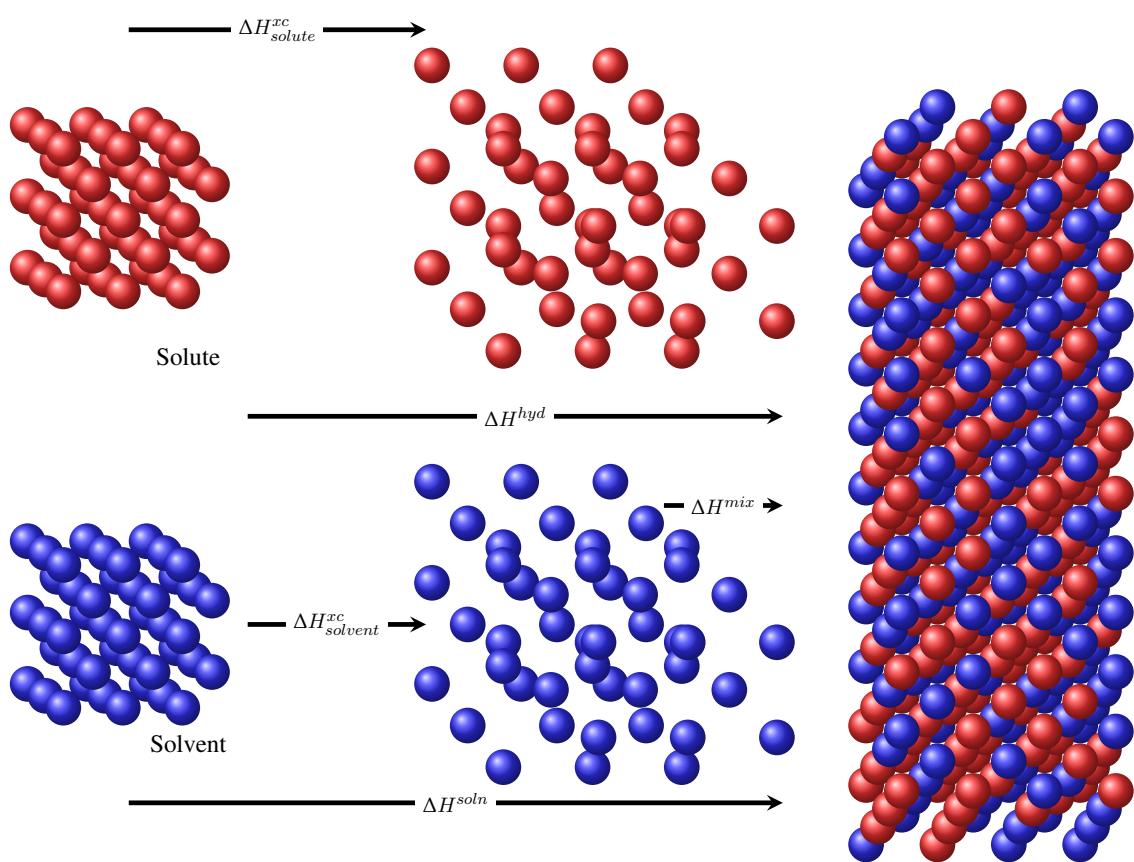


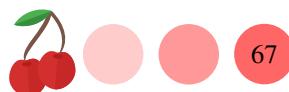
Figure 2.7 Representation of the steps involved in dissolution

2.9 Enthalpy of solution

Some chemicals favorably mix. For example, table salt and water or oil and cyclohexane. Others such as water and cyclohexane do not mix. Like dissolves like is the rule behind miscibility. Understanding why chemicals mix at the molecular level is the key to understanding solubility. Thermodynamics can give some insight into why chemicals mix. In particular, an enthalpy analysis of mixing, and understanding the energy effects involved in solubility can give some partial insight into solubility. Still, it is important to acknowledge that energetics—energy considerations—is only part of the answer, and the spreading of energy has to be included in this analysis to achieve a complete picture of solubility.

★★★★★ NEW FEATURE!

Dissolution steps We will address here the steps involved in the process of dissolution of a compound in a general solvent such as water. This process involves the disaggregation of the molecules of the solute into dissolved particles, that is, particles solvated by the molecules of the solvent. The molecules of the solute and the solvent interact through intermolecular forces. These forces play a key role in dissolution. In the case of the solute, strong intermolecular forces hinder dissolution. It takes more energy to separate the solute particles when intermolecular forces in the solute are strong. Similarly, for the solvent, intermolecular forces also hinder dissolution. It takes more energy to separate the solvent particles when intermolecular forces in the solvent are strong. Once the solute is disaggregated into dissolved particles, the energetics involved in the hydration play a role in dissolution. Particles that do not hydrate easily are less soluble than particles with a large tendency to be surrounded by water molecules. This way, we can understand the dissolution process, characterized by the enthalpy of



solution (ΔH^{soln}), using three steps: first, the energy involved in expanding the solute into separate entities (ΔH_{solute}^{xp}); second, the energy involved in expanding the solvent into separate entities ($\Delta H_{solvent}^{xp}$); third, the energy involved in mixing the separate solute and solvent particles into hydrated ions (ΔH^{mix}). Overall we have that

$$\Delta H^{soln} = \Delta H_{solute}^{xp} + \Delta H_{solvent}^{xp} + \Delta H^{mix} = \Delta H_{solute}^{xp} + \Delta H^{hyd}$$

Steps two and three combined represent the energy of hydrating (ΔH^{hyd}) of the solute:

$$\Delta H^{hyd} = \Delta H_{solvent}^{xp} + \Delta H^{mix}$$

At the same time, the energy of expanding the solute has a clear meaning when the solute is ionic. This is called the negative value of the lattice energy ($\Delta H_{lattice}$), the energy needed to form a solid ionic lattice from the separated ions:

$$\Delta H_{solute}^{xp} = -\Delta H_{lattice}$$

Figure 2.8 displays enthalpy profiles for an endo and exothermic dissolution process.

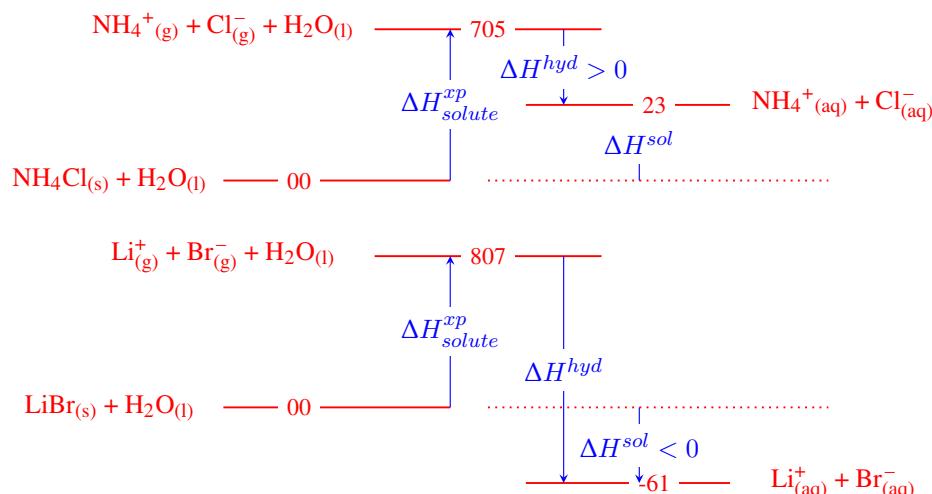


Figure 2.8 Enthalpy diagrams for the dissolution process. (Top) an endothermic dissolution; (Bottom) an exothermic dissolution. Enthalpy values are listed in KJ/mol.

Enthalpy of solution Large, positive ΔH^{soln} values correspond to endothermic solution processes, that is, the solute would absorb energy when dissolving (e.g. NH_4Cl). Small, negative ΔH^{soln} values correspond to exothermic solution processes, that is, the solute would release energy when dissolving (e.g. LiBr). ΔH^{soln} values for numerous solutes are given in Table 2.5. For the case of LiBr we have that the enthalpy of solution is -61KJ/mol, while the energy needed to expand the solute is 807KJ/mol (the lattice energy of LiBr is -807KJ/mol). The enthalpy of hydration for Li^+ is -520KJ/mol and for Br^- is -348KJ/mol. The overall enthalpy of hydration (-682KJ/mol) is smaller in absolute value than the energy needed to expand the solute giving an overall, negative enthalpy of solution. Therefore, the large solvation energy of the salt makes the dissolution of LiBr exothermic.

Enthalpy of hydration The enthalpy of hydration represents the energy involved in the reaction of an ion with water to produce an hydrated ion. For single ions, this property is impossible to measure directly, as we cannot recreate the process of dissolution of a single ion, those are found in the form of ionic compounds and not separate ions. Still, simulations can give insight into the factors that impact these

▼ Heat pads contain a supersaturated solution of sodium acetate in water.



© www.flickr.com

▼ Instant cold packs contain ammonium nitrate and water.



wikipedia



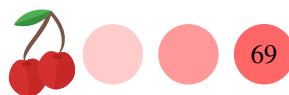
property. In general terms, the electronegativity of the ion impact hydrations: more electronegative ions tend to have smaller, more negative, hydrations energies. ΔH^{hyd} values for numerous solutes are given in Table 2.6. We can see that ΔH^{hyd} for F^- is -524 KJ/mol, while being -308 KJ/mol for I^- , a less electronegative ion.

Table 2.6 Enthalpy of hydration in KJ/mol for several ions *

Ion	ΔH^{hyd}						
H^+	-1091	Li^+	-520	Na^+	-406	K^+	-320
Rb^+	-296	Cs^+	-264	In^+	-344	Tl^+	-328
Cu^+	-593	Ag^+	-473	Au^+	-615	NH_4^+	-307
Be^{2+}	-2484	Mg^{2+}	-1926	Ca^{2+}	-1579	Sr^{2+}	-1446
Ba^{2+}	-1309	Ti^{2+}	1862	Cr^{2+}	-1908	Mn^{2+}	-1851
Fe^{2+}	-1950	Co^{2+}	-2010	Ni^{2+}	-2096	Cu^{2+}	-2099
Pt^{2+}	-2100	Zn^{2+}	-2047	Cd^{2+}	-1809	Pb^{2+}	-1485
Hg^{2+}	-1829	Sn^{2+}	-1554	Y^{3+}	-4105	Tl^{3+}	-4108
Al^{3+}	-4680	Sc^{3+}	-3930	NO_3^-	-314	OH^-	-460
F^-	-524	Cl^-	-378	Br^-	-348	I^-	-308

* D.W. Smith, J. Chem. Educ., 54, 540 (1977).

Heat packs Athletes take advantage of the energetics of dissolution by using hot and cold packs to treat injuries. Both packs consist on a solid chemical that dissolves in a pouch of water when the pack is squeezed. Calcium chloride or magnesium sulfate is used in hot packs, whereas ammonium nitrated is mainly used on cold packs.



CHAPTER 2

SOLUTIONS AND COLLOIDS

2.1 For the following colloids, indicate the nature of the dispersed and dispersing medium (liquid, solid or gas) :
 (a) soda water (b) cake (c) midst (d) smoke (e) froth

2.2 For the following colloids, indicate the nature of the dispersed and dispersing medium (liquid, solid or gas) :
 (a) pumice stone lava (b) cheese (c) paint (d) clouds

2.3 Classify as:

(i) Foam colloid (ii) Solid foam colloid (iii) Aerosol colloid (iv) Emulsion colloid (v) Gel colloid (vi) Sol colloid (vii) Solid-sol colloid (viii) A solution

the following series of mixtures:

(a) Soda (b) Soap Lather (c) Whipped cream (d) Pumice stone (e) Rubber (f) Cloud (g) Mist (h) Fog (i) Milk (j) Cream

2.4 Classify as:

(i) Foam colloid (ii) Solid foam colloid (iii) Aerosol colloid (iv) Emulsion colloid (v) Gel colloid (vi) Sol colloid (vii) Solid-sol colloid (viii) A solution

the following series of mixtures:

(a) Mayonnaise (b) Jelly (c) Butter (d) Curd (e) Cheese (f) Smoke (g) Haze (h) Gold sol (i) Sulphur sol (j) Colored glasses (k) Gems (l) Ruby glass

UNITS OF CONCENTRATION

2.5 Calculate: (a) the percent by mass of a solution made of 5g of NaBr in 70g of solution (b) the percent by mass of a solution made of 5g of NaBr with 20g of water(c) the percent by mass of a solution made of 5g of NaBr with 10mL of water

2.6 Calculate the molality for: (a) a solution made of 5moles of NaBr(MW=103g/mol) in 200g of water (b) a solution made of 20g of NaBr(MW=103g/mol) in 200g of water (c) a solution made of 10g of NaBr(MW=103g/mol) in 20mL of water

2.7 Calculate the density of a solution: (a) containing 3g of solute and 100g of water in 101mL (b) containing 1g of solute and 100mL of water in 103mL

2.8 Calculate the mole fraction of solute of a solution:

- (a) containing 3g of solute (MW=16g/mL) and 100g of water
- (b) containing 2 moles of solute and 30 moles of solvent
- (c) containing 4 moles of solute and 45 moles of solution

2.9 Calculate normality for the following cases: (a) a 1M KMnO₄ solution given it provides 5 e⁻ in a redox
 (b) a 2M K₂Cr₂O₇ solution given it provides 6 e⁻ in a redox
 (c) a 3M KOH solution (d) a 3M Ca(OH)₂ solution

2.10 Calculate normality for the following cases: (a) a 2M HCl solution (b) a 1M H₂CO₃ solution (c) a 2M H₃PO₄ solution

2.11 Use the List feature of your graphing calculator to fill the table below carrying calculations in bulk:

Solution	g solute	g solvent	% _{solute}	% _{solvent}
a	10	10		
b	20	9		
c	30	8		
d	40	7		
e	50	6		
f	60	5		

2.12 Use the List feature of your graphing calculator to fill the table below carrying calculations in bulk:

Solution	g solute	g solvent	% _{solute}	% _{solvent}
a	15	10		
b	25	9		
c	35	8		
d	45	7		
e	55	6		
f	65	5		



RELATING UNITS OF CONCENTRATION

2.13 Calculate: (a) the molarity of a 0.2m solution of density 1.2g/mL made of a NaCl(MW=58g/mol) (b) the molality of a 0.2M solution of density 1.2g/mL made of a NaCl(MW=58g/mol) (c) the percent by mass of a 0.1M solution of density 1.2g/mL made of a NaCl(MW=58g/mol)

2.14 Calculate: (a) the molarity of a 20% solution of density 1.1g/mL made of a Na₂SO₄(MW=142g/mol) (b) the mole fraction of a 20% aqueous solution of density 1.1g/mL made of a Na₂SO₄(MW=142g/mol) (c) the percent by mass of an aqueous solution of density 1.1g/mL and 0.4mole fraction, made of a Na₂SO₄(MW=142g/mol)

2.15 We prepare a C₆H₁₂O₆ (MW=180g/mL) solution by mixing 5g of solute in 100mL of water giving 102mL of solution. Calculate: (a) the molarity (b) the molality

2.16 We prepare a C₆H₁₂O₆ (MW=180g/mL) solution by mixing 5g of solute in 100mL of water giving 102mL of solution. Calculate: (a) the percent by mass (b) the mole fraction

2.17 Calculate the molar weight of the solute of a solution with 0.9g/mL density, 2M and 2.9m.

2.18 Calculate the molar weight of the solute of a solution with 0.9g/mL density, 0.5 mole fraction and 90% of solute by mass.

2.19 Use the List feature of your graphing calculator to fill the table below carrying calculations in bulk (these are water-based solutions):

Solute	Xylene	toluene	benzene	styrene
MW (g/mol)	106	92	78	104
d (g/mL)	1.1	1.3	1.5	1.7
m	1.1	0.9	0.8	0.7
M				
% _m				
χ				

2.20 Use the List feature of your graphing calculator to fill the table below carrying calculations in bulk (these are water-based solutions):

Solute	Acetic Ac.	Acetone	Acetaldehyde	Ammonia
MW (g/mol)	60	58	44	17
d (g/mL)	2.0	1.0	0.5	0.3
m	0.4	0.3	0.2	0.1
M				
% _m				
χ				

2.21 Demonstrate that the relationship between %_m (the mass percent) and %_v (the volume percent) of a solution made from two liquids is given by:

$$\%_v = \%_m \times \frac{d}{d_{solute}}$$

where d_{solute} is the solute density and d is the solution density.

2.22 Demonstrate that the relationship between χ (the mole fraction) and m (molality) of a solution is given by:

$$\chi = \frac{18m}{1000 + 18m}$$

where d_{solute} is the solute density and d is the solution density.

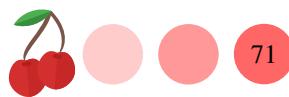
2.23 You mix 10mL of ethanol (a solute with density 0.7g/mL and MW of 46g/mol) with 100mL of water giving 109.5 mL of solution. Calculate: (a) %_v (b) d in g/mL (c) %_m (d) M

2.24 You mix 15mL of ethanol (a solute with density 0.7g/mL and MW of 32g/mol) with 100mL of water giving 115.7 mL of solution. Calculate: (a) %_v (b) d in g/mL (c) %_m (d) M

2.25 A solution is 10% in mass and its solute has a MW of 100g/mol. Calculate: (a) the mole fraction of the solution if it's a water-based solution (b) the mole fraction of the solution if it's an ethanol-based solution and ethanol's MW is 32g/mol

2.26 A solution is 5% in mass and its solute has a MW of 150g/mol. Calculate: (a) the mole fraction of the solution if it's a water-based solution (b) the mole fraction of the solution if it's an ethanol-based solution and ethanol's MW is 32g/mol

SOLUTIONS OF ELECTROLYTES AND

**EFFECTIVE SOLUTE PARTICLES**

2.27 Break down the following electrolytes in ions, if possible: (a) CaI_2 (b) KNO_3 (c) CaSO_4 (d) FeSO_4

2.28 Break down the following electrolytes in ions, if possible: (a) SnCl_4 (b) CuCl_2 (c) Ba(OH)_2 (d) CuSO_3 (e) MgSO_4

2.29 Calculate the i factor for the following chemicals: (a) NaNO_3 (b) NaCl (c) CaI_2 (d) MgCl_2

2.30 Calculate the i factor for the following chemicals: (a) $\text{Mg}(\text{NO}_3)_2$ (b) CuSO_4 (c) FeCl_3

2.31 We dissolve 3 moles of solute in 1L of solution. Given that Van't Hoff factor of the solute is 3, calculate the nominal solute concentration and the effective concentration of particles on solution.

2.32 We dissolve 0.5 moles of solute in 1L of solution reaching a effective concentration of solute particles of 0.9M. Calculate the Van't Hoff factor.

2.33 Can the percent dissociation of a electrolyte be negative? Elaborate.

2.34 Can the percent dissociation of a electrolyte be more than 1? Elaborate.

COLLIGATIVE PROPERTIES

2.35 Calculate the boiling point of a 3m $\text{C}_6\text{H}_{12}\text{O}_6$ aqueous solution. $T_b^{\text{solvent}}=100^\circ\text{C}$ and $k_b=0.512^\circ\text{C}/\text{m}$.

2.36 Calculate the boiling point increase of a 8m $\text{C}_6\text{H}_{12}\text{O}_6$ aqueous solution. $T_b^{\text{solvent}}=100^\circ\text{C}$ and $k_b=0.512^\circ\text{C}/\text{m}$.

2.37 Calculate the boiling point of a 3m CaCl_2 aqueous solution. $T_b^{\text{solvent}}=100^\circ\text{C}$ and $k_b=0.512^\circ\text{C}/\text{m}$.

2.38 Calculate the boiling point increase of a 8m KCl aqueous solution. $T_b^{\text{solvent}}=100^\circ\text{C}$ and $k_b=0.512^\circ\text{C}/\text{m}$.

2.39 Calculate the freezing point of a 2m I_2 solution on benzene. $T_f^{\text{solvent}}=5.5^\circ\text{C}$ and $k_f=4.9^\circ\text{C}/\text{m}$.

2.40 Calculate the freezing point depression of a 2m I_2 solution on benzene. $T_f^{\text{solvent}}=5.5^\circ\text{C}$ and $k_f=4.9^\circ\text{C}/\text{m}$.

2.41 The vapor pressure of cyclohexane is 100hPa at 20°C . Calculate the vapor pressure in hPa of the solution resulting of mixing 3 moles of cyclohexane and 4 moles of I_2 .

2.42 The vapor pressure of cyclohexane is 100hPa at 20°C . Calculate the vapor pressure lowering of the solution resulting of mixing 3 moles of cyclohexane and 3 moles of I_2 .

2.43 The vapor pressure of cyclohexane is 100hPa at 20°C . Calculate the vapor pressure of the solution resulting of mixing 6 moles of cyclohexane and 1 moles of I_2 .

2.44 The vapor pressure of cyclohexane is 100hPa at 20°C . Calculate the vapor pressure lowering of the solution resulting of mixing 6 moles of cyclohexane and 1 moles of I_2 .

2.45 The vapor pressure of a solution made with 1moles of KCl in 2 moles of ethanol is 3.88 kPa at 20°C . Calculate the vapor pressure of pure ethanol at that temperature.

2.46 The vapor pressure of a solution made with 74.5g of KCl in 88g of Acetaldehyde (CH_3CHO) is 3.88 kPa at 20°C . Calculate the vapor pressure of pure ethanol at that temperature.

2.47 The normal boiling point of o-xylene is 144.4°C . A solution made of KCl in o-xylene has a vapor pressure of 608Torr at 144.4°C . Calculate the mole fraction of the solution.

2.48 The normal boiling point of isobutyl alcohol is 107.8°C . A solution made of NaCl in o-xylene has a vapor pressure of 500Torr at 107.8°C . Calculate the mole fraction of the solution.



2.49 Which of the following solutions will have a lower vapor pressure: (a) Pure water at 25°C (b) Pure water at 98°C (c) A solution of C₆H₁₂O₆ in water with $\chi_{C_6H_{12}O_6}=0.1$ at 25°C (d) A solution of C₆H₁₂O₆ in water with $\chi_{C_6H_{12}O_6}=0.01$ at 25°C (e) A solution of KCl in water with $\chi_{KCl}=0.01$ at 25°C (f) A solution of KCl in water with $\chi_{KCl}=0.1$ at 15°C

2.50 Which of the following solutions will have a highest vapor pressure: (a) Pure water at 25°C (b) Pure water at 98°C (c) A solution of C₆H₁₂O₆ in water with $\chi_{C_6H_{12}O_6}=0.1$ at 25°C (d) A solution of C₆H₁₂O₆ in water with $\chi_{C_6H_{12}O_6}=0.01$ at 25°C (e) A solution of KCl in water with $\chi_{KCl}=0.01$ at 25°C (f) A solution of KCl in water with $\chi_{KCl}=0.1$ at 15°C

2.51 Calculate the osmotic pressure of a 3M NaCl solution at 298K.

2.52 The osmotic pressure of a solution is 146.6 atm at 298K. Calculate the effective concentration of solute in the solution.

2.53 The osmotic pressure of a NaCl solution is 200 atm at 298K. Calculate the effective and nominal concentration of solute in the solution.

2.54 A semipermeable membrane separate two NaCl solutions with concentration 0.2M (on the left) and 0.1M (on the right). What side of the membrane will receive an osmotic flow of water?

2.55 A semipermeable membrane separate two solutions, 0.1M NaCl (on the left) and 0.1M CaCl₂ (on the right). What side of the membrane will receive an osmotic flow of water?

2.56 You want to calculate the molar mass of an unknown chemical by dissolving 1.01 g of the chemical and adding water until reaching 100.mL of solution. The osmotic pressure of this solution at 25°C was 10. Torr. Calculate the molar mass of the solute.

2.57 You want to calculate the molar mass of an unknown chemical by dissolving 11.2 g of the chemical and adding water until reaching 100.mL of solution. The osmotic pressure of this solution at 25°C was 15.1 Torr.

Calculate the molar mass of the solute.

2.58 Indicate the concentration of a NaCl solution isotonic with blood at 25°C ($\Pi=1.70$ atm).

2.59 Indicate the concentration of a glucose (C₆H₁₂O₆) solution isotonic with blood at 25°C ($\Pi=1.70$ atm).

2.60 You have two solutions with different concentration separated by a semipermeable membrane, a more concentrated (0.01M) and a less concentrated (0.001M). We apply a series of external pressure to the most concentrated solution at 25°C. Indicate for each pressure, if this will stop the osmotic flow of water, assuming the van't Hoff factor to be one: (a) 0.24 atm (b) 0.02 atm (c) 0.22 atm (d) 0.29 atm

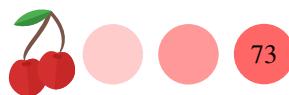
2.61 You have a solution (0.01M) in contact with the pure solvent separated by a semipermeable membrane. We apply a series of external pressure to the solution at 25°C. Indicate for each pressure, if this will stop the osmotic flow of water, assuming the van't Hoff factor to be one: (a) 0.24 atm (b) 0.02 atm (c) 0.22 atm (d) 0.29 atm

2.62 How much mass of solute would you need to prepare 100mL of a KCl (MW=74.5 g/mol) solution with osmotic pressure of 10 torr at 25°C.

2.63 How would you prepare 100mL of a sucrose C₁₂H₂₂O₁₁ (MW=342.29g/mol) solution with osmotic pressure of 7 torr at 20°C.

2.64 We measured the change of osmotic pressure with concentration for a given solute at a fixed temperature. Use the data below to experimentally compute van't Hoff's factor *i* for an unknown solute at 25°C given that R is 62.32 torr/(mol· K). Assume *i* does not change for the molarity range given.

M	Π (torr)
0.010	223
0.011	245
0.012	267
0.013	290
0.014	312



2.65 We measured the change of osmotic pressure with concentration for a given solute at a fixed temperature. Use the data below to experimentally compute van't Hoff's factor i for an unknown solute at 25°C given that R is 62.32 torr/(mol· K). Assume i does not change for the molarity range given.

M	Π (torr)
0.010	464
0.011	511
0.012	557
0.013	603
0.014	650

2.66 We measured the change of the boiling point of a solution with concentration at a fixed temperature. Use the data below to experimentally compute $i \cdot k_b$ for the solution and the boiling point of the pure solvent. Assume $i \cdot k_b$ does not change for the molarity range given.

m	T_b (°C)
0.010	34.02020
0.011	34.02222
0.012	34.02424
0.013	34.02626
0.014	34.02828

2.67 We measured the change of the boiling point of a solution with concentration at a fixed temperature. Use the data below to experimentally compute $i \cdot k_b$ for the solution and the boiling point of the pure solvent. Assume $i \cdot k_b$ does not change for the molarity range given.

m	T_b (°C)
0.010	208.059
0.011	208.065
0.012	208.071
0.013	208.076
0.014	208.083

2.68 We measured the change of the freezing point of a solution with concentration at a fixed temperature. Use the data below to experimentally compute $i \cdot k_f$ for the solution and the freezing point of the pure solvent. Assume $i \cdot k_b$ does not change for the molarity range given.

m	T_f (°C)
0.010	5.448
0.011	5.444
0.012	5.438
0.013	5.433
0.014	5.428

2.69 We measured the change of the freezing point of a solution with concentration at a fixed temperature. Use the data below to experimentally compute $i \cdot k_f$ for the solution and the freezing point of the pure solvent. Assume $i \cdot k_b$ does not change for the molarity range given.

m	T_f (°C)
0.010	-23.30
0.011	-23.33
0.012	-23.36
0.013	-23.39
0.014	-23.41

2.70 From the following solutions: (i) 0.1m KCl in water (ii) 0.2m NaCl in water (iii) 0.3m KOH in water select the one with: (a) lowest freezing point (b) highest freezing point (c) highest boiling point (d) lowest boiling point (e) lowest vapor pressure (f) highest vapor pressure (g) highest osmotic pressure (h) lowest osmotic pressure

2.71 From the following solutions: (i) 0.1m $C_6H_{12}O_6$ in water (ii) 0.1m KCl in water (iii) 0.1m K_2SO_4 in water select the one with: (a) lowest freezing point (b) highest freezing point (c) highest boiling point (d) lowest boiling point (e) lowest vapor pressure (f) highest vapor pressure (g) highest osmotic pressure (h) lowest osmotic pressure

2.72 From the following solutions: (i) 0.1m KCl in water (ii) 0.1m CaF_2 in water (iii) 0.1m $Ca_3(PO_4)_2$ in water select the one with: (a) lowest freezing point (b) highest freezing point (c) highest boiling point (d) lowest boiling point (e) lowest vapor pressure (f) highest vapor pressure (g) highest osmotic pressure (h) lowest osmotic pressure

2.73 From the following solutions: (i) 0.2m LiF in water (ii) 0.1m HF in water (iii) 0.3m Na_2SO_4 in water select the one with: (a) lowest freezing point (b) highest freezing point (c) highest boiling point (d) lowest boiling



point (e) lowest vapor pressure (f) highest vapor pressure
(g) highest osmotic pressure (h) lowest osmotic pressure

2.74 From the following solutions: (i) 0.2m CH₃OH in water (ii) 0.2m NaF in water (iii) 0.1m Ca(NO₃)₂ in water select the one with: (a) lowest freezing point (b) highest freezing point (c) highest boiling point (d) lowest boiling point (e) lowest vapor pressure (f) highest vapor pressure (g) highest osmotic pressure (h) lowest osmotic pressure

2.75 The vapor pressure of acetone and chloroform at 35°C are 345 and 293 torr, respectively. Calculate the corresponding vapor pressure of the following mixtures of both at 35°C, assuming the mixture is ideal: (a) 1 mol of acetone with 1 mole of chloroform (b) 2 mol of acetone with 1 mole of chloroform (c) 1 mol of acetone with 2 mole of chloroform

2.76 The vapor pressure of benzene and toluene at 20°C are 74 and 22 torr, respectively. A certain solution of both at 20°C has a vapor pressure of 50 torr. Assuming the mixture is ideal, (i) calculate the mole fraction of benzene in the mixture. (ii) calculate the mole fraction of toluene in the mixture.

IDEAL AND REAL SOLUTIONS

2.77 Which of the following mixtures would you expect to give the most ideal solution: (a) CH₃OH and H₂O or CH₃COCH₃ and H₂O (b) 0.001M KOH solution or 0.001M Ca(OH)₂ solution in water (c) CH₃F and HF or CH₄ and CH₃CH₃

2.78 Which of the following mixtures would you expect to give the most ideal solution: (a) 0.001M I₂ solution in benzene or 2M I₂ solution in benzene (b) 0.001M KCl solution or 0.001M HF solution in water (c) CH₃(CH₂)₃CH₃ and CH₃(CH₂)₇CH₃ or CH₃(CH₂)₃CH₃ and water

2.79 Data below lists the vapor pressure of mixtures of benzene and ethylene chloride at fixed temperature.

Mixture	$\chi_{C_2H_5Cl}$	P (torr)
a	0.0	268
b	0.25	260
c	0.50	252
d	0.75	244
e	1.00	236

Answer the following questions: (a) Which solution will have the lowest normal boiling point (b) Which solution will have the highest normal boiling point (c) Estimate the sign of ΔH_{sol} (d) Are the intermolecular forces weaker, stronger or similar than those of the pure substances

2.80 Data below lists the vapor pressure of mixtures of benzene and carbon disulfide at 25° temperature.

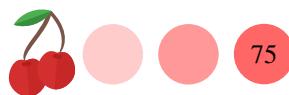
Mixture	χ_{CS_2}	P (mmHg)
a	0.0	100
b	0.25	175
c	0.50	245
d	0.75	275
e	1.00	350

Answer the following questions: (a) Which solution will have the lowest normal boiling point (b) Which solution will have the highest normal boiling point (c) Estimate the sign of ΔH_{sol} (d) Are the intermolecular forces weaker, stronger or similar than those of the pure substances

2.81 Data below lists the vapor pressure of mixtures of acetone ((CH₃)₂CO) and chloroform (CHCl₃) at 308.32 K temperature.

Mixture	χ_{CHCl_3}	P (torr)
a	0.0	350
b	0.25	300
c	0.50	260
d	0.75	250
e	1.00	285

Answer the following questions: (a) Which solution will have the lowest normal boiling point (b) Which solution will have the highest normal boiling point (c) Estimate the sign of ΔH_{sol} (d) Are the intermolecular forces weaker, stronger or similar than those of the pure substances



2.82 Data below lists the vapor pressure of mixtures of benzene (C_6H_6) and toluene (C_6H_5OH) at fixed temperature.

Mixture	$\chi_{C_6H_6}$	P (torr)
a	0.0	60
b	0.25	80
c	0.50	110
d	0.75	150
e	1.00	180

Answer the following questions: (a) Which solution will have the lowest normal boiling point (b) Which solution will have the highest normal boiling point (c) Estimate the sign of ΔH_{sol} (d) Are the intermolecular forces weaker, stronger or similar than those of the pure substances

FACTORS AFFECTING THE SOLUBILITY OF SOLIDS AND GASES

2.83 The solubility of a gas in water at 298K when its partial pressure is 0.9atm is $1.26 \times 10^{-3}M$. Calculate: (a) Henry's law constant at that temperature (b) The solubility at a partial pressure of 0.5atm

2.84 The solubility of a gas in water at 298K when its partial pressure is 1.9atm is $2.65 \times 10^{-4}M$. Calculate: (a) Henry's law constant at that temperature (b) The solubility at a partial pressure of 0.9atm

2.85 The table below provides solubility data in water for a series of alcohols. Rationalize the trends based on what you have learned on this chapter.

Compound	$s (g/100gH_2O)$
$CH_3(CH_2)_3OH$	9
$CH_3(CH_2)_4OH$	2.7
$CH_3(CH_2)_5OH$	0.6
$CH_3(CH_2)_6OH$	0.18

2.86 The table below provides solubility data in water for a series of alcohols. Rationalize the trends based on what you have learned on this chapter.

Compound	$s (g/100gH_2O)$
$CH_3(CH_2)_3OH$	5.9
$C_6H_{11}-OH$	36

ENTHALPY OF SOLUTION

2.87 Which of the species of the following pairs would you expect to have a larger, more positive, enthalpy of hydration, corresponding to a less favored hydration? (a) Na^+ or Mg^{2+} (b) H^+ or NH_4^+ (c) Mg^{2+} or Ca^{2+} (d) Cl^- or ClO_4^-

2.88 Which of the species of the following pairs would you expect to have a larger, more positive, enthalpy of hydration, corresponding to a less favored hydration? (a) Li^+ or Na^+ (b) Rb^+ or K^+ (c) Li^+ or Cs^+ (d) Li^+ or Be^{2+}

2.89 Which of the species of the following pairs would you expect to have a larger, more positive, enthalpy of expansion—defined in the context of hydration enthalpy, as the energy needed to separate the molecules of a compound into its gas state? (a) $H_2O(l)$ or $CaCl_2(s)$ (b) $CH_3(CH_2)_2CH_3(g)$ or $CH_3(CH_2)_9CH_3(g)$ (c) $H_2O(l)$ or $SO_2(g)$

2.90 Which of the species of the following pairs would you expect to have a larger, more positive, enthalpy of expansion—defined in the context of hydration enthalpy, as the energy needed to separate the molecules of a compound into its gas state? (a) $H_2O(l)$ or $NaCl(s)$ (b) $H_2O(l)$ or $C_6H_{10}(l)$ (c) $C_6H_5OH(l)$ or $C_6H_{10}(l)$

2.91 The lattice energy of NaF, the solute, is -910 KJ/mol, whereas the enthalpy of hydration of Na^+ and F^- are -406 and -524 KJ/mol, respectively. (a) Calculate the hydration energy of NaF (b) Calculate the energy needed to expand the solute (c) Calculate the enthalpy of solution. Is the dissolution endothermic or exothermic?

2.92 The lattice energy of KF, the solute, is -808 KJ/mol, whereas the enthalpy of hydration of K^+ and F^- are -320 and -524 KJ/mol, respectively. (a) Calculate the hydration energy of KF (b) Calculate the energy needed to expand the solute (c) Calculate the enthalpy of solution. Is the dissolution endothermic or exothermic?



Ch. 3. Chemical kinetics

THE rate at which a chemical reaction occurs is a critical parameter at an industrial and laboratory-level as the faster the speed the sooner one can commercialize or sell a given chemical product. Slow chemical reactions are, in general, less desirable as it takes more time for the reagents to react. On the other hand, too fast chemical reactions can also be less desirable. Think, for example, in an explosion in which gas and a spark quickly generate carbon dioxide with water and a lot of heat in a way that is not easy to control. This chapter deals with the rate of reactions. You will learn how to calculate what we call a rate law which is a mathematical formula that gives the numerical rate value. You will also learn the collision theory that explains the factors that affect the speed of chemical reactions.

3.1 Rate of reaction

Some chemical reactions are fast such as the explosive reaction between cooking gas and oxygen, happening almost instantaneously. Other reactions are slow such as the rusting of iron, taking months to occur. Chemical kinetics is a chemistry discipline that studies the speed of chemical reactions and the factors that affect this measure. The overall goal here is to understand the factors that control the rate of reactions with the ultimate goal of maximizing the generation of products. This section covers the principles of reaction rates, defining two different types of rates, and showing how to interconvert rates of reaction.

Two different ways of defining the reaction rate When a chemical reaction proceeds, reactants decompose into products. Therefore, the concentration of reactants decreases with time as reactant molecules become products, and the concentration of products increases with time as products are being formed. This change in concentration with time is what we call reaction rate. There are two different ways of defining the rate of a reaction. We can define the average reaction rate \bar{r} as the change in concentration with time or as an instantaneous rate r when the time interval is very small (we call this derivative):

$$\bar{r} = \frac{\Delta c}{\Delta t} \quad \text{or} \quad r = \lim_{\Delta t \rightarrow 0} \frac{\Delta c}{\Delta t} = \frac{dc}{dt} \quad (3.1)$$

Both types of rates are not numerically the same. The average rate is an average change in concentration between two different times. At the same time, the time interval for the average can be large or small. Differently, the instantaneous rate is calculated as the slope in the concentration vs. time plot at a given time—using mathematical terms



we call this the derivative. Instantaneous rates represent more accurately the changes in concentration happening in a reaction. For this reason, from now on, whenever we describe a reaction rate we will refer to the instantaneous rate.

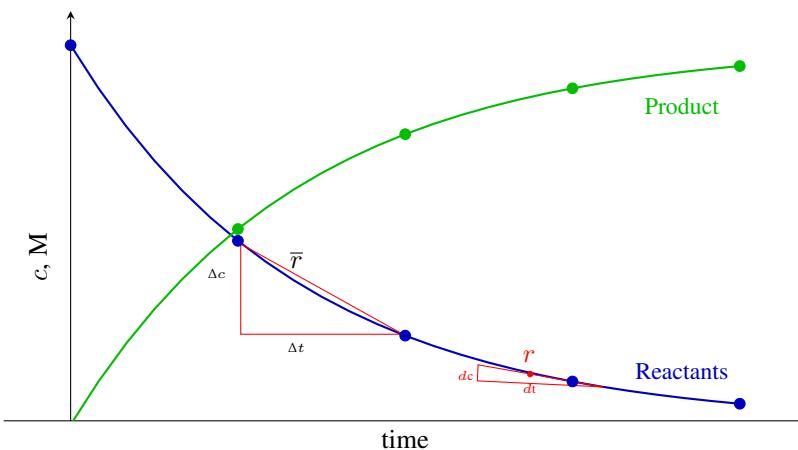


Figure 3.1 Change of the concentration of reactants and products with time showing the average and instantaneous velocity.

Rate of appearance and disappearance At the beginning of a reaction, the molecules of reactants will be consumed while the molecules of products will form (see Figure 3.1). There are three different ways to measure the reaction rate. We can measure the amount of reactants that disappear per unit of time and this would give you the rate of disappearance of a reactant. We can also measure the amount of products formed per unit of time and that would give you the rate of appearance of a product. As a note, rates of disappearance are negative (as the molarity of reactants decreases with time) whereas rates of appearance are positive. Finally, we can measure the amount of reactants that interconvert into products and that would give you the overall rate of reaction, which is always a positive number. Overall, by measuring concentration changes of reactants and products we can compute three types of rates: rates of disappearance, rates of appearance, and rates of reaction. Let us work on a sample reaction:



We can think of the rate of disappearance of $\text{I}_{(\text{aq})}^-$ that should be written as:

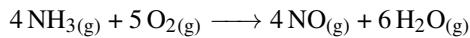
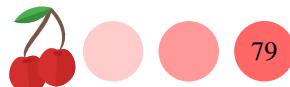
$$r_{\text{I}^-} = \frac{d[\text{I}^-]}{dt}$$

Similarly, we have that the rate of appearance of Cl^- is:

$$r_{\text{Cl}^-} = \frac{d[\text{Cl}^-]}{dt}$$

As chemical rates represent the change of concentration of a given reactant with time, the units for a chemical rate are M/s.

Relating rates of appearance and disappearance We can relate the rates of any two reactants or products in a chemical reaction and, at the same time, we can relate the rate of reaction with the rate of any product or reactant—remember there is a single rate of reaction and multiple rates of appearance and disappearance of products and reactants. For example, for the following reaction:



We can relate r_{NH_3} and $r_{\text{H}_2\text{O}}$:

$$-\frac{1}{4}r_{\text{NH}_3} = +\frac{1}{6}r_{\text{H}_2\text{O}}$$

Overall, a negative sign should be included before the rate of any reactant and a positive sign before the rate of any product. You also need to divide by the stoichiometric coefficients of each reactant and product. Similarly, we can relate r_{O_2} with the rate of reaction r :

$$-\frac{1}{5}r_{\text{O}_2} = r$$

For a general equation such as:



we have that the general relationship between any rate and the overall reaction rate is:

$$r = -\frac{1}{a}r_A = -\frac{1}{b}r_B = +\frac{1}{c}r_C = +\frac{1}{d}r_D \quad (3.2)$$

Sample Problem 33

For the reaction below, the rate of disappearance of A is -0.1M/s . Calculate:

- (a) The rate of disappearance of B.
- (b) The rate of appearance of C.
- (c) The rate of appearance of D.
- (d) The rate of reaction.



SOLUTION

In order to calculate the rate of disappearance of B, we will use the following relationship, in which the rate of disappearance of A and B have a negative sign and carries the respective stoichiometric coefficient

$$-\frac{1}{2}r_A = -\frac{1}{3}r_B$$

We know r_A and hence we can solve for r_B :

$$-\frac{1}{2}(-0.1) = -\frac{1}{3}r_B$$

We have that r_B is -0.15M/s . We will now use a similar relationship to calculate r_C :

$$-\frac{1}{2}(-0.1) = +\frac{1}{4}r_C$$

We have that r_C is $+0.2\text{M/s}$. Finally, we will calculate r_D and r :

$$-\frac{1}{2}(-0.1) = +\frac{1}{5}r_D \text{ and } -\frac{1}{2}(-0.1) = r$$

We have that r_D is $+0.25\text{M/s}$ and r is 0.05M/s . Mind the rate of disappearance of reactants are negative, whereas the rate of appearance of products and the overall rate of reaction are positive numbers.

❖ STUDY CHECK

For the reaction below, the rate of appearance of C is 0.3M/s . Calculate: (a) The rate of disappearance of A and B. (b) The rate of appearance of D. (c) The rate of reaction.



► Answer: $r_A = -1.5 \text{ M/s}$, $r_B = -0.6 \text{ M/s}$, $r_D = 0.6 \text{ M/s}$, and $r = 0.3 \text{ M/s}$

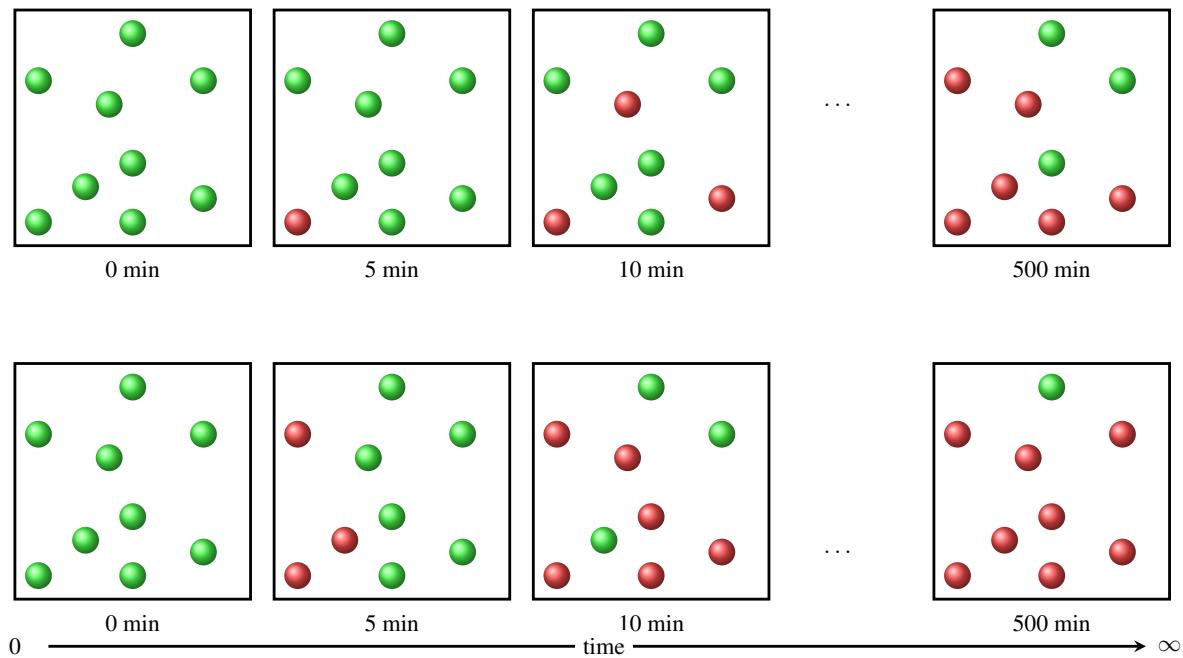


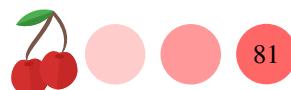
Figure 3.2 A fast and a slow reaction

3.2 Rate law

Some chemical reactions double their rate by increasing the concentration of reactants, whereas, for the same change of concentration, others quadruple their rate. The rate law of a reaction is an experimental formula that explicitly includes the power dependence of the rate of reaction on the concentration of reactants and products. You can find rate laws in a differential form and in an integrated form. On one hand, the differential rate law, or simply the rate law, is convenient when we want to assess the impact of concentration on the rate of reaction. On the other hand, integral rate laws give the time dependency of the concentration, being convenient to track how the reactants disappear with time. This section will cover how to interpret rate laws and how to differentiate rate laws from integral rate laws. It will also introduce the concept of the partial and the total order of reaction, as well as the idea of reaction rate constant.

The rate law The rate law is an experimental expression, a formula that comes from an experiment, relating the rate of reaction with the concentration of the chemicals that impact the rate. An example of a rate law would be:

$$r = k[\text{NO}]^2[\text{O}_2]$$



where:

r is the overall rate of reaction

k is the rate constant

$[NO]$ is the molarity of NO

$[O_2]$ is the molarity of O₂

So, what is the purpose of a rate law? Let us use the following rate law as an example:

$$r = 0.002[NO]^2[O_2]$$

By means of the rate law above, we can compute the numerical value of the rate of reaction for different concentrations. As such, rate laws help predict the value of the reaction rate.

Partial and overall reaction orders The powers in the rate law are called reaction order. For example, in the rate law below

$$r = k[NO]^2[O_2]$$

the order of NO is 2 as the power of NO in the rate law is 2. Similarly, the partial order of O₂ is 1 as the power of O₂ in the rate law is 1. The overall reaction order is 3, and this number results in adding all partial orders. Regarding the way we describe the reaction order, if the reaction order is one, we would say that the reaction is first order. Similarly, if the reaction order is two, we would say the reaction is second order, and so on. The reaction order can also be zero when the power in the rate law is zero. Reaction orders tend to be integer numbers such as 0, 1, or 2, mostly in educational problems. However, using realistic kinetic data, the partial and total orders can be any number and even have a negative sign. The reaction orders are very important as they indicate how the reaction rate responds to changes in concentration. For example, using the rate law above, if we double the concentration of O₂ the rate law will double, but if we double the concentration of NO, the reaction rate would quadruple, that is, it would be four times larger.

The rate constant, k The rate constant is a critical parameter of a rate law as it tells how the reaction responds to changes in molarity. For example, look at these two different rate laws:

$$r_A = 0.01[N_2O_5] \quad \text{and} \quad r_B = 0.001[N_2O_5]$$

We have that as the rate constant in r_A is larger the changes in the concentration of N₂O₅ will have a stronger impact on the rate than in r_B .

Sample Problem 34

Given the following rate law. Indicate: (a) The rate constant giving the correct units. (b) The partial order of all species. (c) The total order of the reaction. (d) If [F₂] is doubled how would the reaction rate be affected?

$$r = 0.002[Cl_2][F_2]^3$$

SOLUTION

Given the information provided in the rate law, we have that the reaction is first



order with respect to Cl_2 and third order with respect to F_2 . The overall reaction order is four. The rate constant is $0.002 \text{ 1/M}^2\text{s}$.

◆ STUDY CHECK

Given the following rate law. Calculate: (a) The rate constant giving the correct units. (b) The partial order of all species. (c) The total order of the reaction. (d) If $[\text{A}]$ is doubled how would the reaction rate be affected?

$$r = 0.056[\text{A}]^4[\text{B}]^2[\text{C}]^2$$

►Answer: Orders: A(4), B(2), C(2), overall(8); $k=0.056 \text{ 1/M}^7\text{s}$; 16 times larger

The rate constant units The units of a rate constant are determined by the reaction order. In other words, given a reaction order, we will have a given unit for the rate constant. At the same time, given the units of a rate constant, we can also determine the order of the reaction. The following formula gives the constant units for a given reaction order n :

$$\frac{\text{M}^{1-n}}{\text{s}} \quad (3.3)$$

where:

n is the reaction order

For example, for first-order reaction ($n=1$) the units of the reaction constant are $1/\text{s}$ and for a second-order reaction, the units are $1/\text{M}\cdot\text{s}$. For a reaction of zero-order, the units of the constant are M/s . This formula results from a dimensional analysis given that the units of reaction rate r are M/s and the units of concentration is molarity, M . As a side note, here we will use second as a unit of time, however, one can envision a similar formula for different time units.

Sample Problem 35

Given the following rate constants indicate the reaction order: (a) $k=0.04 \text{ M/s}$ (b) $k=0.09 \text{ 1/M}\cdot\text{s}$ (c) $k=0.03 \text{ 1/M}^4\cdot\text{s}$

SOLUTION

We will use Formula 3.3 to calculate the reaction order. We have that 0.04 M/s is order zero, $0.09 \text{ 1/M}\cdot\text{s}$ is second order and $0.03 \text{ 1/M}^4\cdot\text{s}$ is fifth order.

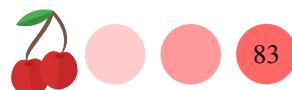
◆ STUDY CHECK

Given the following rate constants indicate the reaction order: (a) $k=0.03 \text{ 1/s}$ (b) $k=3 \times 10^{-4} \text{ L/s}\cdot\text{mol}$ (c) $k=3 \times 10^{-5} \text{ 1/s}\cdot\text{M}^2$

►Answer: (a) Order 1 (b) Order 2 (c) Order 3

Integral reaction law The reaction law is more specifically called a differential reaction law as it represents a differential equation—this is a mathematical term to describe equations in terms of derivatives. For a differential rate law, there is an integral rate law. The integral rate law is obtained using a mathematical technique called integration—this technique is out of the scope of this class. For example, below we have an example of a differential and integral rate law for a first-order reaction.

$$r = 0.01[\text{N}_2\text{O}_5] \quad \text{and} \quad \ln[\text{N}_2\text{O}_5] = -0.01 \cdot t + \ln(0.1)$$



In the differential rate law, we have the explicit reaction rate r accompanied by molarities ($[N_2O_5]$), whereas in the corresponding integral rate law we have molarities ($[N_2O_5]$) accompanied of time. The integral rate law gives the change of the concentration with time, whereas the differential rate law gives the change of the reaction rate with concentration. Each type of law has its purpose and differential rate laws are more common and used when we have experimental data in terms of reaction rates and molarities. The integrated rate law is used when we have data in terms of molarity and time. Overall, differential rate laws and integral rate laws are exchangeable. To convert a differential rate law into its corresponding integral rate law we just need the initial concentration of the species involved in the law, $[A]_0$. For example, the corresponding differential and integral rate law for a zeroth-order reaction are: Table 3.1 reports the corresponding differential and integral rate laws for different orders.

Table 3.1 Corresponding differential, integral rate laws and half-life formulas

Order	Differential rate law	Integral rate law	Half-life ($t_{1/2}$) formula
0	$r = k$	$[A] = -k \cdot t + [A]_0$	$\frac{[A]_0}{2k}$
1	$r = k[A]$	$\ln[A] = -k \cdot t + \ln[A]_0$	$\frac{0.693}{k}$
2	$r = k[A]^2$	$\frac{1}{[A]} = k \cdot t + \frac{1}{[A]_0}$	$\frac{1}{k[A]_0}$

Sample Problem 36

Identify the following rate law as differential or integral and switch into the other form.

$$\frac{1}{[C_2H_6]} = 4 \times 10^{-4} \cdot t + \frac{1}{0.03}$$

SOLUTION

As the equation contains time this would be a integrated rate law. We can use Table 3.1 to identify the order and compute the differential law. This is a second order reaction with rate constant 4×10^{-4} 1/s, therefore:

$$r = 4 \times 10^{-4}[C_2H_6]$$

❖ STUDY CHECK

Identify the following rate law as differential or integral and switch into the other form for an initial concentration of 0.3M.

$$r = 5 \times 10^{-2}$$

►Answer: $[A] = -5 \times 10^{-2} \cdot t + 0.3$

Half-life, $t_{1/2}$ When a reaction starts to happen, the concentration of reactants decreases with time. Half-life is the time at which the initial concentration of reactants



is half its initial value. Reactions with small half-life are fast, as they take a short time to reduce the concentration of reactants to half. Differently, reactions with large half-life are slow as they need longer times to proceed. This way, the numerical value of half-life helps you compare the speed of reactions. At the same time, the half-life is a transformation of the rate constant into a time value. That is, by rate constants can be converted into half-lives. There is a single half-life formula for each reaction order and Table ?? reports some half-life formulas. If you wonder, where these formulas come from, one can obtain all these formulas by using $[A] = [A]_0/2$ in any integral rate law. For example, for a first order reaction we have that:

$$\ln[A] = -k \cdot t + \ln[A]_0$$

When $[A] = [A]_0/2$ we have that $t = t_{1/2}$ and therefore:

$$\ln\left(\frac{[A]_0/2}{[A]_0}\right) = -k \cdot t_{1/2}$$

that leads to

$$t_{1/2} = -\frac{\ln(0.5)}{k}$$

Sample Problem 37

Calculate the half-life for a second order reaction with initial concentration of 5.99×10^3 M if the rate constant is 0.005 1/Ms?

SOLUTION

As we deal with a second order reaction, we will use $\frac{1}{k[A]_0}$ given that $[A]_0 = 5.99 \times 10^3$ M and $k=0.005$ 1/Ms. We have that

$$t_{1/2} = \frac{1}{0.005 \cdot 5.99 \times 10^3} = 0.03s$$

◆ STUDY CHECK

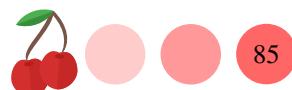
Calculate the half-life for a first order reaction with initial concentration of 5.99×10^3 mol/L if the rate constant is 0.02 1/s?

►Answer: 34.65s

3.3 The differential and integral methods for obtaining rate laws

Up to now, we analyzed the importance of using rate laws. However, before this point, all rate laws were given. This section will cover how to experimentally obtain rate laws by analyzing experimental data. There are two main methods for obtaining rate laws: the differential method and the integral method and each method differs not only on the nature of the experimental data gathered but also on how this data is processed.

The differential method The differential method also called the method of the initial rates measures velocities for different concentrations, and in particular, measures initial velocities. These are velocities at very short times after the reaction starts. This method is convenient when there are parasite reactions that compete with the reaction one wants to study. By using initial rates, we can minimize the impact of competing reactions on the kinetic data. In this method, by comparing different velocities for



different concentrations one can calculate the reaction order and the rate constant, that is, one can construct the rate law. The next example will show you how to use this method. As a note, one can only use the differential method when reaction rates data is supplied.

Sample Problem 38

Use the data below to calculate the rate law of the following reaction:



Experiment	r (M/s)	$[A]$, (M)
1	0.5	0.5
2	0.72	0.6

SOLUTION

As they provide values of $[A]$ the rate law should be $r = k[A]^n$. In order to calculate the rate law we need the values of k and n . We will apply the rate law to the two different experiments and divide:

$$\begin{aligned} 0.5 &= k0.5^n & (\text{Experiment 1}) \\ 0.72 &= k0.6^n & (\text{Experiment 2}) \end{aligned} \left\{ \frac{0.5}{0.72} = \frac{k}{k} \cdot \left(\frac{0.5}{0.6} \right)^n \right.$$

This approach will cancel k leaving only n .

$$0.694 = (0.833)^n$$

Remember that if we divide two numbers with the same exponent we can combine the numbers and share the exponents. In order to solve for n we need to apply natural logarithms (or simply log) to both sides of the equation in order to move the exponent down:

$$\ln(0.694) = n \cdot \ln(0.833) \text{ that gives } n = \frac{\ln(0.694)}{\ln(0.833)} = 1.99 = 2$$

Remember the orders are normally integer numbers so you can round to the closest integer. Now that we have the order, we can use the rate law again to obtain the rate constant using for example: $r=0.5\text{M/s}$ and $[A]=0.5\text{M}$, and given that now we know $n=2$

$$0.5 = k0.5^2$$

Solving for k we have $k=2\text{ 1/Ms}$. We have that the reaction law is: $r = 2[A]^2$

◆ STUDY CHECK

Use the data below to calculate the rate law of the following reaction: $\text{A} \longrightarrow \text{B}$

Experiment	r (M/s)	$[A]$, (M)
1	0.5	2.5
2	0.6	3.0

►Answer: $r = 0.2[A]^1$



was useful to obtain the rate law using data involving only the concentration of one reactant. In other words, the previous example was useful to obtain simple rate law such as:

$$r = k[A]^x$$

The next example will cover how to calculate the rate law when the data provided involved the concentration of two reactants and therefore the rate law contains the orders of two species. In other words, the next example will show how to obtain more complex rate laws such as:

$$r = k[A]^x[B]^y$$

in which we do not know the reaction constant and two of the order.

Sample Problem 39

Use the data below to calculate the rate law of the following reaction: A + B \longrightarrow C

Experiment	[A] (M)	[B] (M)	r (M/s)
1	0.5	0.2	0.25
2	0.6	0.2	0.36
3	0.5	0.3	0.375
4	0.6	0.3	0.54

SOLUTION

As they provide values of [A] and [B] the rate law should be $r = k[A]^n[B]^m$. In order to calculate the rate law we need the values of k , n and m . We will apply the rate law to the two different experiments and divide. But this time we will sort the data appropriately. In order to calculate the order of A we will select the data with different values of [A] and the same value of [B]:

Experiment	[A] (M)	[B] (M)	r (M/s)
1	0.5	0.2	0.25
2	0.6	0.2	0.36

Again, we will apply the rate law to each Experiment:

$$\begin{aligned} 0.25 &= k \cdot 0.5^n \cdot 0.2^m & (\text{Experiment 1}) \\ 0.36 &= k \cdot 0.6^n \cdot 0.2^m & (\text{Experiment 2}) \end{aligned}$$

$$\frac{0.25}{0.36} = \frac{k \cdot (0.5)^n \cdot (0.2)^m}{k \cdot (0.6)^n \cdot (0.2)^m}$$

$$\frac{0.25}{0.36} = \left(\frac{0.5}{0.6}\right)^n$$

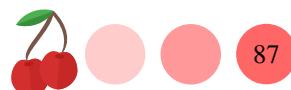
This approach will cancel k and [B] leaving only n giving

$$0.694 = (0.833)^n$$

In order to solve for n we need to apply natural logarithms (or simply log) to both sides of the equation in order to move the exponent down:

$$\ln(0.694) = n \cdot \ln(0.833) \text{ that gives } n = \frac{\ln(0.694)}{\ln(0.833)} = 1.99 = 2$$

Again, remember the orders are normally integer numbers so you can round to the closest integer. In order to calculate the order of B we will select the data with different values of [B] and the same value of [A]:



Experiment	[A] (M)	[B] (M)	r (M/s)
1	0.5	0.2	0.25
3	0.5	0.3	0.375

Again, we will apply the rate law to each Experiment:

$$\left. \begin{array}{l} 0.25 = k0.5^n0.2^m \quad (\text{Experiment 1}) \\ 0.375 = k0.5^n0.3^m \quad (\text{Experiment 3}) \end{array} \right\} \frac{0.25}{0.375} = \frac{k}{k} \cdot \left(\frac{0.5}{0.5} \right)^n \cdot \left(\frac{0.2}{0.3} \right)^m$$

We have that $0.666 = (0.66)^m$. The order of B is $m=1$. Now that we have the order, we can use the rate law again to obtain the rate constant using any of the experiments:

$$0.25 = k0.5^20.2^1 \quad (\text{Experiment 1})$$

$r=0.5\text{M/s}$ and $[A]=0.5\text{M}$, and given that now we know $n=2$

$$0.5 = k0.5^2$$

Solving for k we have $k=2 \text{ 1/M}^2\text{s}$. We have that the reaction law is: $r = 2[A]^2[B]^1$

❖ STUDY CHECK

Use the data below to calculate the rate law of the following reaction: A + B \longrightarrow C

Experiment	[A] (M)	[B] (M)	r (M/s)
1	0.5	0.2	2×10^{-4}
2	0.6	0.2	2×10^{-4}
3	0.5	0.3	4.5×10^{-4}
4	0.6	0.3	4.5×10^{-4}

►Answer: $r = 5 \times 10^3[B]^2$

Table 3.2 The integral method

Order	y	x	Slope	Slope Sign	Intersect
0	$[A]$	t	$-k$	—	$[A]_0$
1	$\ln([A])$	t	$-k$	—	$\ln([A]_0)$
2	$\frac{1}{[A]}$	t	$+k$	+	$\frac{1}{[A]_0}$

The integral method: an introduction The integral method is used to calculate the rate law if data reporting concentration and time are given. To understand the use of the integral method, it is convenient to learn more about integral rate laws. Let us analyze the integral rate law for a zeroth-order reaction:

$$[A] = -k \cdot t + [A]_0$$

If you look carefully you could notice that this integral rate law is indeed a linear relationship. The term $[A]_0$ and k are constants. Differently, the terms $A]$ and t are variables. Linear relationships are mathematical relationships with an independent variable represented in the horizontal axes and a dependent variable represented in the



vertical axis. In the rate law above the independent variable is t and the dependent variable is $[A]$ and for every value of t we would have a given value of $[A]$. Moreover, $-k$ is the slope of the relationship, and $[A]_0$ is the intersect. Let us analyze another integral rate law, this time for a first-order reaction:

$$\ln[A] = -k \cdot t + \ln[A]_0$$

we have that this law also represent a linear relationship as well, with t as independent variable (the x) and $\ln([A])$ as the dependent variable (the y). The slope is $-k$ and the intersect is $\ln([A]_0)$. Overall, we have that all integral rate laws are linear relationship with t as the x and different properties as the y : $[A]$ for a zeroth-order, $\ln([A])$ for a first-order reaction and $\frac{1}{[A]}$ for a second-order reaction. We also have that the slope of the lines in absolute value always gives k . This information is summarized in Table 3.2.

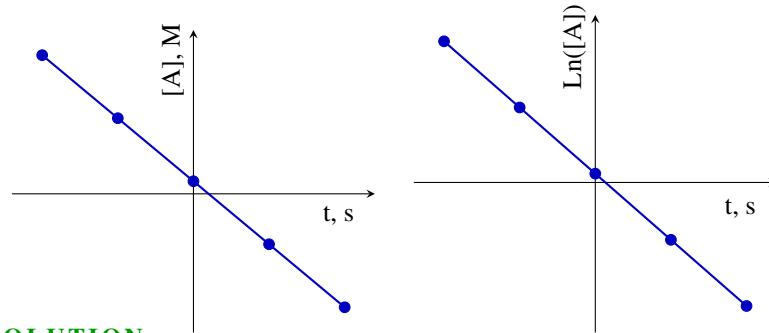
The integral method is based on plotting some kinetic data, for example, concentration vs. time, and fitting the data into a linear relationship. If the quality of the fit is good enough, by reading the slope of the line and the intersect one can compute the rate law that rules the reaction. To associate the experimental data into a line we use linear regression, a statistical tool that gives the equation of the best line that fits the experimental data. At the same time, linear regression gives an estimate of the goodness of the fit through a regression parameter, r or r^2 , depending on the statistics software employed. Overall, is good to keep in mind that every plot ($[A]$ vs. t , $\ln[A]$ vs. t or $1/[A]$ vs. t) is associated to a specific order.

The integral method: associating a linear plot with an order

The base of the integral method is to create three different plots: (a) $[A]$ vs. t (b) $\ln[A]$ vs. t and (c) $\frac{1}{[A]}$ vs. t . In all plots, time is always indicated in the horizontal axis. Based on the data, only one of the plots will be the best linear plot with a regression coefficient r^2 closer to one. The perfect linear plot will be associated with an order (here, either 0, 1, or 2). If the plot $[A]$ vs. t gives a perfect line the reaction will be zeroth-order. If the plot $\ln([A])$ vs. t gives a perfect line the reaction will be first order. If the plot $\frac{1}{[A]}$ vs. t gives a perfect line the reaction will be second-order. It is convenient to practice identifying the different plots and associating them with an order. The following example covers just that.

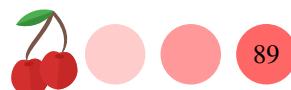
Sample Problem 40

The following plots results from processing kinetic data by means of the integral method. They are all perfect lines with $r^2=0.99$. Indicate the order of the reaction.



SOLUTION

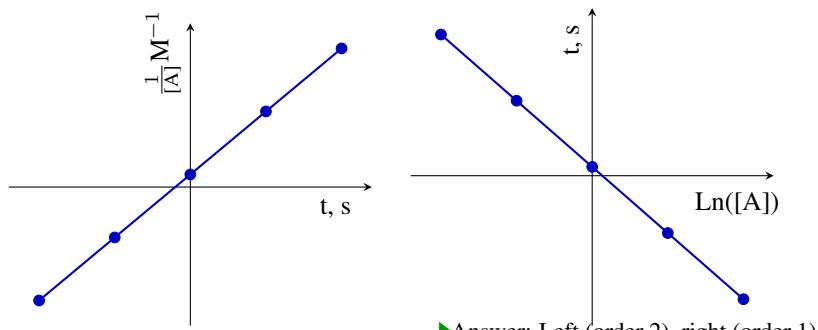
We will inspect the linear plot and based on what is represented on the vertical and horizontal axis we will conclude the reaction order. The plot on the left represents molarity on the vertical axis and time on the horizontal. This is a



zeroth-order reaction. On the other hand, the plot on the right represents the logarithm of molarity on the vertical axis and time on the horizontal axis. This is a first-order reaction.

STUDY CHECK

The following plots results from processing kinetic data by means of the integral method. They are all perfect lines with $r^2=0.99$. Indicate the order of the reaction.



►Answer: Left (order 2), right (order 1)

How to carry out a linea regresion with a calculator First and foremost, to carry out a linear regression, you need a graphing calculator. In general, Casio calculators are very user-friendly and easy to use. Differently, Texas calculators tend to be hard to employ. Here I will show how to carry out a linear regression displaying the correlation coefficient r^2 parameter on the screen first using a Casio calculator and then using a Texas calculator. You need to follow the following steps to carry out a linear regression in a Casio fx 9750GII:

- 1 **Step one:** Enter the data: start the calculator and press menu+2 (stat) to access the list menu. You will follow all the steps on this menu. Type the X values in List 1 and Y in List 2.
- 2 **Step two:** Press Calc (F2) on the bottom menu of the screen, then press Reg (F3) to press X (F1) and then $ax + b$ (F1).
- 3 **Step three:** At this point, you will have all the results from the regression on the screen.

You need to follow the following steps to carry out a linear regression in a TI 84:

- 1 **Step one:** Enter the data: press Stat and Enter. Type the X values in List 1 and Y in List 2.
- 2 **Step two:** Press Second and Zero to access the catalog. Now, go down the menu until you find DiagnosticOn and select it.
- 3 **Step three:** Now carry out the regression by pressing Stat and Calc. Now go down on the menu until you find $ax + b$ and press it.
- 4 **Step four:** At this point, you will have all the results from the regression on the screen.

The integral method: extracting data from linear regressions

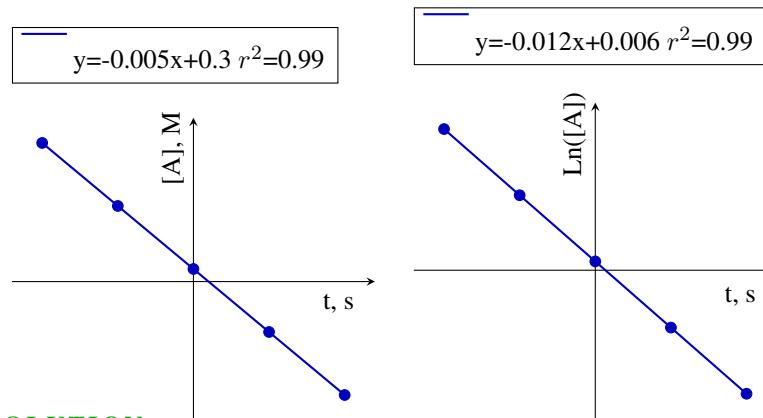
We will practice the integral method by extracting the rate constant and the initial reactant concentration from the linear regression data. Linear regression software will



give the equation of a line and the associated r coefficient. We will have to read the slope and the intercept of the equation and infer the rate constant and the initial reactant concentration $[A]_0$. The rate constant will be obtained from the slope of the line, whereas $[A]_0$ is related to the intercept. For all cases, the absolute value of the slope of the line equation will correspond to the rate constant k . The relationship between $[A]_0$ and the intercept differs based on the order. For a zeroth-order plot, the intersect directly corresponds to the initial concentration. Differently, for a first-order reaction, the intercept corresponds to $\ln([A]_0)$. Therefore, to obtain $[A]_0$ you will have to compute the exponential of the intersect: $[A]_0 = e^{Intercept}$. Finally, for a second-order reaction, the slope will correspond to the inverse of the initial concentration, and hence, to obtain $[A]_0$ we will have to compute the inverse of the intersect: $[A]_0 = \frac{1}{Intercept}$. The following example shows how to obtain the rate constant and $[A]_0$ using regression results.

Sample Problem 41

The following plots results from processing data by means of the integral method. Interpret the linear regressions and indicate the rate law.

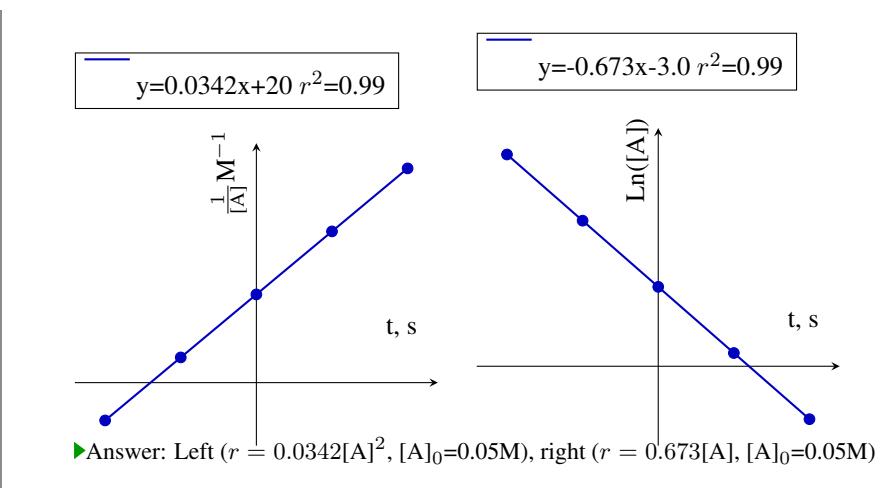


SOLUTION

We will inspect the linear regression to identify the reaction order. From the absolute value of the slope, we will obtain the rate constant. The plot from the left represents molarity and hence this is a zeroth-order reaction with a rate constant $k=0.005\text{M/s}$. The rate law would be: $r = 0.005$. The plot from the right displays the logarithm of the concentration and hence this would be a first-order reaction, with a rate constant $k=0.012\text{ 1/s}$. The rate law would be: $r = 0.012[A]$. We can also calculate the initial concentration for each plot. On the left plot, we have that as this is a zeroth-order reaction the intercept directly gives you the initial concentration of reactants: $[A]_0=0.3\text{M}$. On the right plot, we have that as this is a first-order reaction the intercept gives you the logarithm of the initial concentration of reactants. We have that $\ln([A]_0)=0.006$ and hence $[A]_0=e^{0.006}=1.006\text{M}$.

❖ STUDY CHECK

The following plots results from processing data by means of the integral method. Interpret the linear regressions and indicate the rate law and the initial concentration of reactants.



▼ Speed is a critical concept in chemistry



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▼ Explosions are fast reactions



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▼ Sparks can activate reactions



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Sample Problem 42

Using the following data, apply the integral method to calculate the order and rate constant and write down the rate law.

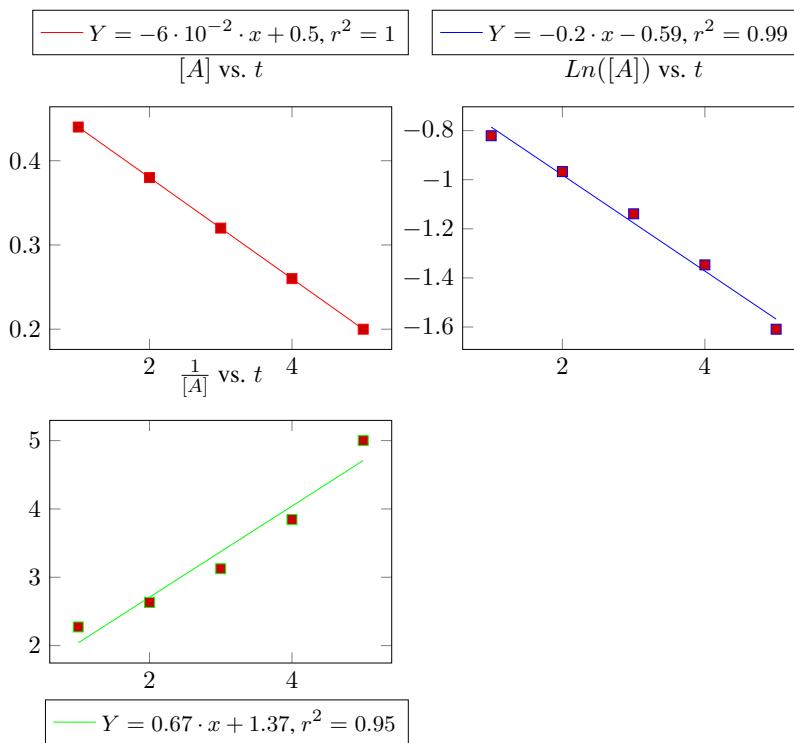
t (s)	1	2	3	4	5
$[A]$, (M)	0.44	0.38	0.32	0.26	0.20

SOLUTION

We will apply the integral method and will process the data calculating the logarithm of the molarity and the inverse of molarity. It is recommended to use three digits in order for the regression to be consistent:

t (s)	$[A]$, (M)	$\ln([A])$	$\frac{1}{[A]}$, (M^{-1})
1	0.440	-0.821	2.273
2	0.380	-0.967	2.631
3	0.320	-1.139	3.125
4	0.260	-1.347	3.846
5	0.200	-1.609	5.000

Now we will create three different plots and carry linear regressions for each:



We have the reaction can be order zero or order one, as for both cases r^2 is larger or equal to 0.99. However, the fit for zeroth-order is better, so we will choose that possibility. For an order zero plot, the absolute value of the slope gives the rate constant. The final rate law would be: $r = 6 \times 10^{-2}$.

❖ STUDY CHECK

Using the following data, apply the integral method to calculate the order and rate constant and write down the rate law.

t (s)	0	6	12	18	24
$[A]$, (M)	1.0000	0.5000	0.2500	0.1250	0.0625

►Answer: $r = 0.115[A]$

The integral method in action Now we are ready to work from scratch on a set of data from the integral method. Normally, data involving concentration and time will be given. To apply the integral method, we need to process these data into three different columns, reporting the concentration, the logarithm of the concentration, and the inverse of the concentration. Next, we will do three plots and we will obtain the regression line for each plot. We will compare the goodness of the fit by assessing the value of r^2 . The closer this value to one the better the fit. This analysis will lead to the reaction order. Finally, after we have selected the plot that corresponds to the best fit, we will analyze the regression line and extract the rate constant and initial molarity of reactants.

The integral method for more than one reactant The integral methods can also be applied to obtain rate laws involving more than one reactant (e.g. $r = k[A][B]^x$). For this case we will obtain pseudo rate-constants. In general rate constants only depend on the temperature and not on concentration. However, let us assume we want to calculate a rate law that depends on two reactants ($[A]$ and $[B]^x$),

and we start the experiment by using a very large molarity of one of them so that during the reaction this value do not change much. On the other hand, we use a smaller molarity for the other reactant and we want to apply the integral method to his molarity. We will have that $[A]$ is approximately constant (let us call this $[A]_0$), whereas $[B]$ is not. We can include the constant molarity in the rate law (as it is constant) so that we have

$$r = k[A]_0[B]^x \simeq k'[B]^x$$

And we have that

$$k' = k[A]_0$$

Applying the integral method we can find out the order of B and the pseudo rate constant. Once we have the pseudo constant, as we control $[A]_0$ we can always obtain the real rate constant.

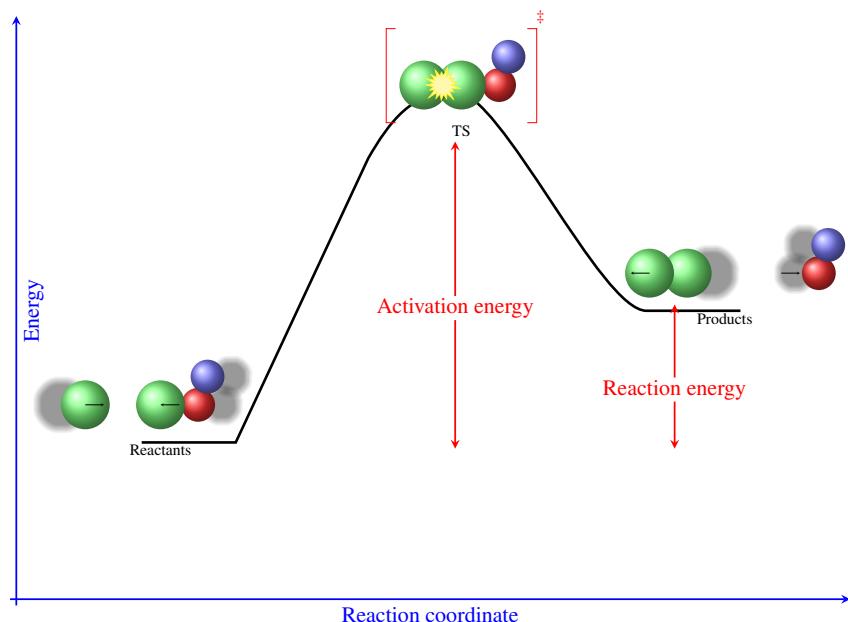


Figure 3.4 Energy diagram showing the conversion of reactants into products

3.4 Collision theory

The rate of reaction depends on temperature and reactions proceed at a higher speed at higher temperatures. This is the reason we use refrigerators and freezers to keep food for a longer time. The collision theory provides a microscopic understanding of chemical reactions. A pivotal element of this theory is the transition state also called the activated complex. This is an ephemeral state between reactants and products so that if the reaction proceeds until this point, reactants will certainly evolve into products. The energy difference between the reactants and the transition state of a reaction is called the activation energy. Energy diagrams are useful representations of the energy changes involved in a reaction. By analyzing an energy diagram we can predict whether a reaction is endo or exothermic and estimate the energy involved in the activation of a reaction. This section covers the fundamental principles of collision theory.

Collision theory Chemical reactions proceed at a molecular level by means of the collision of reactant molecules. The frequency of collisions is directly related to the reaction rate so that the more collisions per second the faster the reaction would proceed

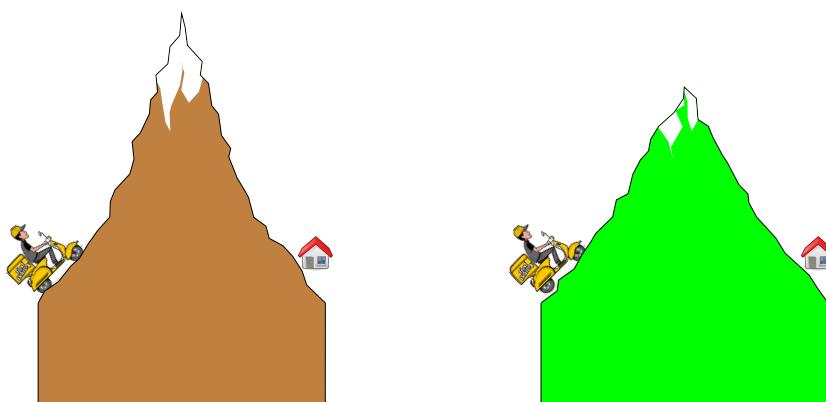


as the higher would be the chance for a reaction to occur. The collision theory of the chemical reactions associates the rate to the frequency of collisions. By increasing the concentration of reactants the number of collisions would increase and that is the reason why there is a concentration dependency on the reaction rate. However, not all collisions are equally effective and only effective collisions will contribute to chemical reactions. Two main factors control the effectiveness of the molecular collisions. First, the orientation of the collisions is critical and only certain orientations will produce successful collisions. The second factor is the energy of the molecules colliding. Only molecules with energy beyond a threshold will be able to form products. In other words: a successful collision should have the right orientation while having enough energy. Let us elaborate on the role of the orientation for the reaction:



We have that a Cl atom reacts with a NOCl molecule to produce Cl_2 , as represented in the image below. Only with the Cl atoms hit the NOCl molecule through the Cl atom, the collision will proceed with the right orientation in order to produce the Cl_2 molecule. At the same time, if the orientation is correct and the molecules have enough energy a transition state will form. We will discuss more this state during the next sections.

Transition state and activation energy We have discussed that the energy of reactants is a key parameter during a reaction. The minimum energy needed to activate the reactants so that they can produce products is called activation energy. The higher the activation energy the more energy is needed for a reaction to happen and hence the lower the reaction rate will be. When reactants get together they increase their energy from reactants until a state of maximum energy before producing the products. This state of maximum energy is called an activated complex or transition state. Transition states are very ephemeral states that exist for a very short amount of time in comparison to reactants and products. An example of activation happens during the ignition of a gas burner. Cooking gas and oxygen can react together to produce water and carbon dioxide only with the help of a spark. A spark is needed to activate the reactants so that their molecules can reach the transition state and hence produce products. Transition states are normally indicated with a \ddagger sign to indicate they have a very different nature than normal molecules. The figure below represents two reaction pathways with different activation energy.



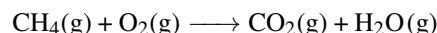
Effect of temperature As temperature increases the kinetic energy of the molecules reacting increases as well and with this the energy involved in the collisions also increases. Molecules move faster at higher temperature and hence the frequency of collisions between reactants and molecules increases with temperature.

Overall, the reaction rate increases with temperature. In other words, we can speed up chemical reactions by increasing temperature.

Concentration of reactants Another way to favor the collision between the molecules of reactants is to increase its concentration. The larger the concentration of reactants the higher the probability of their molecules to collide with each other potentially producing products.

Sample Problem 43

Methane (CH_4) reacts with oxygen (O_2) to produce carbon dioxide (CO_2) and water (H_2O) according to the following reaction



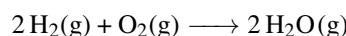
- (a) What happens to the number of collision between CH_4 and O_2 when you add extra oxygen?; (b) How would increasing temperature impacts the rate of the reaction?

SOLUTION

(a) The more reactants the more collisions between their molecules. (b) Increasing temperature would increase the rate of the combustion reaction, as increasing temperature increases collisions.

◆ STUDY CHECK

How would the following changes affect the rate of this reaction:



- (a) Removing oxygen; (b) Decreasing temperature

►Answer: (a) slow down; (b) slow down.

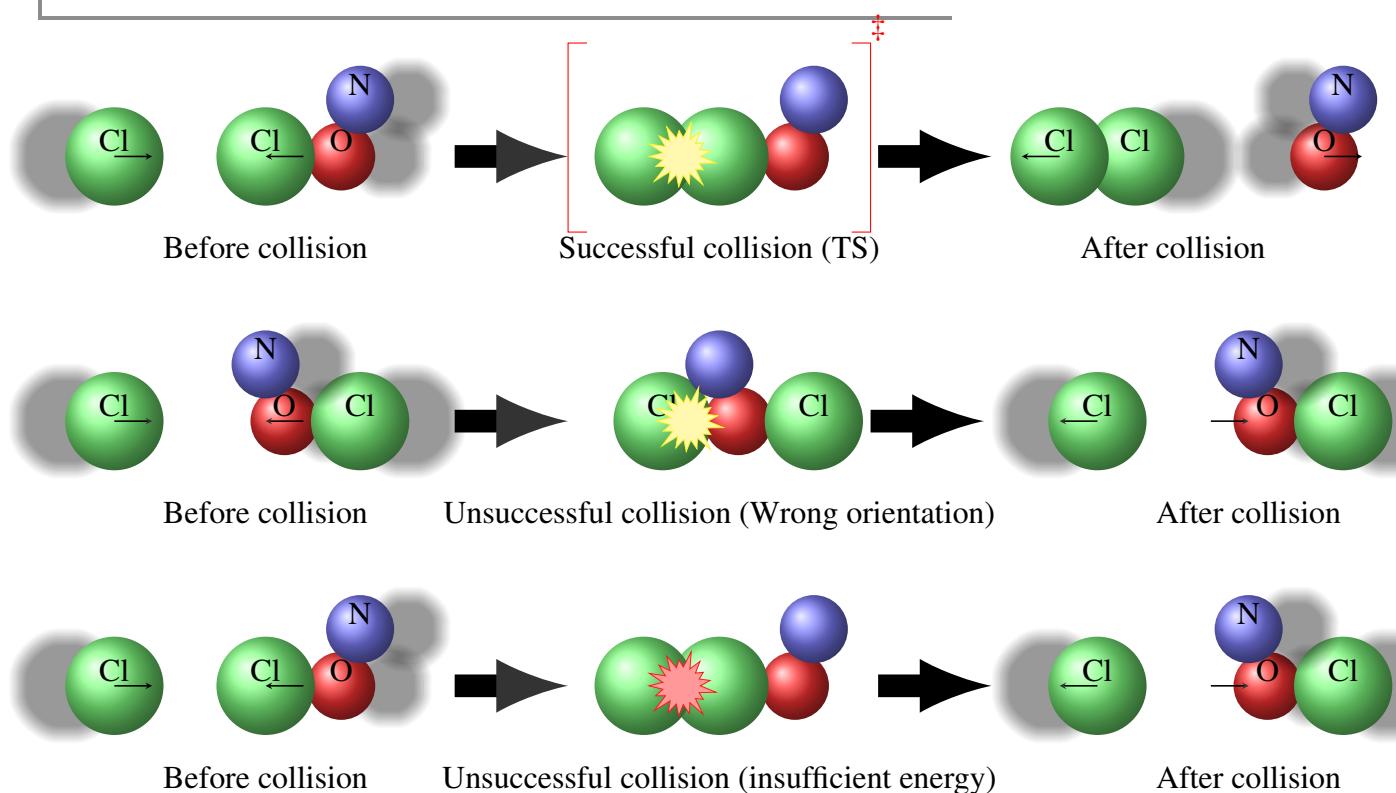


Figure 3.5 Example of three collisions, a successful collision that leads to a transition state and the products and two unsuccessful collisions due to an ineffective molecular arrangement and insufficient energy.



Catalysts Catalysts are chemicals that are not directly involved in a reaction—they are neither reactants nor products and as such, they are not consumed during a reaction. Still, they have the ability to increase the rate of reactions. Each catalyst is specific to a given reaction. As such, a catalyst can speed up a reaction without affecting other reactions. Enzymes are biological catalysts that support chemical reactions happening in the body. Most of the biological reactions involved in the chemistry of life are very slow. It is only with the help of biological catalysts that these reactions can indeed happen at reasonable rates. Every single metabolic reaction has associated an enzyme responsible for speeding up the process. Similarly, catalysts are well-known compounds in the chemical industry. The production of chemicals in the industry is also supported by the help of catalysts which make the chemical processes more economically beneficial. For example, catalysts are used in the manufacturing of margarine from vegetable oils. In the same line, the synthesis of ammonia is catalyzed by iron, the manufacturing of sulfuric acid uses catalysts based on nitrogen(II) oxide and platinum, and the oxidation of hydrocarbons in automobile exhausts are catalyzed by platinum. Enzymes are also added to detergents in order to speed up the breaking of protein molecules in stains. How do catalysts work? Catalyst function by providing alternative reaction pathways with more favorable—normally lower—activation energy. This way, in the presence of a catalyst, reactions proceed by means of two different reaction pathways, the catalyzed and non-catalyzed pathways. Still, as the catalyzed pathway is more favorable the overall speed of the reaction is higher. Catalysts can be classified as homogeneous, heterogeneous, and acid catalysts.

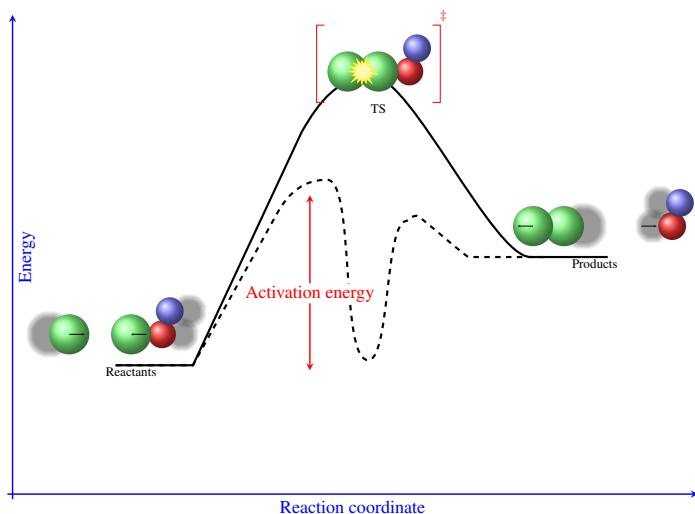


Figure 3.6 Energy diagram showing the catalyzed and non-catalyzed pathways

Heterogeneous catalysis A heterogeneous catalyst is a material with catalytic properties which has a different state of matter than the main reaction. For example, the synthesis of ammonia is carried in the chemical industry by means of reacting hydrogen and nitrogen. The catalyst for this process is iron, which is a solid. The reaction proceeds in a gas phase, whereas the catalyst employed is solid. This is an example of heterogeneous catalysis. Another example of the hydrogenation of alkenes by means of molecular hydrogen. This process is used for example in the production of saturated fats or shortenings such as Crisco. As hydrogen hardly dissociates in gas, this reaction proceeds at a very low rate without the help of a catalyst. Differently, in the presence of platinum, the dissociation energy of hydrogen is lower what makes the process function at a faster rate. The necessary steps for a reaction to happen on

a heterogeneous catalyst are: (a) the adsorption of the reactants on the surface (the words adsorption refers to the attachment of a gas onto a solid) (b) the activation of the reactants in which its molecular geometry changes due to the adsorption (c) the migration of the adsorbed reactants (d) the surface reaction (e) the desorption of the products

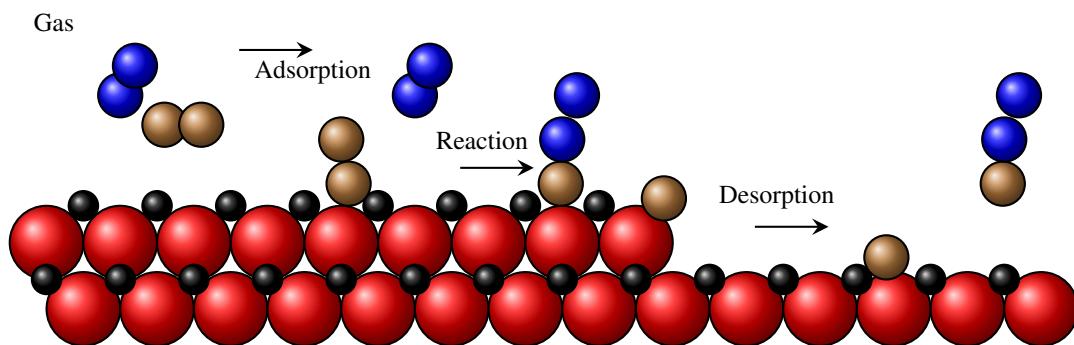
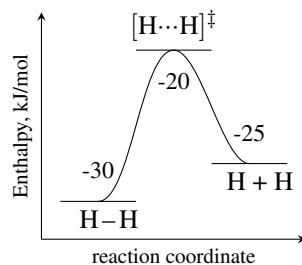


Figure 3.7 Steps in a heterogeneously catalyzed reaction

3.5 Use of energy diagrams

Energy diagrams Energy profile, or energy diagrams, are a visual representation of the advancing of a reaction (see Figure 3.4). Reactions advance through changes in the geometry of the reaction and during a reaction, for example, some bonds are being formed while others are being broken. The horizontal axis of the diagram represents the reaction coordinate, representing how the reaction proceeds, from reactants on the left to products on the right. The vertical axis represents the energy, oftentimes the enthalpy of the different steps of the reaction. Transition states are maxima in the energy diagrams, that is, points between two minima connecting reactants and products.

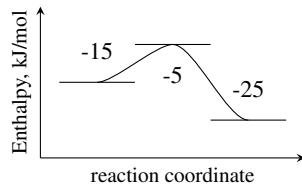


We can extract two types pf properties from energy diagrams. First, the reaction energy ΔH_R is the difference in energy between the products and reactants. If this value is negative, the reaction will be exothermic, releasing heat. The opposite is true for an endothermic reaction that consumes heat. Second, we can obtain the activation energy as the energy of the transition state with respect to the energy of the reactants. The activation energy will always be a positive number which value is related with the reaction rate: in general small activation energies lead to fast reactions and large activation energies lead to slow reactions. Below are two examples showing an exothermic and endothermic reactions, as well as a diagram showing the activation energy.



Sample Problem 44

For the energy profile below



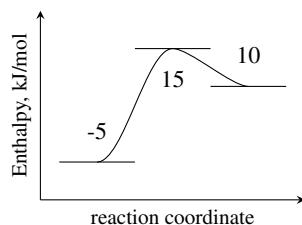
- Calculate (a) The energy of the reactants (b) The energy of the products (c) The energy of the transition state (d) The activation energy (e) The reaction energy (f) Indicate whether the reaction is endothermic or exothermic

SOLUTION

We have that the energy of the reactants is -15kJ/mol, the energy of the products is -25kJ/mol and the energy of the transition state (TS) is -5kJ/mol. The reaction energy represents the energy of the products concerning the reactants: $-25 - (-15) = -10\text{ kJ/mol}$. This is an exothermic reaction. The activation energy represents the energy of the TS concerning the reactants: $-5 - (-15) = 10\text{ kJ/mol}$.

◆ STUDY CHECK

For the energy profile below



- Calculate (a) The energy of the reactants (b) The energy of the products (c) The energy of the transition state (d) The activation energy (e) The reaction energy (f) Indicate whether the reaction is endothermic or exothermic

►Answer: (a) -5kJ/mol (b) 10kJ/mol (c) 15kJ/mol (d) 20kJ/mol (e) 15kJ/mol (f) Endothermic

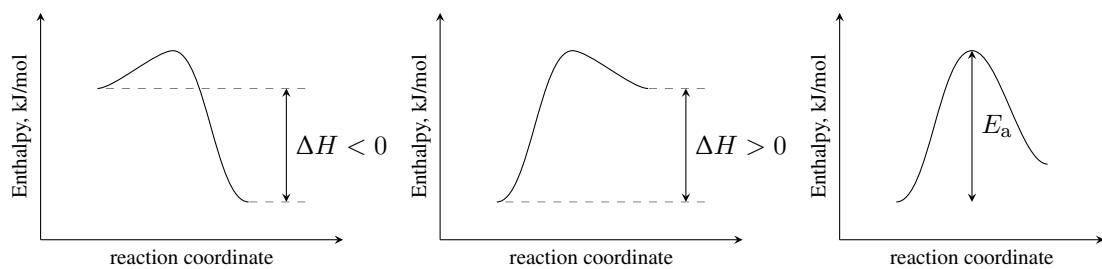
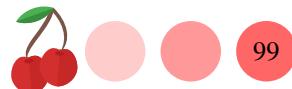


Figure 3.8 A set of reaction energy profiles displaying the energy of reaction and the activation energy: exothermic (left), endothermic (center), and endothermic (right)

3.6 The Arrhenius equation



The Arrhenius equation on its exponential form The Arrhenius equation gives the dependency of the rate constant with the frequency factor and the activation energy. We will introduce this equation in two forms: an exponential and a linear form. However, in this section we will focus on the exponential form of this equation:

$$k = A e^{-\frac{E_a}{RT}} \quad \text{and} \quad \ln(k) = \ln(A) - \frac{E_a}{R} \cdot \left(\frac{1}{T} \right) \quad (3.4)$$

where:

r is the overall rate of reaction

A is the frequency (or pre-exponential) factor

E_a is the activation energy in kJ/mol

R is the constant of the gases in energy units (8.314 J/molK)

T is the temperature in Kelvins

Based on Arrhenius equation, the larger the activation energy the smaller the rate constant. Similarly, as the temperature increases the rate constant increases, and therefore the reaction rate increases too. The following example shows how to use this equation in its exponential form. The linear form of the equation results simply from applying logarithms to both sides of the regular Arrhenius equation and is useful to obtain data graphically as it represents a linear relationship with $\frac{1}{T}$ as x and $\ln(k)$ as y . The slope of the resulting line is $-\frac{E_a}{R}$ (mind the negative sign) and the intercept is $\ln(A)$. In the Arrhenius equation, the pre-exponential factor represents the frequency of collision between molecules, in s^{-1} .

Sample Problem 45

The rate constant at 325K for the decomposition reaction $C_4H_8 \longrightarrow 2 C_2H_4$? is $6.1 \times 10^{-8} \text{ s}^{-1}$, and the frequency factor is $3.9 \times 10^{-5} \text{ s}^{-1}$. Calculate: (a) the activation energy (b) the rate constant at 200K

SOLUTION

We will use the Arrhenius equation on its exponential form:

$$k = A e^{-\frac{E_a}{RT}}$$

As we know the frequency factor ($A = 3.9 \times 10^{-5} \text{ s}^{-1}$) and the rate constant at a given temperature ($k = 6.1 \times 10^{-8} \text{ s}^{-1}$ at 325K), we can solve for the activation energy:

$$6.1 \times 10^{-8} = 3.9 \times 10^{-5} e^{-\frac{E_a}{8.314 \cdot 325}}$$

We have that

$$1.56 \times 10^{-3} = e^{-\frac{E_a}{8.314 \cdot 325}}$$

Using logarithms to solve for E_a :

$$\ln(1.56 \times 10^{-3}) = -\frac{E_a}{8.314 \cdot 325}$$

And solving for E_a :

$$\ln(1.56 \times 10^{-3}) = -\frac{E_a}{8.314 \cdot 325}$$



we have that $E_a = 17463.5 \text{ J/mol}$ in another words 17 kJ/mol .

◆ STUDY CHECK

The Arrhenius parameters for the gas-phase reaction below are $6 \times 10^{-12} \text{ s}^{-1}$ and 665 J/mol .



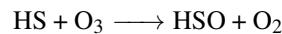
Calculate: (a) the rate constant at 300K. (b) the temperature in Kelvins at which the rate constant is $5 \times 10^{-12} \text{ s}^{-1}$

►Answer: (a) $4.6 \times 10^{-12} \text{ s}^{-1}$ (b) 439K

The following example shows how to use rate constant and temperature data in order to graphically compute the Arrhenius parameters.

Sample Problem 46

Using the following data, calculate the Arrhenius parameters (the activation energy and the frequency factor) for the following gas-phase reaction using the graphic method:



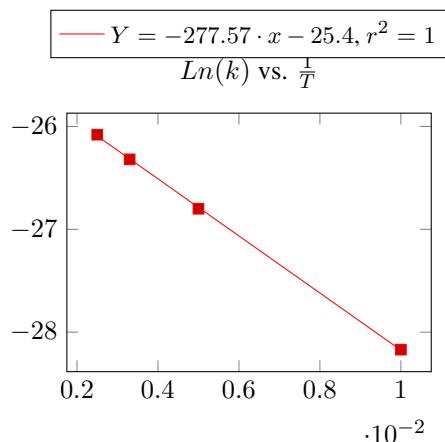
$T \text{ (K)}$	$k, (\text{s}^{-1})$
100	5.8×10^{-13}
200	2.3×10^{-12}
300	3.7×10^{-12}
400	4.7×10^{-12}

SOLUTION

As they provide with rate constant and temperature data, we will use the linearized form of Arrhenius equation in order to calculate the activation energy and the frequency factor. We will first process the data and compute the natural logarithm of the rate constant and the inverse of temperature.

$T \text{ (K)}$	$\frac{1}{T} \text{ (K}^{-1}\text{)}$	$k, (\text{s}^{-1})$	$\ln(k)$
100	1.0×10^{-2}	5.8×10^{-13}	-28.17
200	5.0×10^{-3}	2.3×10^{-12}	-26.80
300	3.3×10^{-3}	3.7×10^{-12}	-26.32
400	2.5×10^{-3}	4.7×10^{-12}	-26.08

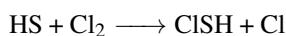
Now we are ready to graph the Arrhenius plot with $\frac{1}{T}$ in the horizontal (x) axis and $\ln(k)$ in the vertical (y) axis.



From the slope of the graph we will calculate $-\frac{E_a}{R}$ and from the intersect we will calculate $\ln(A)$. We have that $\frac{E_a}{R} = 227.57$ and $\ln(A) = -25.4$. We have that the Arrhenius parameters are: $E_a = 1892\text{J/mol}$ and $A = 9.3 \times 10^{-12}\text{s}^{-1}$.

◆ STUDY CHECK

Using the following data, calculate the Arrhenius parameters (the activation energy and the frequency factor) for the following gas-phase reaction using the graphic method:



$T (\text{ K})$	$k, (\text{s}^{-1})$
100	1.1×10^{-15}
200	1.4×10^{-13}
300	6.9×10^{-13}
400	1.5×10^{-12}

►Answer: $E_a = 7990\text{J/mol}$, $A = 1.7 \times 10^{-11}\text{s}^{-1}$.

3.7 Reaction mechanisms

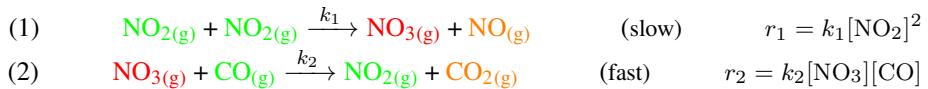
Most chemical reactions do not occur in a single step but in a series of steps that connect reactants with products in the form of a reaction mechanism. Some of the steps of the mechanism are slow—heavily impacting the experimentally measured rate law—others proceed quickly or are equilibrated hence going backwards. A proper reaction mechanism will justify the experimental rate law while matching the overall reaction stoichiometry. This section will gain insight into the different nuances involving reaction mechanisms, first giving an example of a reaction mechanism, then describing two of the most important steps of mechanisms: the rate-limiting step and the equilibrated steps. The first step gives the experimental rate law whereas the second is useful to calculate the concentration of reaction intermediates.

An example of a reaction mechanism Let us analyze the reaction between nitrogen dioxide and carbon monoxide, with the experimental rate law indicated below:

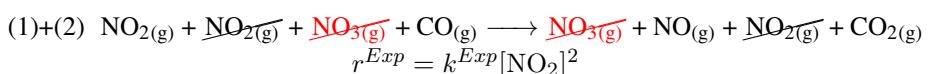
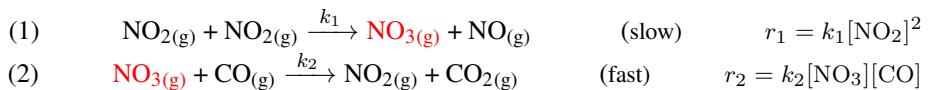


$$r^{Exp} = k^{Exp}[\text{NO}_2]^2$$

The experimental rate law demonstrates that this is a second order reaction. The reaction mechanism associated with the overall reaction is shown below. It consists of two steps. The first step involves the reaction of two nitrogen dioxide molecules (NO_2)—one of the reactants—to produce a molecule of nitrogen trioxide and a nitrogen monoxide molecule (NO_3)—one of the products. The second step involves the reaction of nitrogen trioxide (NO_3) and carbon monoxide (CO)—a second reactant—to produce nitrogen dioxide and carbon dioxide—the second product.



All reactions in a mechanism are called elemental steps and hence they proceed in a single step. At the same time, for each step, the number of molecules involved in the reactants is called molecularity and directly corresponds to the order or the rate law for a given step. Reactions involving a single molecule are called unimolecular, whereas reactions involving two molecules are called bimolecular. Reactions involving three molecules are called termolecular and are very rare. We have that every single step of the mechanism has a reaction constant (k_1 and k_2) and a rate law (r_1 and r_2). The rate law of each step of the mechanism simply results from multiplying the rate constant by the molarity of all reactants, using the stoichiometric coefficients as powers. For example the first step involves two NO_2 molecules and hence the rate law involves $[\text{NO}_2]^2$. At the same time, every step is characterized by a certain speed. Some steps are slower (step 1) than other (step 2). By combining the different steps and eliminating the repeated species we can obtain the overall reaction:



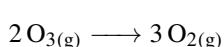
Finally, there are three different types of molecules in a mechanism: overall reactants, overall products and intermediates. Overall reactants are the reactants of the overall reaction (indicated in green). Overall products are the products of the overall reaction (indicated in orange). Intermediates (indicated in red) are generated only inside the mechanism and are not involved in the overall reaction. They are very ephemeral states that exist only temporally and they are never part of any experimental rate law.

Rate limiting step The rate limiting step of a mechanism approximately corresponds to the slowest step as this step will determine the experimental rate law:

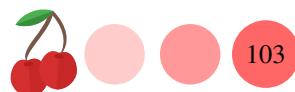
$$r^{Exp} \sim r^{slow} \quad (3.5)$$

The sign \sim indicated that this is an approximation. Rate limiting steps represent bottlenecks of chemical mechanisms limiting the overall advance of the reaction. Hence the rate limiting step is crucial to obtain the overall experimental rate law.

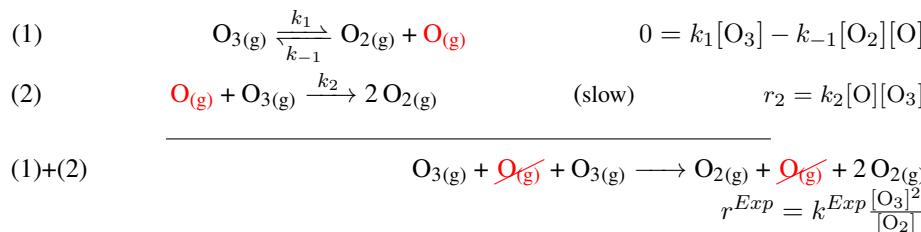
Equilibrated steps Often times we encounter equilibrated steps in mechanisms. Let us analyze the decomposition of ozone to produce molecular oxygen:



$$r^{Exp} = k^{Exp} \frac{[\text{O}_3]^2}{[\text{O}_2]}$$



This reaction proceed by means of the following mechanism the steps of which combined gives the overall reaction:



The reactant is O_3 , whereas O_2 is the product and O is an intermediate. The first step, the step indicated with a double arrow, is equilibrated, that means that the forward reaction (\longrightarrow) proceeds fast enough in order to be able to proceed backwards (\longleftarrow). At this point the forwards reaction is characterize by a rate constant k_1 and the backwards by another rate constant k_{-1} . Equilibrated steps are employed to compute the concentration of the reaction intermediates. As both reactions are equilibrated we have that the forwards and backwards reaction proceed at the same speed giving: $0 = k_1[\text{O}_3] - k_{-1}[\text{O}_2][\text{O}]$. We can compute the concentration of the intermediate by means of the rate law of the equilibrated step:

$$0 = k_1[\text{O}_3] - k_{-1}[\text{O}_2][\text{O}] \implies [\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]}$$

Now let us calculate the expression of the experimental rate law in terms of the different mechanistic steps. The second step is the rate limiting reaction so we have that:

$$r^{\text{Exp}} \sim r^{\text{slow}} = k_2[\text{O}][\text{O}_3]$$

Using the concentration of the intermediate recently calculates we have:

$$r^{\text{Exp}} = \frac{k_2 \cdot k_1}{k_{-1}} \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

We have that the mechanism justifies the experimental rate law with $k^{\text{Exp}} = \frac{k_2 \cdot k_1}{k_{-1}}$.

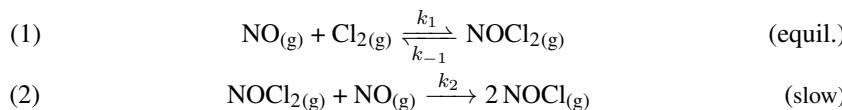
How to verify a possible mechanism Imagine we suggest a possible mechanism for a reaction with an experimental rate law and we want to make sure this is an appropriate mechanism. An appropriate chemical mechanism follows two rules: (a) the combination of all steps gives the overall reaction and (b) the experimental rate law can be justified by means of the mechanistic steps.

Sample Problem 47

Assess whether the reaction below:



is correctly represented by the following mechanism:

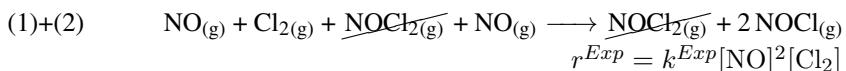
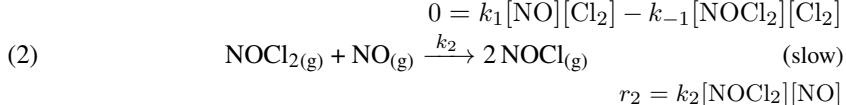
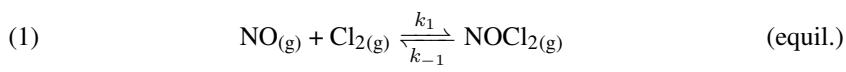


SOLUTION

We will verify two criteria: that the combination of the mechanistic steps gives the overall reaction and that the rate law is correctly described by the mechanism, using the rate determining step approximation—this means that the slow step



determines the experimental rate law. We will first write down the rate laws for each individual step and we will combine both steps:



We have that the first criteria is met as the overall reaction is obtained by combining both steps. Now we will use the rate limiting approach in order to reproduce the experimental rate law:

$$r^{\text{Exp}} \sim r^{\text{slow}} = k_2[\text{NOCl}_2][\text{NO}]$$

and we will use the equilibrated step in order to calculate $[\text{NOCl}_2]$:

$$0 = k_1[\text{NO}][\text{Cl}_2] - k_{-1}[\text{NOCl}_2][\text{Cl}_2] \implies [\text{NOCl}_2] = \frac{k_1}{k_{-1}}[\text{NO}][\text{Cl}_2]$$

Now we are able to compute r^{slow} :

$$r^{\text{slow}} = \frac{k_2 \cdot k_1}{k_{-1}}[\text{NO}]^2[\text{Cl}_2]$$

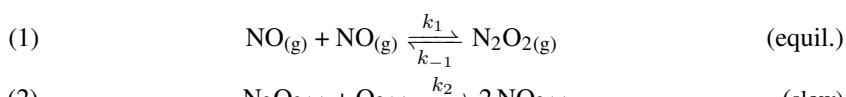
We have that the rate limiting step gives the experimental rate law. Hence this is an appropriated mechanism with $k^{\text{Exp}} = \frac{k_2 \cdot k_1}{k_{-1}}$.

❖ STUDY CHECK

Assess whether the reaction below:



is correctly represented by the following mechanism:



►Answer: yes with $k^{\text{Exp}} = \frac{k_2 \cdot k_1}{k_{-1}}$



CHAPTER 3

RATE OF REACTION

3.1 A is the reactant of two different reactions. Plot the data below in order to compare the rate of the two reaction.

	Reaction I	Reaction II
Time, s	[A] (M)	[A] (M)
0	100	100
1	7×10^{-1}	36.78
2	4×10^{-3}	13.53
3	3×10^{-5}	4.90
4	2×10^{-7}	1.80

3.2 Use the data below to identify reactants and products in a reaction.

Time, s	[A] (M)	[B] (M)
0	0	3
1	2×10^{-2}	2.4
2	3×10^{-2}	2.0
3	6×10^{-2}	1.64
4	8×10^{-2}	1.34

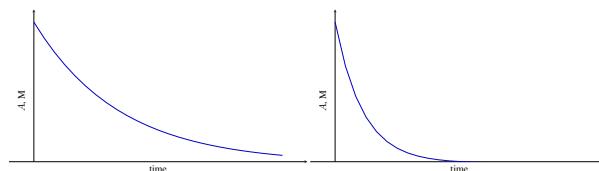
3.3 Use the data below to identify reactants and products in a reaction.

Time, s	[A] (M)	[B] (M)
0	2	0
1	1.996	4×10^{-3}
2	1.992	8×10^{-3}
3	1.988	1.2×10^{-2}
4	1.984	1.6×10^{-2}

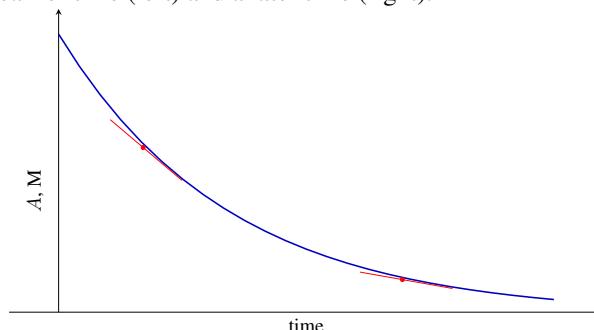
3.4 Use the data below to identify reactants and products in a reaction.

Time, s	[A] (M)	[B] (M)
0	4	0
1	3.6	2×10^{-3}
2	2.2	1×10^{-2}
3	1.3	1×10^{-2}
4	0.8	2×10^{-3}

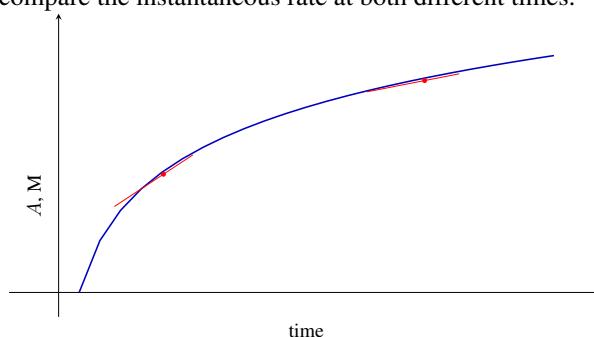
3.5 The concentration plots below represent two different reaction. Indicate which has the fastest initial reaction rate.



3.6 Using the concentration vs. time plot shown below, compare the instantaneous rate at both different times, an earlier time (left) and a later time (right).



3.7 Using the concentration vs. time plot shown below, compare the instantaneous rate at both different times.





3.8 For a given reaction the differential rate is measured for a set of species. Given the numerical values indicated next, identify the specie as reactant or product: (a) $r_A=0.3\text{M/s}$ (b) $r_B=-0.1\text{M/s}$ (c) $r_C=-1.2\text{M/s}$ (d) $r_D=0.6\text{M/s}$

3.9 For the reaction below: $2\text{a} + 3\text{b} \longrightarrow 4\text{c} + 5\text{d}$ and given that the rate of disappearance of b is $r_B=-0.3\text{M/s}$, calculate: (a) the rate of disappearance of A, r_A (b) the rate of appearance of C, r_C (c) the rate of appearance of D, r_D (d) the rate of reaction r

3.10 For the reaction below: $2\text{a} + 2\text{b} \longrightarrow 3\text{c} + \text{d}$ and given that the rate of appearance of d is $r_D=0.2\text{M/s}$, calculate: (a) the rate of disappearance of A, r_A (b) the rate of disappearance of B, r_B (c) the rate of appearance of C, r_C (d) the rate of reaction r

RATE LAWS

3.11 Given the following rate law

$$r=0.04[\text{A}]^2[\text{B}][\text{C}]^3$$

indicate: (a) the reaction order of A (b) the reaction order of B (c) the reaction order of C (d) the overall reaction order (e) the value of the reaction constant including its units

3.12 Given the following rate law

$$r=0.4[\text{Cl}_2][\text{F}_2]^2$$

indicate: (a) the reaction order of Cl_2 (b) the reaction order of F_2 (c) the overall reaction order (d) the value of the reaction constant including its units

3.13 Given the following rate law

$$r=k[\text{A}]^4[\text{B}]^2[\text{C}]^2$$

indicate the impact on the rate of the following: (a) to double [A] (b) to triple [B] (c) to double [C]

3.14 Given the following rate law

$$r=k[\text{A}][\text{B}]^2[\text{C}]$$

indicate the impact on the rate of the following: (a) to double [B] (b) to triple [A] (c) to quadruple [C]

3.15 Given the following rate constant values, identify the reaction order: (a) $k=3 \times 10^{-4} \text{ L/(s}\cdot\text{mol)}$ (b) $k=0.03 \text{ M/s}$ (c) $k=3 \times 10^{-5} \text{ 1/(s}\cdot\text{M}^2)$

3.16 Given the following rate constant values, identify the reaction order: (a) $k=0.04 \text{ M/s}$ (b) $k=0.001 \text{ 1/s}$ (c) $k=0.09 \text{ 1/s}\cdot\text{mol}\cdot\text{M}$

3.17 Identify the following rate laws as integral or differential, and given a rate law form obtain the other corresponding type of form (i.e. if the integral form is given then obtain the differential form and viceversa): (a) $r = 0.0023$, $[\text{A}]_0=0.3$ (b) $\ln([\text{A}]) = -0.045 \cdot t + 0.45$ (c) $r = 0.3[\text{A}]^2$, $[\text{A}]_0=25$

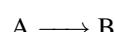
3.18 Identify the following rate laws as integral or differential, and given a rate law form obtain the other corresponding type of form (i.e. if the integral form is given then obtain the differential form and viceversa): (a) $[\text{A}] = 0.045 - 0.34 \cdot t$ (b) $r = 0.9[\text{A}]^1$, $[\text{A}]_0=1.49$ (c) $\frac{1}{[\text{A}]} = 0.3 + 0.04 \cdot t$

3.19 Compute the half-life for the following reactions: (a) a first order reaction with $k=0.234 \text{ 1/s}$ (b) a zeroth-order reaction with $k=0.34 \text{ M/s}$ and initial concentration 0.1M (c) a second-order reaction with $k=0.067 \text{ M/s}$ and initial concentration 0.01M

3.20 Compute the half-life for the following reactions: (a) a zeroth-order reaction with $k=0.045 \text{ M/s}$ and initial concentration 0.05M (b) a first order reaction with $k=0.947 \text{ 1/s}$ and initial concentration 0.05M (c) a second-order reaction with $k=0.0087 \text{ M/s}$ and initial concentration 0.087M

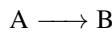
THE DIFFERENTIAL AND INTEGRAL METHODS OF OBTAINING RATE LAWS

3.21 Use the data below to calculate the rate law of the following reaction:



Experiment	$r (\text{M/s})$	$[\text{A}], (\text{M})$
1	0.03	1
2	0.12	2

3.22 Use the data below to calculate the rate law of the following reaction:



Experiment	r (M/s)	$[A]$, (M)
1	5×10^{-3}	0.5
2	5×10^{-3}	0.6

3.23 Use the data below to calculate the rate law of the following reaction:



Experiment	r (M/s)	$[A]$, (M)
1	0.03	0.01
2	0.30	0.1

3.24 Use the data below to calculate the rate law of the following reaction:



Experiment	r (M/s)	$[A]$, (M)
1	0.5	0.253
2	1	0.320

3.25 Use the data below to calculate the rate law:

Experiment	$[A]$ (M)	$[B]$ (M)	r (M/s)
1	0.1	0.02	2.08×10^{-5}
2	0.1	0.04	8.32×10^{-5}
3	0.2	0.01	1.04×10^{-5}
4	0.4	0.01	2.08×10^{-5}

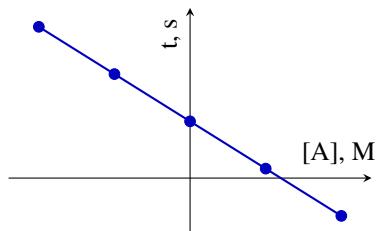
3.26 Use the data below to calculate the rate law:

Experiment	$[A]$ (M)	$[B]$ (M)	r (M/s)
1	0.1	0.02	1.03×10^{-3}
2	0.1	0.04	2.08×10^{-3}
3	0.2	0.01	1.04×10^{-3}
4	0.4	0.01	2.08×10^{-3}

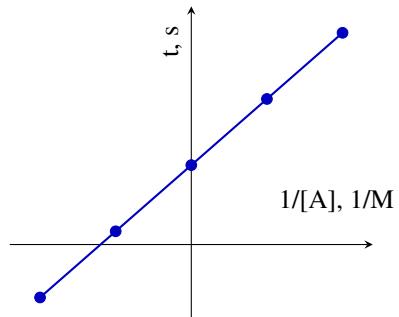
3.27 Use the data below to calculate the rate law:

Experiment	$[A]$ (M)	$[B]$ (M)	r (M/s)
1	0.1	0.02	1.03×10^{-3}
2	0.1	0.04	2.08×10^{-3}
3	0.2	0.01	1.04×10^{-3}
4	0.4	0.01	2.08×10^{-3}

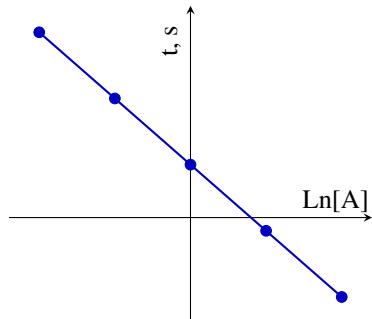
3.28 The plot below resulting from integral method represent a perfect line with $r^2=0.99$. Indicate the order of the reaction.



3.29 The plot below resulting from integral method represent a perfect line with $r^2=0.99$. Indicate the order of the reaction.

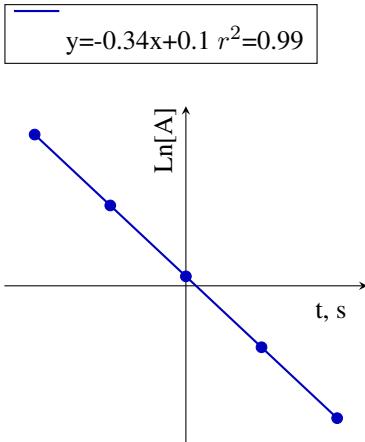


3.30 The plot below resulting from integral method represent a perfect line with $r^2=0.99$. Indicate the order of the reaction.



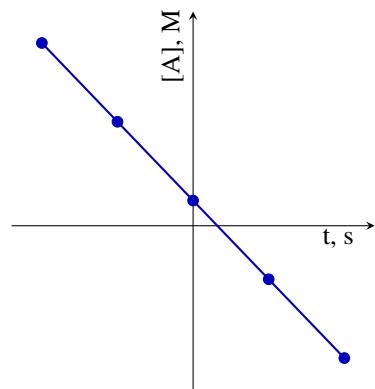


3.31 The following plot results from processing data by means of the integral method. Interpret the linear regressions and indicate the rate law.



3.32 The following plot results from processing data using the integral method. Interpret the linear regressions, paying particular attention to the statistics behind the regression, and indicate the rate law.

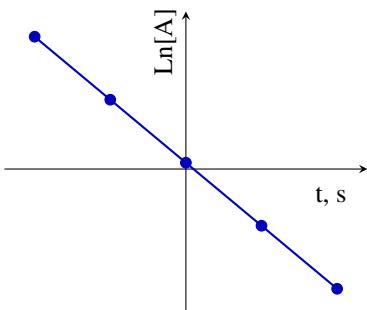
$$y=-0.56x+0.05 \ r^2=0.99$$



3.34 Using the following data, calculate the order and rate constant and write down the rate law.

t (s)	[A], (M)
5	0.952
10	0.625
15	0.465
20	0.370
25	0.308
35	0.230

$$y=-0.04x+0.91 \ r^2=0.97$$

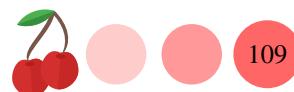


3.35 Using the following data, calculate the order and rate constant and write down the rate law.

t (s)	[A], (M)
0	9.90×10^{-2}
5	4.97×10^{-2}
10	3.32×10^{-2}
15	2.49×10^{-2}
20	1.66×10^{-2}
25	1.43×10^{-2}

3.33 The following plot results from processing data by means of the integral method. Interpret the linear regressions and indicate the rate law.

3.36 Calculate the rate law for the following reaction using the given data: $2 \text{ClO}_2 + 2 \text{I}^- \longrightarrow 2 \text{ClO}_2^- + \text{I}_2$



<i>t</i> (s)	[ClO ₂], (M)
0	4.77 × 10 ⁻⁴
1	3.31 × 10 ⁻⁴
2	3.91 × 10 ⁻⁴
3	3.53 × 10 ⁻⁴
5	2.89 × 10 ⁻⁴
10	1.76 × 10 ⁻⁴
30	2.40 × 10 ⁻⁵
50	3.20 × 10 ⁻⁶

3.37 Calculate the rate law for the following reaction using the given data: CH₃COOCH₃ + OH⁻ → CH₃COO⁻ + CH₃OH

<i>t</i> (s)	[CH ₃ COOCH ₃], (M)
0	1.00 × 10 ⁻²
3	7.40 × 10 ⁻³
4	6.83 × 10 ⁻³
5	6.34 × 10 ⁻³
10	4.63 × 10 ⁻³
20	3.04 × 10 ⁻³
30	2.24 × 10 ⁻³

3.38 Calculate the rate law for the following reaction using the given data: 2 NO₂ → 2 NO + O₂

<i>t</i> (s)	[NO ₂], (M)
0	1.00 × 10 ⁻²
60	6.83 × 10 ⁻³
120	5.18 × 10 ⁻³
180	4.18 × 10 ⁻³
240	3.50 × 10 ⁻³
300	3.01 × 10 ⁻³
360	2.64 × 10 ⁻³

3.39 Calculate the rate law for the following reaction using the given data: 2 HI → H₂ + I₂

<i>t</i> (s)	[HI], (M)
0	1
1000	0.11
2000	0.061
3000	0.041
4000	0.031

3.40 Calculate the rate law for the following reaction using the given data: H₂ + I₂ → 2 HI

<i>t</i> (s)	[H ₂], (M)
0	1
1	0.43
2	0.27
3	0.20
4	0.16

3.41 Calculate the rate law for the following reaction using the given data: C₃H₅ → C₃H₆

<i>t</i> (s)	[C ₃ H ₆], (M)
0	1.5 × 10 ⁻³
5	1.24 × 10 ⁻³
10	1.0 × 10 ⁻³
15	0.83 × 10 ⁻³

3.42 Calculate the rate law for the following reaction using the given data: 2 P + Q → W

<i>t</i> (s)	[P], (mM)
0	1
15	0.97484
30	0.9504
45	0.92676
60	0.90379
75	0.881
90	0.8596

3.43 Calculate the rate law for the following reaction using the given data: 2 O₃ → 3 O₂

<i>t</i> (h)	[O ₃], (M)
5	0.952
10	0.625
15	0.465
20	0.37
25	0.308
35	0.23

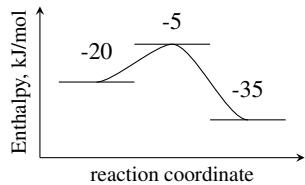


3.44 Calculate the rate law for the following reaction using the given data: $2X \longrightarrow Y + Z$

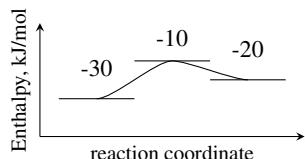
t (s)	[X], (M)
5	0.0990
10	0.0497
15	0.0332
20	0.0249
25	0.0200
30	0.0166
35	0.0143
40	0.0125

COLLISION THEORY

3.45 For the energy profile below, indicate the activation energy and the reaction energy. Does this diagram corresponds to an exothermic or endothermic reaction?



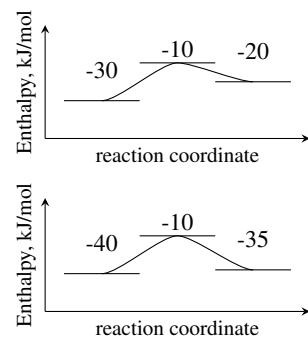
3.46 For the energy profile below, indicate the activation energy and the reaction energy. Does this diagram corresponds to an exothermic or endothermic reaction?



3.47 Sketch an energy profile in which reactants are located at -10 kJ/mol , the activation energy is 15 kJ/mol and the energy of reaction is 10 kJ/mol .

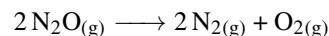
3.48 Sketch an energy profile in which reactants are located at -15 kJ/mol , the activation energy is 10 kJ/mol and the energy of reaction is -10 kJ/mol .

3.49 Compare both energy profiles top and bottom and indicate: (a) What reaction proceeds faster (b) What reaction exchanges more energy



3.50 The reaction energy of a process, going from reactants into products, is 10 kJ/mol and its activation energy is 15 kJ/mol . Calculate the reaction energy and the activation energy of the reverse process, starting from products and going to reactants. Is this reverse reaction exothermic or endothermic. How about the direct reaction, starting from reactants and going to products?

3.51 The rate constant for the gas-phase decomposition of N_2O has the following temperature dependence:

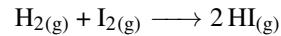


has the following temperature dependence:

T (K)	k , (s^{-1})
1500	9214
1400	2175
1300	411
1200	58.9

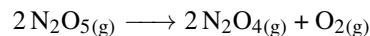
Indicate the reaction order, and compute the activation energy in (kJ/mol) and the frequency factor.

3.52 For the gas-phase reaction between hydrogen and iodine

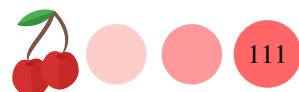


the rate constant at 500 K was found to be $9.36 \times 10^{-7} \text{ 1/(M}\cdot\text{s)}$ and the rate constant at 600 K was found to be $5.69 \times 10^{-4} \text{ 1/(M}\cdot\text{s)}$. Calculate the activation energy in kJ/mol and the frequency factor of the reaction.

3.53 For the decomposition of dinitrogen pentoxide



the rate constant at 500 K is 345.43 s^{-1} and at different temperature, the rate constant is 24.84 s^{-1} . Given that



the activation energy of this reaction is 103.03 kJ/mol, calculate the second temperature value.

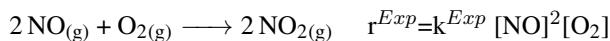
3.54 For a given reaction, when temperature increases from 100K to 200K, its rate constant triples. Calculate the activation energy for this process.

REACTION MECHANISMS

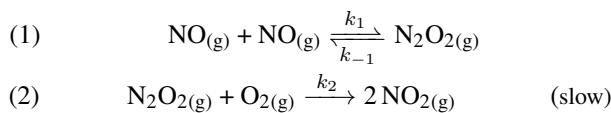
3.55 For the following elemental reaction steps indicate the molecularity and give the rate law: (a) $\text{N}_2\text{O} \longrightarrow \text{NO} + \text{O}$ (b) $\text{N}_2\text{O} + \text{O} \longrightarrow \text{N}_2 + \text{O}_2$ (c) $2\text{NO} \longrightarrow \text{N}_2\text{O}_2$ (d) $\text{N}_2\text{O}_2 + \text{H} \longrightarrow \text{N}_2\text{O} + \text{HO}$

3.56 For the following elemental reaction steps indicate the molecularity and give the rate law: (a) $\text{SiH}_4 + \text{SiH}_2 \longrightarrow \text{Si}_2\text{H}_6$ (b) $\text{SiH}_2 + \text{H} \longrightarrow \text{SiH} + \text{H}_2$ (c) $\text{Si}_2\text{H}_3 + \text{H}_2 \longrightarrow \text{Si}_2\text{H}_5$

3.57 The experimental rate law for the reaction of nitrogen monoxide and molecular oxygen given by the following reaction

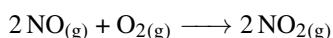


is second order with respect to dinitrogen oxide and first order with respect to oxygen. A plausible mechanism would be:

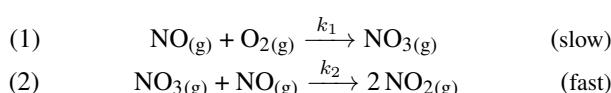


Calculate: (a) the molecularity of each reaction step
 (b) the rate law for each reaction step
 (c) identify all intermediates
 (d) justify whether the suggested mechanism is valid and if so give k^{Exp} in terms of the rate constants in the mechanism

3.58 A possible mechanism for the reaction of nitrogen monoxide and molecular oxygen to produce nitrogen dioxide given by the following reaction



could be:



Calculate: (a) the molecularity of each reaction step
 (b) the rate law for each reaction step
 (c) identify all intermediates
 (d) give the experimental rate law



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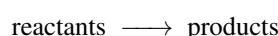
Ch. 4. Chemical equilibrium

REACTIONS rarely occur to completion. Once products form, they can follow a backward reaction to regenerate the reactants, and at the same time, reactants regenerate and produce products. Overall, chemical reactions proceed until reaching equilibrium. The equilibrium conditions determine how profitable a reaction can be as they describe how much of the products stay as products. This chapter covers the idea and basic principles of chemical equilibrium. We will describe the role of an equilibrium constant, which gives insight into the mixtures of reactants and products in equilibrium. Also, we will discuss the different types of equilibrium constants in terms of molarity and pressure and the role of a reaction quotient that gives insight into the direction in which a chemical reaction proceeds towards the equilibrium. Finally, we will cover Le Châtelier principle that describes the direction in which a chemical reaction proceeds to recover the equilibrium state, after equilibrium is altered.

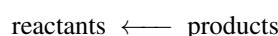
4.1 Chemical Equilibrium

This section covers basic ideas about chemical equilibrium. First, we will introduce the concept of the forward and reverse reactions. Next, we will define the idea of equilibrium, based on the speed of the forward and reverse reactions.

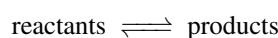
Forward and reverse reactions In chemical reactions, reactants form products. We call this the *forward reaction*:

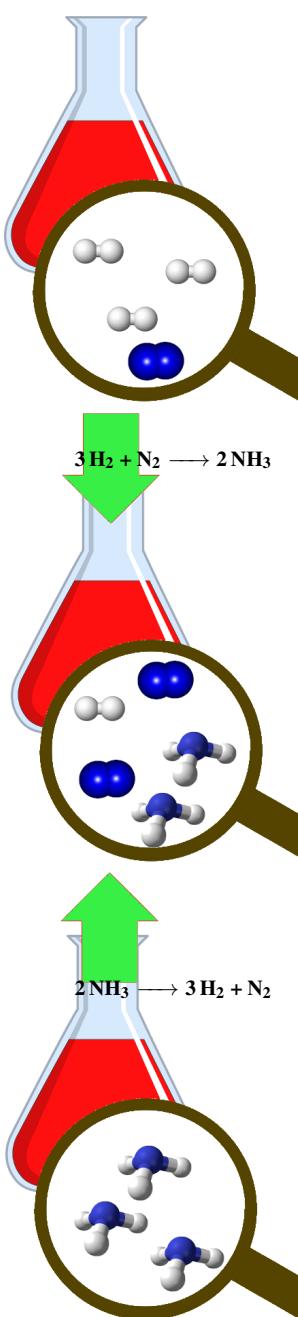


However, once the products form they can also generate reactants through the *reverse reaction*:



Equilibrium In chemical reactions, both the forward and the reverse reactions happen synchronously, so that when products form they also generate reactants. However, both the reverse and forward reactions have different speeds. In the beginning, the forward reaction proceeds at a faster pace than the reverse so that the reaction advances. Once products form, the reverse reaction will start speeding. A reaction reaches *chemical equilibrium* when both the forward and reverse reactions proceed at the same speed. Chemical reactions normally are written down with a double arrow that indicates equilibrium:





▼ The forward reaction goes from reactants to products whereas the reverse reaction goes from products to reactants.

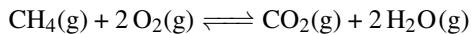
For example, the chemical process that forms ammonia from nitrogen and hydrogen can proceed using the forward and reverse reaction



Equilibrium and concentration It is just a matter of time before a reaction reaches equilibrium. Initially, the forward process normally proceeds at high speed as products start to form. This is because initially there is an abundance of reactants. Once the products start to accumulate the forward process will start happening. This is because at that point there is an increasing amount of product molecules that can go back to reactants. Eventually, the forward and reverse rates become equal as the reaction reaches equilibrium. When the equilibrium has been reached, reactants and products have very specific concentrations that depend on temperature. At the same time, a reaction in equilibrium contains a mixture of reactants and products.

Sample Problem 48

Write down the forward and reverse reactions for:

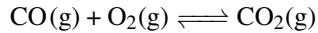


SOLUTION

(a) The forward reaction is $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$ and the reverse $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \leftarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$

◆ STUDY CHECK

Write down the forward and reverse reactions for the reaction:



► Answer: $\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ and $\text{CO}(\text{g}) + \text{O}_2(\text{g}) \leftarrow \text{CO}_2(\text{g})$

4.2 The equilibrium constant

Reactions in equilibrium are characterized by an equilibrium constant. This next section will show how to interpret and calculate the value of the equilibrium constant of a reaction.

Equilibrium mixtures Imagine you start a chemical reaction. Initially, products will form while reactants disappear. At equilibrium, you will have a mixture of reactants and products with the forward and reverse processes happening at the same rate. Would an equilibrium mixture contain more reactants or more products? The equilibrium constant helps predict just that.

Table 4.1 Different K_c values at 298K

Reaction		K_c	Equilibrium mixture
$2 \text{NH}_3(\text{g})$	\rightleftharpoons	$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g})$	17 Products > Reactants
$\text{H}_2(\text{g}) + \text{I}_2(\text{g})$	\rightleftharpoons	$2 \text{HI}(\text{g})$	50 Products > Reactants
$2 \text{SO}_3(\text{g})$	\rightleftharpoons	$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g})$	0.3 Products < Reactants
$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{H}_2\text{O}(\text{g})$	0.2 Products < Reactants

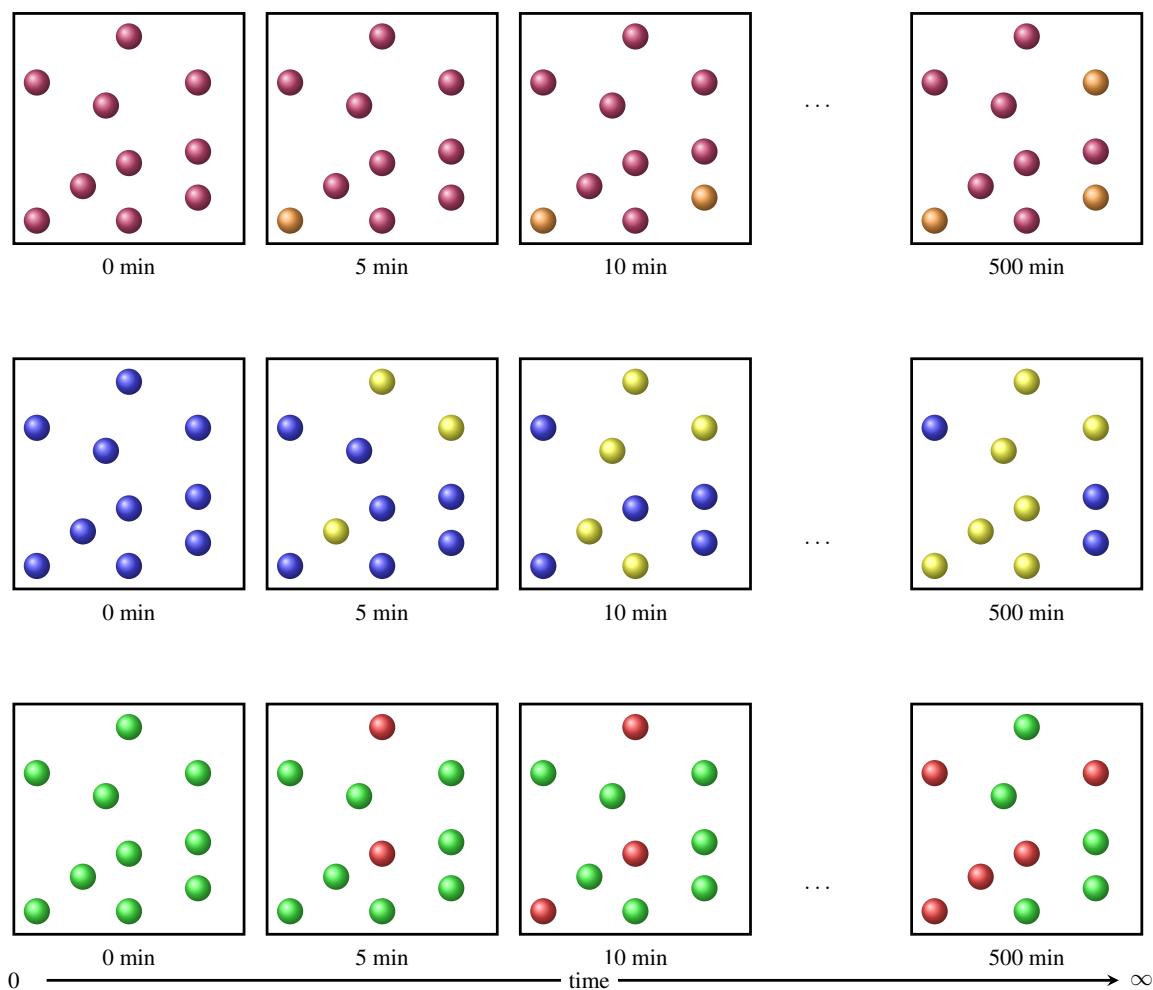
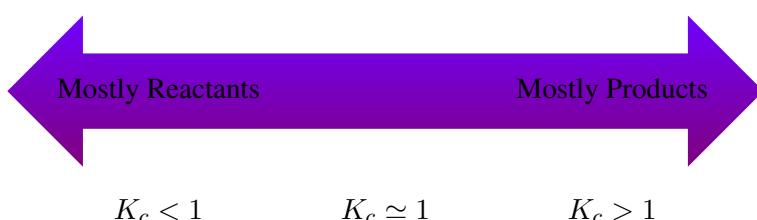
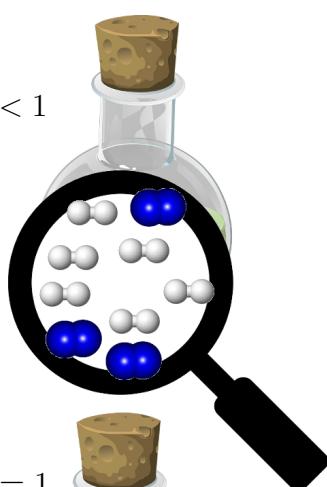
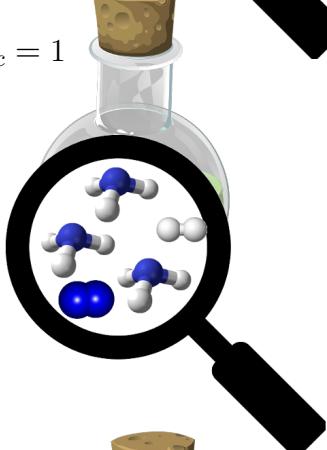
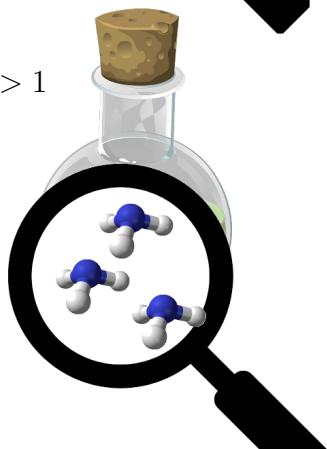


Figure 4.1 Three equilibrium situations

The *equilibrium constant of a reaction* The equilibrium constant associated with a reaction K_c indicates whether reactants or products are abundant at equilibrium. Each reaction has one K_c value that depends only on temperature and the subscript c represents concentration. On one hand, if K_c is larger than one there will be a larger concentration of products than reactants in the equilibrium mixture (see Figure 4.1). On the other hand, if K_c is smaller than one there will be a larger concentration of reactants than products in the equilibrium mixture. If K_c is close to one then both reactants and products will have the same concentration in the equilibrium mixture (see Table 4.1 for examples).



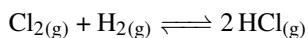
In terms of units, equilibrium constants are unitless numbers—a number without units. In other words, they have no unit and they are simply expressed as a number.

 $K_c < 1$  $K_c = 1$  $K_c > 1$ 

▼ The magnitude of the equilibrium constant indicates whether there is more products or reactants in an equilibrium mixture.

Sample Problem 49

The value of K_c for the following reaction at 300K is 4×10^{31} . Indicate whether the equilibrium mixture will contain mostly reactants, mostly products or both.



SOLUTION

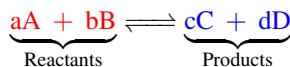
As K_c is larger than one, an equilibrium mixture of Cl_2 , H_2 and HCl will contain mainly products, that is will be mainly made of HCl .

◆ STUDY CHECK

The value of K_c for $\text{F}_2(g) \rightleftharpoons 2 \text{F}(g)$ at 500K is 7×10^{-13} . Indicate whether the equilibrium mixture will contain mostly reactants, mostly products or both.

► Answer: mostly reactants.

Equilibrium constant expression Let's consider a general equilibrium reaction in which A and B react to form C and D



The stoichiometric coefficients of the reaction are a , b , c , and d . The expression for the equilibrium constant depends only on the concentration of the reactants and products. To refer to concentration we will use square brackets. For example, $[A]$ means the concentration of A . Hence, the expression of the equilibrium constant will be:

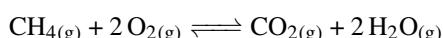
$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[\text{C}]^c \cdot [\text{D}]^d}{[\text{A}]^a \cdot [\text{B}]^b} \quad \text{Equilibrium constant} \quad (4.1)$$

Let us break down the expression of K_c . On top of the fraction, we have the equilibrium concentration of the products to the power of its coefficients. For example $[\text{C}]^c$ means the equilibrium concentration of C to the power of the coefficient c . On the bottom of the fraction, we have the concentration of the reactants to the power of its coefficients. All concentrations in K_c are timed.

$$K_c = \frac{[\text{C}]^c \cdot [\text{D}]^d}{[\text{A}]^a \cdot [\text{B}]^b}$$

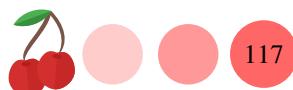
↗ product concentration
↗ reactant coefficient

Let's focus on the reaction below:



The expression of the equilibrium constant would be:

$$K_c = \frac{[\text{CO}_2] \cdot [\text{H}_2\text{O}]^2}{[\text{CH}_4] \cdot [\text{O}_2]^2}$$



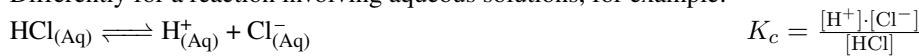
Equilibrium involving solids, liquids and solutions Let us analyze an example of a reaction involving solids or liquids:



Solids and liquids have no concentration and hence they should not be included in the expression of K_c . For the example above:

$$K_c = [\text{CO}_2]$$

Differently for a reaction involving aqueous solutions, for example:



Overall, remember that in the expression of K_c , you can only include gases (g) or aqueous solutions (aq) as you can ignore solids and liquids without a well-defined concentration.

Sample Problem 50

Write down the expression of K_c for the following reactions:

- (a) $2 \text{NO}_{2(\text{g})} \rightleftharpoons \text{N}_2\text{O}_{4(\text{g})}$
- (b) $\text{C}_3\text{H}_{8(\text{g})} + 5 \text{O}_{2(\text{g})} \rightleftharpoons 4 \text{H}_{2\text{O}}_{(\text{g})} + 3 \text{CO}_{2(\text{g})}$
- (c) $\text{Zn}_{(\text{s})} + 2 \text{HCl}_{(\text{aq})} \rightleftharpoons \text{ZnCl}_{2(\text{aq})} + \text{H}_{2(\text{g})}$

SOLUTION

Remember you can only include gas and aqueous solution in the expression of K_c . For the first example

$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

For the second example,

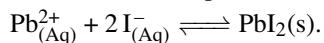
$$K_c = \frac{[\text{H}_2\text{O}]^4 \cdot [\text{CO}_2]^3}{[\text{C}_3\text{H}_8] \cdot [\text{O}_2]^5}$$

For the last example:

$$K_c = \frac{[\text{ZnCl}_2] \cdot [\text{H}_2]}{[\text{HCl}]^2}$$

◆ STUDY CHECK

Write down the expression of K_c for the following reaction:

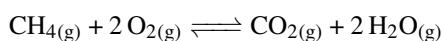


► Answer: $\frac{1}{[\text{Pb}^{2+}] \cdot [\text{I}^-]^2}$

Equilibrium constant in terms of pressures The equilibrium constant K_c is the ratio of the concentration of products and reactants. As concentration is related to pressure—remember the chapter about gases—we can also express an equilibrium constant in terms of pressures, we call this K_p .

$$K_p = \frac{P_{\text{Products}}}{P_{\text{Reactants}}} = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \quad \text{Equilibrium constant} \quad (4.2)$$

Let's focus on an example. Think about the reaction below that involved just gases:





The expression of the equilibrium constant would be:

$$K_p = \frac{P_{\text{CO}_2} \cdot P_{\text{H}_2\text{O}}^2}{P_{\text{CH}_4} \cdot P_{\text{O}_2}^2}$$

K_p values larger than one implies that in the mixture the pressure of products is larger than the pressure of reactants and the opposite is true for values smaller than one.

Relating K_c and K_p The values of K_c and K_p are related by the following formula:

$$K_p = K_c(RT)^{\Delta n} \quad (4.3)$$

where:

K_p is the equilibrium constant in terms of pressure

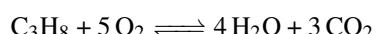
K_c is the equilibrium constant in terms of concentration

R is the constant of the gases in pressure units (0.082 atmL/molK)

T is the absolute temperature (in Kelvins)

Δn is the change of stoichiometry of the reaction

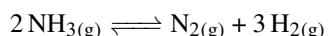
Let us analyze the role of Δn for the reaction:



Δn represents the number of molecules of products with respect to the number of molecules of reactants: 7-6=1. For this reaction, we have that $K_p = K_c(RT)$. However, the power of the relationship will depend on the stoichiometry of the reaction. At the same time, the relationship between both constants depends on the temperature.

Sample Problem 51

For the following reaction



The value of K_c at 300K is 17. Calculate the value of K_p at the same temperature.

SOLUTION

First we will write down the expression of both equilibrium constants:

$$K_c = \frac{[\text{N}_2] \cdot [\text{H}_2]^3}{[\text{NH}_3]^2} \quad K_p = \frac{P_{\text{N}_2} \cdot P_{\text{H}_2}^3}{P_{\text{NH}_3}^2}$$

We will also calculate Δn in order to establish the relationship between both constants:

$$\Delta n = 1 + 3 - 2 = 2$$

We have that:

$$K_p = K_c(RT)^{\Delta n} = K_c(RT)^2$$

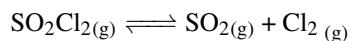
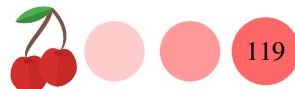
Given that K_c at 300K is 17:

$$K_p = K_c(RT)^{\Delta n} = 17(0.082 \cdot 300)^2 = 10287$$

In equilibrium, the pressure of products will be larger than the pressure of reactants.

❖ STUDY CHECK

For the following reaction



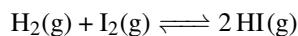
The value of K_p at 300K is 0.05. Calculate the value of K_c at the same temperature.

►Answer: 2×10^{-3}

4.3 Using equilibrium constants

We saw that the equilibrium constant of a reaction tells you whether there are more reactants or products in an equilibrium mixture. At the same time, one can use K_c to quantitatively calculate the value of the equilibrium concentration of reactants and products. This section will explain how to do this.

Solving from K_c Let's analyze the reaction of hydrogen (H_2) and iodine (I_2) to produce hydrogen iodide (HI):



The equilibrium constant at 300K is $3 \cdot 10^{-1}$. Analyzing a reaction mixture we find that the concentration of H_2 is 1M and the concentration of I_2 is 2M. We want to calculate how much HI we have in the mixture. As the concentrations of reactants and products are linked together through K_c we can certainly solve for $[\text{HI}]$. The expression for K_c is:

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2] \cdot [\text{I}_2]}$$

and we know that $[\text{H}_2] = 1\text{M}$ and $[\text{I}_2] = 2\text{M}$. Plugging the values in the expression of K_c , and given the numerical value of K_c we have:

$$3 \cdot 10^{-1} = \frac{[\text{HI}]^2}{1 \cdot 2}$$

Solving for $[\text{HI}]$ we have

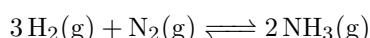
$$[\text{HI}]^2 = 0.6$$

To solve for $[\text{HI}]$ we have to use an square root:

$$[\text{HI}] = \sqrt[2]{0.6} = 0.77\text{M}$$

Sample Problem 52

The value of the equilibrium constant for the reaction



is $3 \cdot 10^8$ at 300K. An analysis of an equilibrium mixture gave a concentration of nitrogen and ammonia of 2M, respectively. Calculate the equilibrium concentration of hydrogen at 300K.

SOLUTION



The value of the equilibrium constant for the formation of ammonia is:

$$K_c = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3 \cdot [\text{N}_2]}$$

We know $[\text{NH}_3]$ and $[\text{N}_2]$ and both values are 2M, and we also know $K_c = 3 \cdot 10^8$. Plugging these values into the previous equations we obtain:

$$3 \cdot 10^8 = \frac{2^2}{[\text{H}_2]^3 \cdot 2}$$

we can solve for $[\text{H}_2]$:

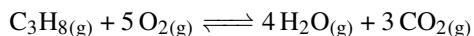
$$[\text{H}_2]^3 = 6.6 \cdot 10^{-9}$$

In order to obtain $[\text{H}_2]$ we need a cubic root:

$$[\text{H}_2] = \sqrt[3]{6.6 \cdot 10^{-9}} = 1.9 \cdot 10^{-3} M$$

◆ STUDY CHECK

The value of the equilibrium constant for the reaction



is 500 at a given temperature. An analysis of an equilibrium mixture gave a concentration of water, carbon dioxide and C_3H_8 of 1M. Calculate the equilibrium concentration of oxygen at that temperature.

►Answer: $[\text{O}_2] = 0.29 M$

4.4 Concentration or pressure ratio

In a chemical reaction, if we prepare a mixture of reactants they will generate products. At equilibrium reactants and products exist at a very specific ratio given by the equilibrium constant. What if we would prepare a mixture containing both reactants and products? Given that both reactants and products are related by an equilibrium, how would the concentrations change? In other words, would the reaction proceed toward the right, hence producing products, or the left to produce reactants? This section introduces the use of a concentration (or pressure) ratio that helps predict the direction in which a mixture of reactants and products will proceed toward equilibrium.

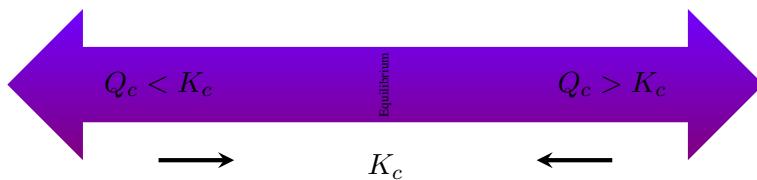
Definition of concentration ratio Equilibrium constants are ratios of equilibrium concentration or pressure of products over reactants measured after the system has reacted for an infinite time. Concentration ratios Q_c are the ratio of the concentration of products over reactants away from the equilibrium. In other words, they represent the reaction away from the equilibrium.

$$Q_c = \frac{[\text{Products}]_{\text{noneq}}}{[\text{Reactants}]_{\text{noneq}}} = \frac{[C]_{\text{noneq}}^c \cdot [D]_{\text{noneq}}^d}{[A]_{\text{noneq}}^a \cdot [B]_{\text{noneq}}^b}$$

concentration ratio (4.4)



Use of concentration ratios Concentration ratios help predict whether a reaction will proceed toward the left or toward the right when we start with a mixture of reactants and products away from equilibrium.



If Q_c is larger than K_c the reaction will proceed towards the left producing reactants. On the other hand, if Q_c is smaller than K_c the reaction will proceed towards the right producing products. If Q_c equals K_c then the reaction is in equilibrium.

Sample Problem 53

In two different experiments, we prepare mixtures of four chemicals interconnected by the following equilibrium:



Indicate if any of the mixtures is in equilibrium. If it is not, indicate whether the reaction will evolve towards the left or the right to reach equilibrium.

Experiment	1	2
[CO ₂]	0.0040	0.037
[H ₂]	0.0040	0.046
[CO]	0.0203	0.011
[H ₂ O]	0.0203	0.0011

SOLUTION

We will compute the concentration ratio for each experiment and compare the value with k_c . If Q_c is larger than k_c the reaction will proceed to the left whereas if Q_c is smaller than k_c the reaction will proceed to the right.

Experiment	1	2
[CO ₂]	0.0040	0.037
[H ₂]	0.0040	0.046
[CO]	0.0203	0.011
[H ₂ O]	0.0203	0.0011
Q_c	3.8×10^{-4}	140

None of the mixtures are in equilibrium as Q_c differs from k_c . In the first experiment the reaction will proceed to the right and in the second experiment the reaction will proceed to the left.

STUDY CHECK

We prepare mixtures of four chemicals in an experiment. These chemicals are interconnected by the following equilibrium:

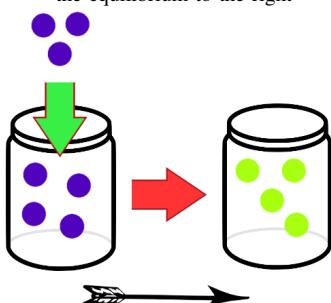


Indicate if the mixture is in equilibrium. If it is not, indicate whether the reaction will evolve towards the left or the right to reach equilibrium.

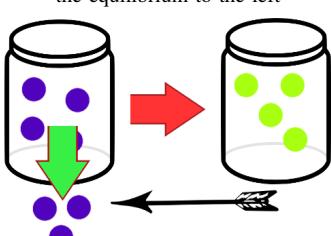


▼Henry Louis Le Châtelier was a french chemist who devised a principle used by chemists to predict the effect a changing condition has on a system in chemical equilibrium.

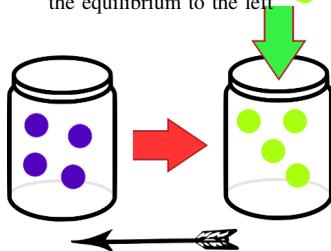
Adding reactants shifts the equilibrium to the right



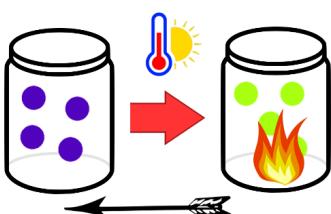
Removing reactants shifts the equilibrium to the left



Adding products shifts the equilibrium to the left



Warming an exothermic reaction shifts the equilibrium to the left



▼Le Châtelier principle helps predicts the outcome of altering an equilibrium mixture.

Experiment	1
[CO ₂]	0.0005
[H ₂]	0.0076
[CO]	0.0094
[H ₂ O]	0.0025

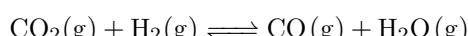
►Answer: to the right

4.5 Le Chatelier principle

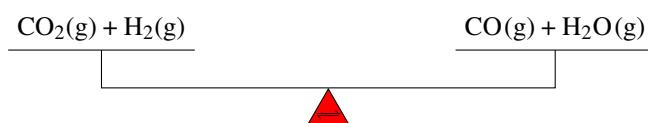
At this point, we have covered the idea of equilibrium and we have seen that the forward and reverse reactions have the same rate at equilibrium. Now, what happens if you alter this equilibrium? Le Châtelier principle claims a reaction will go back to its original equilibrium state by shifting left or right.

Le Chatelier principle When a reaction is in equilibrium the forward and reverse reactions proceed at the same speed. Also in an equilibrium state, the concentrations of reactants and products have very specific values. Imagine that you create stress conditions by adding reactants or products or even changing the temperature. This stress will have an impact on the equilibrium and the reaction eventually will reach a new state of equilibrium by somehow counteracting this stress. Le Châtelier principle says that when stress is placed in a reaction (adding or removing reactant or products, increasing or decreasing temperature) the equilibrium will be shifted in the direction that relieves that stress. Table 4.2 displays different aspects regarding Le Châtelier's principle in terms of parameter change and consequence.

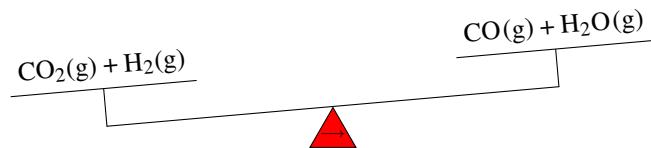
Change in concentration Let us consider the following equilibrium:



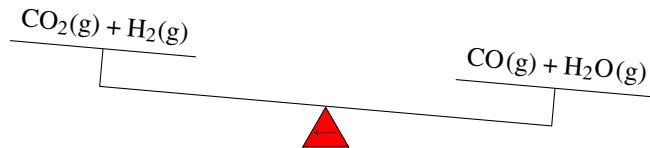
K_c for this reaction equals one at 1200K. This means that the concentration of reactants and products are the same. We can represent this using this balance or seesaw



If we add some CO₂ the equilibrium will be affected. To counteract this stress, the reaction will restore the equilibrium by decreasing the amount of CO₂. This can only be achieved by displacing the equilibrium to the right so that CO₂ is removed. Mind that CO₂ is consumed if the reaction moves from reactants → to products and it is produced when going from products ← to reactants. We can represent this with the following seesaw.



As we added CO₂ the reactants now weigh more and hence the reaction has to proceed to the right → . Now imagine we remove some CO₂(g). Again, the equilibrium will be affected and the reaction will restore its equilibrium state by doing the opposite, that is producing CO₂(g) as the reaction proceeds from reactants ← to products. Again using the seesaw:

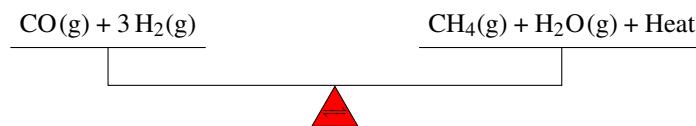


We can also add a different chemical that is not involved in the equilibrium. In this case, the equilibrium will not be affected by this change.

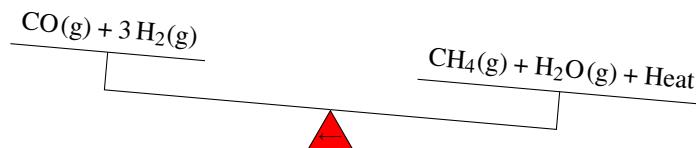
Temperature change Let us consider the following equilibrium that produces heat—remember we describe these types of reactions as exothermic:



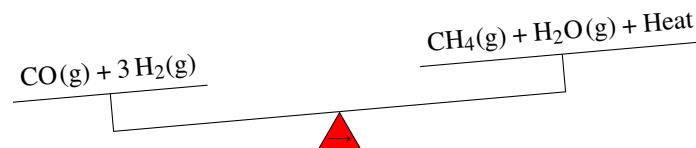
Again, this reaction is in equilibrium so we can use the same seesaw analogy.

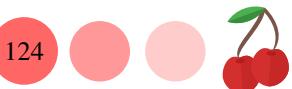


If we increase the temperature of the system, the equilibrium will be affected. To go back to an equilibrium state the reaction will decrease the temperature of the container. As the reaction produces heat, a way to decrease the system temperature is to generate reactants (←). Again, using the scale that means:



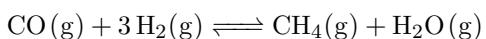
Differently now if we decrease the temperature, the reaction will increase the temperature by going back to its equilibrium state going from reactants → to products. This is because heat is produced as a product



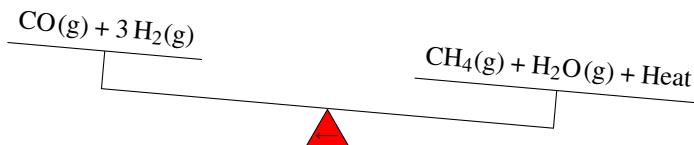


Volume change

We can also think about increasing or decreasing the volume in which the reaction takes place. This change will have an impact on the reaction equilibrium as the concentrations of reactants and products will be altered by this change. Changes in volume will shift the reaction towards the left or right depending on the overall stoichiometric change of the reaction, that is on whether the reaction produces or consumes molecules. For reactions that generate matter, that is, in the case that $\Delta n > 0$, increasing the volume will follow the increase of the number of moles. In other words, by increasing the volume, the equilibrium will shift towards the products, that is towards the right. For reactions that consume matter ($\Delta n < 0$), increasing the volume will shift the equilibrium towards the reactants, that is towards the left. For example, the reaction below consumes molecules:



if we increase the volume of the container in which the reaction takes place, the equilibrium will shift toward the left:



The opposite shift will follow a volume decrease as the reaction shift towards the right.

Sample Problem 54

For the next endothermic reaction indicate whether the reaction will shift right (\longrightarrow) or left (\longleftarrow) after the following changes:



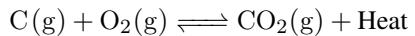
- (a) adding reactants (b) adding products (c) decreasing the temperature.

SOLUTION

(a) Adding reactants always displaces the equilibrium so that reactants are consumed, hence the reaction will proceed \longrightarrow . (b) After adding products the reaction will tend to reduce the amount of products, and hence it will go \longleftarrow . (c) The reaction is endothermic that means that it consumes heat. If we decrease the temperature it will tend to increase the temperature and hence heat needs to be formed. This will only happen if the reaction proceeds (\longleftarrow).

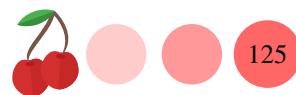
◆ STUDY CHECK

For next exothermic reaction indicate whether the reaction will shift right (\longrightarrow) or left (\longleftarrow) after the following changes:



- (a) removing reactants (b) removing products (c) decreasing the temperature.

►Answer: (a) \longleftarrow ; (b) \longrightarrow ; (c) \longrightarrow .



CHAPTER 4

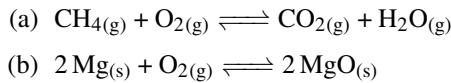
CHEMICAL EQUILIBRIUM

- 4.1** True or false:(a) At equilibrium, the rate of the reverse reaction is twice the rate of the forward reaction
(b) At equilibrium, the concentration of products do not change with time (c) At equilibrium, the concentration of reactants do not change with time (d) At equilibrium, the concentration of reactants and products do not change with time

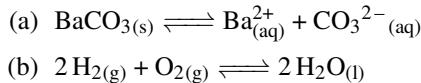
- 4.2** True or false:(a) At equilibrium, the rate of the reverse reaction do not change (b) At equilibrium, the rate of the forward reaction do not change (c) At equilibrium, the rate of the reverse reaction equals the rate of the forward reaction (d) At equilibrium, the concentration of reactants and products are not constant

EQUILIBRIUM CONSTANTS

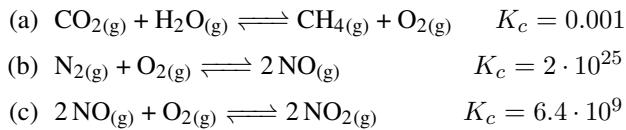
- 4.3** Write down the forward and reverse reactions for the following reactions in equilibrium:



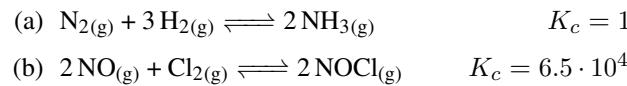
- 4.4** Write down the forward and reverse reactions for the following reactions in equilibrium:



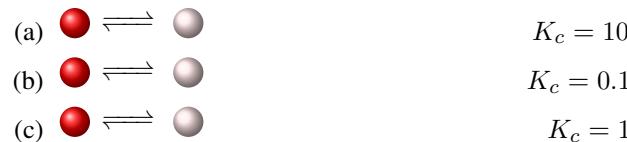
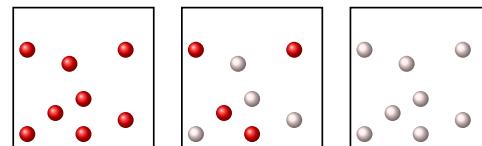
- 4.5** For the reactions below and given the value of the equilibrium constant indicate whether the equilibrium mixture will have: (a) More reactants than products (b) More products than reactants (c) Same amount of products and reactants



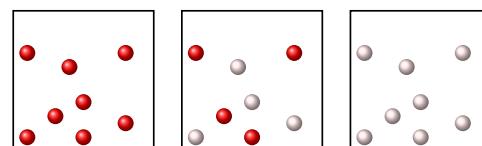
- 4.6** For the reactions below and given the value of the equilibrium constant indicate whether the equilibrium mixture will have: (a) More reactants than products (b) More products than reactants (c) Same amount of products and reactants



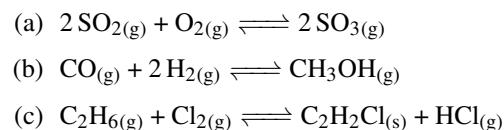
- 4.7** Indicate which of the following diagrams (left, center, right) represent better the system at equilibrium:



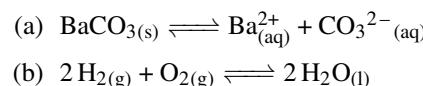
- 4.8** Indicate which of the following diagrams (left, center, right) represent better the system at equilibrium:



- 4.9** Write down the expressions of K_c and K_p for the following reactions:



- 4.10** Write down the expression of K_c for the following reactions:



USING EQUILIBRIUM CONSTANTS

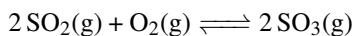


4.11 The reaction of carbon monoxide with hydrogen to produce methanol has a equilibrium constant in terms of concentration that at a certain temperature is larger than one



Calculate: (a) the equilibrium concentration of hydrogen (H_2) given that the equilibrium concentration of methanol (CH_3OH) and carbon monoxide (CO) for the reaction is 2M, respectively. (b) the equilibrium concentration of hydrogen (H_2) given that the equilibrium concentration of methanol (CH_3OH) and carbon monoxide (CO) for the reaction are 3M and 1M, respectively.

4.12 Consider the following reaction:



(a) Write down the expression of K_c . (b) Calculate the numerical value of K_c for the reaction if the concentrations at equilibrium at 1000K are 2M for SO_3 , 0.3M for O_2 and 1M for SO_2 . (c) indicate whether an equilibrium mixture will contain mostly products, mostly reactants or equal amounts of reactants and products.

4.13 Complete the table and calculate K_c and K_p at 300K:

Reaction	K_c	K_p
(a) $2 \text{NH}_3\text{(g)} \rightleftharpoons \text{N}_2\text{(g)} + 3 \text{H}_2\text{(g)}$	17	
(b) $\text{SO}_2\text{Cl}_2\text{(g)} \rightleftharpoons \text{SO}_2\text{(g)} + \text{Cl}_2\text{(g)}$		0.05

4.14 Complete the table and calculate K_c and K_p at 300K:

Reaction	K_c	K_p
(a) $2 \text{SO}_3\text{(g)} \rightleftharpoons 2 \text{SO}_2\text{(g)} + \text{O}_2\text{(g)}$	0.243	
(b) $\text{Cl}_2\text{(g)} + \text{Br}_2\text{(g)} \rightleftharpoons 2 \text{BrCl}_2\text{(g)}$		0.196

CONCENTRATION RATIO

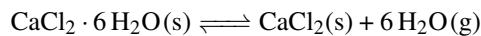
4.15 For the reactions below indicate whether they will evolve towards the right or towards the left in order to reach equilibrium.

Reaction	K_c	Q
(a) $2 \text{NH}_3\text{(g)} \rightleftharpoons \text{N}_2 + 3 \text{H}_2$	17	20
(b) $2 \text{SO}_3\text{(g)} \rightleftharpoons 2 \text{SO}_2\text{(g)} + \text{O}_2\text{(g)}$	0.243	10

4.16 For the reactions below indicate whether they will evolve towards the right or towards the left in order to reach equilibrium.

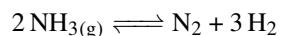
Reaction	K_c	Q
(a) $\text{H}_2\text{(g)} + \text{I}_2 \rightleftharpoons 2 \text{HI(g)}$	50	0.1
(b) $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{O(g)}$	0.196	0.196

4.17 For the decomposition of calcium chloride hexahydrate



we have that $K_c=3.5 \times 10^{-54}$ and $Q=10$ at 300K. Indicate towards which direction the reaction will evolve to reach equilibrium.

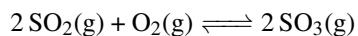
4.18 For the decomposition of calcium chloride hexahydrate



we have that $K_c=17$ and $Q=10$ at 300K. Indicate towards which direction the reaction will evolve to reach equilibrium.

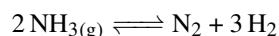
LE CHÂTELIER PRINCIPLE

4.19 Using the Le Châtelier principle indicate whether the reaction below

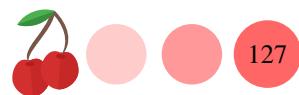


will shift in the direction of products (→) or reactants (←) after the following actions: (a) add SO_2 (b) add SO_3 (c) remove O_2

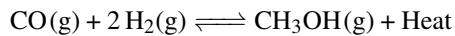
4.20 Using the Le Châtelier principle indicate whether the reaction below



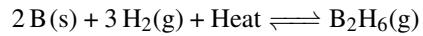
will shift in the direction of products (→) or reactants (←) after the following actions: (a) add NH_3 (b) add N_2 (c) remove H_2



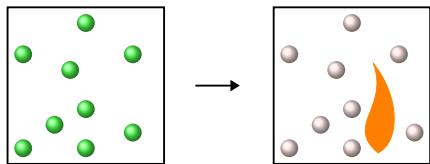
4.21 According to Le Châtelier principle indicate whether the reaction will shift in the direction of products (\longrightarrow) or reactants (\longleftarrow) after we increase temperature:



4.22 According to Le Châtelier principle indicate whether the reaction will shift in the direction of products (\longrightarrow) or reactants (\longleftarrow) after we increase temperature:

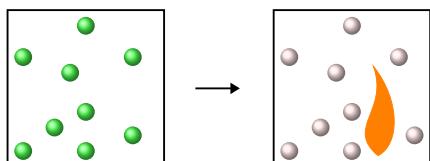


4.23 According to Le Châtelier principle indicate whether the following reaction will shift in the direction of products (\longrightarrow) or reactants (\longleftarrow) after the following changes:



- (a) adding reactants (b) increasing temperature (c) decreasing temperature

4.24 According to Le Châtelier principle indicate whether the following reaction will shift in the direction of products (\longrightarrow) or reactants (\longleftarrow) after the following changes:



- (a) adding products (b) removing products (c) increasing temperature



Ch. 5. Acids & Bases

ACIDS and bases are part of our everyday life, from the vinegar in our salad to many of the candy our kids eat such as Sour Patch Kids. On one hand, vinegar tastes sour as it contains acetic acid. Sour Patch Kids, on the other hand, are coated in a combination of sugar and acids. Acids help us digest food and help bacteria produce yogurt or cottage cheese. Bases on the other hand are used in drain openers, oven cleaners, or the production of soap. This chapter covers the properties of acids and bases qualitatively and quantitatively. You will learn how to identify each of these chemicals and categorize them according to their strength. Yes! acids and bases are strong, and some of them can seriously hurt you. More importantly, this chapter introduces the idea of PH, which quantifies the acidity of a solution. The PH of an acid or base depends on its strength and here we will cover how to compute the PH of solutions of strong and weak acids and bases. Balancing PH is crucial for health. Finally, we will briefly cover the idea of a buffer that helps regulate the PH of solutions and titrations used to elucidate the molarity of an unknown acid or base.

5.1 The nature of acids and Bases

Acids have very different properties than bases. Acids are acidic, have a sour taste, and can sting to the touch. Bases are basic, have a bitter–chalky–taste, and feel soapy–slippery–to the touch. On the one hand, acids are extensively used in the food and perfume industry. For example, vinegar—a liquid solution of acetic acid—is used in pickles and food preparations. On the other hand, lemon and orange juice, containing citric acid, are used to prepare effervescent salts and as food preservatives. Acids are also used in the production of batteries. For example, car batteries contain corrosive sulphuric acid. On the other hand, bases are extensively used in manufacturing. As a first example, sodium hydroxide is used to manufacture soap, medicines, and paper. As a second example, calcium hydroxide—also known as slaked lime—is used to neutralize the acid in water supplies or as an antidote for food poisoning. This hydroxide is also used in the construction industry, mixed with sand and water to make mortar. As a third example, potassium hydroxide (KOH), is used in alkali batteries. Finally, ammonia is an extensively used cleaning product, also used to remove ink spots from clothes or grease from window panes.

Strong and weak acids and bases Strong acids are strong electrolytes that completely dissociate to produce protons. Similarly, strong bases completely dissociate in solution generating hydroxyls. On the contrary, weak acids and bases are just weak electrolytes that dissociate partially in solution generating only a small amount of protons and hydroxyls. The dissociation of strong acids and bases is represented



using a single arrow, whereas the dissociation of weak acids and bases is represented using a double harpoon. For example, hydrochloric acid is a strong electrolyte and its dissociation is represented by



whereas hydrofluoric acid is a weak electrolyte and its dissociation is represented by



Arrhenius acid-base model In general terms, we can identify some acids and bases by inspecting its formula. Svante Arrhenius claimed around 1884 that acids are acidic because contain hydrogen in their structure and when dissolved in water they produce *protons*: H^+ , also called hydronium ion written as H_3O^+ . Let us consider these chemicals: HF, H_2SO_4 and HNO_3 . All these chemicals, named hydrofluoric acid, sulfuric acid, and nitric acid, are Arrhenius acidic. The reaction below described the process of dissociation of hydrogen chloride to produce chloride and a proton:

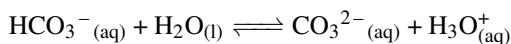


Based on the acid dissociation reaction above, we say chloride is the result of deprotonating hydrochloric acid. In other words, chloride is deprotonated. Based on this dissociation reaction that happens in water, we can say hydrogen chloride also known as hydrochloric acid is an Arrhenius acid, as it produces protons in water. We have that acids are classified as monoprotic, diprotic, and polyprotic. Monoprotic acids have only one acidic H on their molecule (e.g. HNO_3), whereas diprotic acids have two (e.g. H_2NO_4) and polyprotic acids have more than two (e.g. H_3PO_4). Differently, bases are basic because when dissolved in water they produce *hydroxyls*: OH^- . Hydroxides are Arrhenius bases and for example, NaOH and $\text{Ca}(\text{OH})_2$, named sodium hydroxide and calcium hydroxide, are well-known bases. Let us address now the dissociation of sodium hydroxide in water:



This chemical is an Arrhenius base as it produces hydroxyls. Therefore, Arrhenius acids and bases produce protons and hydroxyls in water, respectively. However, the Arrhenius model does not explain why chemicals unsolved in water can also be acidic or even why chemicals such as NH_3 —a molecule without OH on its structure—can be basic.

Brönsted-Lowry acid-base model In 1923 two different chemists Thomas Lowry and Johannes Brönsted proposed what is now known as the Brönsted-Lowry model of acids and bases. The Brönsted-Lowry model is a more advanced acid-base model. This model claims acids are chemicals that give away protons (H^+) whereas bases receive protons. This way, Brönsted-Lowry extends the Arrhenius model to other solvents different than water, as the solvent is not part of the definition. Based on this model, we can understand how $\text{HCO}_3^-_{(\text{aq})}$ can act as an acid giving away protons to water and as a base receiving protons from water. When acting as an acid:



When acting as a base:



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▼ Hydrofluoric acid is a weak acid used to dissolve glass.



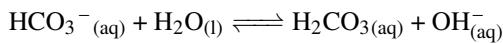
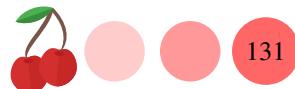
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▼ Citrus such as lemons or oranges are acidic.



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▼ Pickles contain vinegar that is a solution of acetic acid in water.



As you can see, an acid-base reaction is essentially a proton transfer reaction, in which a proton H^+ transfers from an acid into a base. Compounds that can act as acids or bases are referred to as *amphiprotic* as they can act as a proton donor or acceptor. Other examples are: H_2O , HS^- or HSO_4^- . Still, the Brönsted-Lowry model does not explain why chemicals such as ammonia are a base and carbon dioxide an acid. In particular, the model does not justify what structural particularity makes ammonia behave as a base and carbon dioxide (with no hydrogen on its structure) as an acid.

Sample Problem 55

Identify the following chemicals as Arrhenius acids or bases and give their names: HCl, KOH, H_3PO_4 and CH_3COOH .

SOLUTION

The acids are: HCl, H_3PO_4 and CH_3COOH . Their names are: hydrochloric acid, phosphoric acid and acetic acid, the later is a common name. KOH is a base called potassium hydroxide.

◆ STUDY CHECK

Identify the following chemicals as Arrhenius acids or bases and give their names: NaOH and H_2CO_3 .

►Answer: sodium hydroxide (base) and carbonic acid (acid).

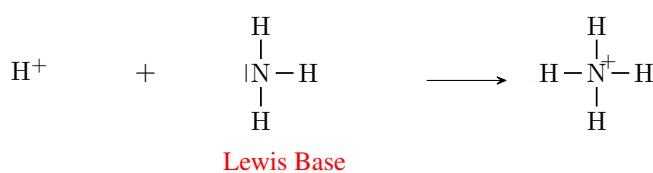
▼ Bath bombs are made of acidic and basic ingredients that combine in water to make a fizzy bath time experience.



© wikipedia

Lewis acid-base model This is the most comprehensive acid-base model that we will cover in this chapter. A Lewis acid is a chemical able to receive electron pairs, whereas a Lewis base can give way to electron pairs. In other words, acids are the electron-pair receiver and bases are electron-pair givers. In the example below you can see why ammonia acts as a base:

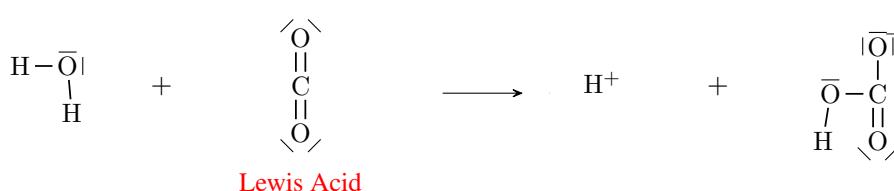
▼ Ashes are basic.



© wikipedia

Ammonia as well as other molecules contain lone pairs. These lone pairs are key in the definition of a Lewis acid-base, as acids and bases receive and give away electron density. Lewis bases contain lone pairs and can give away electron density to an acid. Another example is presented below. The presence of two lone pairs in water makes it a Lewis base that can give electron density to carbon dioxide, a lewis acid.

▼ Limestone reactant with hydrochloric acid to give carbon dioxide bubbles.



© www.wallpaperflare.com

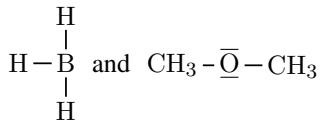


Sample Problem 56

Indicate whether the following chemicals are lewis acid or lewis bases: (a) BH_3 and (b) $\text{CH}_3-\text{O}-\text{CH}_3$.

SOLUTION

The lewis structure of the molecules are:



BH_3 can receive a lone pair to complete the octet of Boron and hence it will be a Lewis acid. Differently, $\text{CH}_3-\overline{\text{O}}-\text{CH}_3$ is a Lewis base as oxygen has two lone pairs that can be given away.

❖ STUDY CHECK

Indicate whether the following chemicals are lewis acid or lewis bases: (a) AlH_3 and (b) OH^- .

► Answer (a) acid and (b) base.

In summary, the Arrhenius definition is based on what is on a solution, whereas the Brönsted-Lowry definition is based on giving and receiving protons (see Table 5.1). Finally, the Lewis definition is based on giving and receiving lone pairs. All these definitions are complementary and all Arrhenius acids are Brönsted-Lowry as well as Lewis acids.

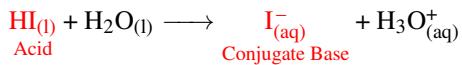
Table 5.1 Acid-base models

Model	Acid definition	Base definition
Arrhenius	H^+ producer	OH^- producer
Brönsted-Lowry	H^+ donor	H^+ acceptor
Lewis	electron-pair acceptor	electron-pair donor

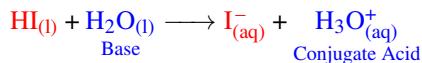
5.2 Dissociation of acids and bases

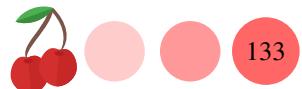
This second section will cover the acid and base dissolution in water. Water plays a key role in the acid-base character of a chemical as these chemicals ultimately react with water. When acids and bases solve in water, they dissociate producing a byproduct called the conjugate base and conjugate acid. We will describe how to set up the dissociation equilibrium and how to identify conjugate acid-base pairs.

Conjugate acids and bases A conjugate acid-base pair are molecules or ions related by the loss of one H^+ . For example: hydroiodic acid HI and iodate I^- or water H_2O and protons H_3O^- . The product of the dissociation of acids is a conjugate base. For example:



Similarly, bases produce a conjugate acid. In the example below, water acts as a base and a proton is the conjugate acid:

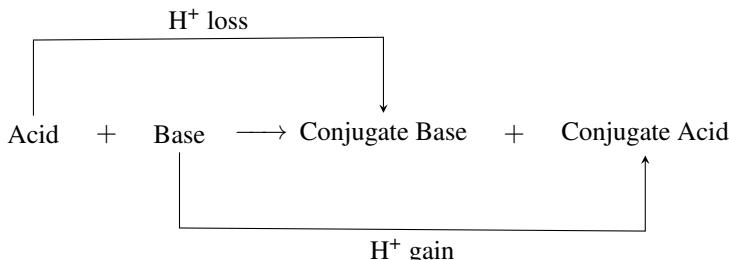




At the same time acids react with bases as they have opposite characters. Following the previous example:

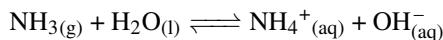


Hence, we have that acid reactants with a base to produce a conjugate base and a conjugate acid. We can use the diagram below to identify the acid-conjugate base pairs:



Sample Problem 57

Identify the acid, the base, the conjugate acid and the conjugate base in the reaction:



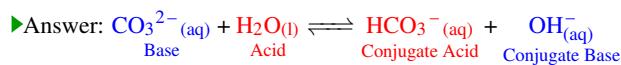
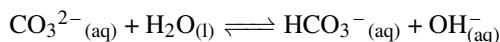
SOLUTION

The trick is first identifying the acid and the base starting for the left side of the formula. In this case $\text{NH}_3_{(g)}$ is the base and hence water is the acid. Now connect the acid and the base with the other side of the arrow, and use conjugate with the opposite term. For example: NH_3 is a base and should be related with NH_4^+ that is the conjugate acid. Similarly, H_2O is an acid, being related with OH^- that is the conjugate base. In summary:



◆ STUDY CHECK

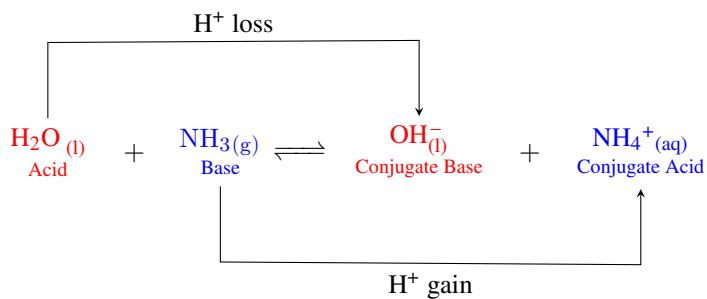
Identify the acid, the base, the conjugate acid and the conjugate base in the reaction:



Writing down acid-base equilibria Now let us address how to write down acid-base equilibria from scratch, starting with the dissociation of ammonia (NH_3). Dissociation reactions are the reaction of an acid or base and water:



We have that ammonia is a base and hence water will act as an acid. Bases receive protons whereas acids give protons away. In the equilibrium, we will remove one proton from water and add it to ammonia, producing respectively a hydroxyl and an ammonium ion:



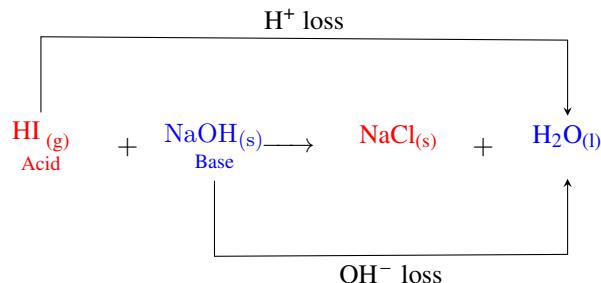
And that will give the dissociation equilibrium of ammonia.



We can now address the reaction between an acid and a base for example, between sodium hydroxide and hydroiodic acid:

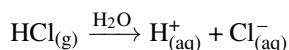


In these types of acid-base reactions, we have that the acid will generate a proton and the base will generate a hydroxyl, which will both combine to produce water and a salt, sodium chloride:

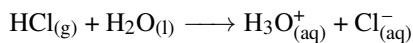


This way, dissociation and acid-base reaction function in a very similar manner.

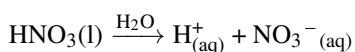
Including water in the dissociation Let us consider an acid such as HCl. We know acids produce protons (H^+ or H_3O^+) so we can express the acid dissociation as:

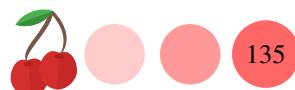


We indicate water on top of the arrow to represent that the dissociation process happens in water. There is an alternative way to represent this process by including explicitly water:

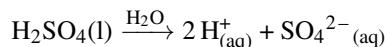


This way we explicitly represent the role of water as a proton receiver. Ultimately, both ways are correct and for some chemicals (e.g. NH_3) it is more convenient to use the role of water whereas for others it makes no difference. In the following, we present more examples. For the case of HNO_3 , nitric acid, we have:

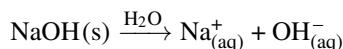




that means once dissolved in water, nitric acid gives a proton and forms a nitrate NO_3^- cation. Some other acids, such as H_2SO_4 are diprotic, as they have two protons and hence they can lose both while reacting with water:



Bases produce hydroxyls (OH^-) and an example of a base dissociation would be:

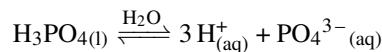


Sample Problem 58

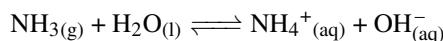
Write down the dissociation reaction using double arrows for the following chemicals: $\text{H}_3\text{PO}_4(\text{l})$ and $\text{NH}_3(\text{g})$.

SOLUTION

Phosphoric acid is a triprotic acid with three possible protons that can be given away:



As the molecules contains protons there is no need to explicitly include water in the equilibrium. Ammonia is a base and needs is the only case in which you need to explicitly use water to help dissociate the base. This is because ammonia does not contain hydroxyls.

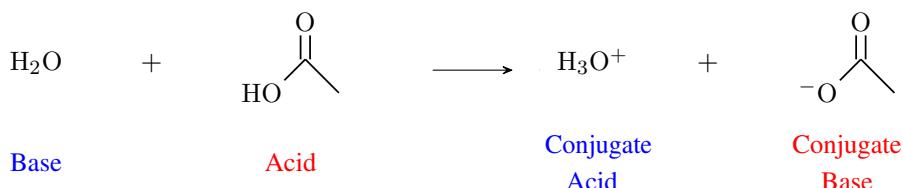


◆ STUDY CHECK

Write down the dissociation reaction using double arrows for the following chemicals: $\text{HI}(\text{g})$ and $\text{HClO}_2(\text{l})$.

► Answer: $\text{HI}(\text{g}) \rightleftharpoons \text{H}_{(\text{aq})}^+ + \text{I}_{(\text{aq})}^-$ and $\text{HClO}_2(\text{l}) \rightleftharpoons \text{H}_{(\text{aq})}^+ + \text{ClO}_2^-(\text{aq})$.

Conjugate organic acids and bases Organic acids are also called carboxylic acids. Amines tend to be organic bases. A conjugate organic acid-base pair are organic molecule or ions related by the loss of one H^+ . For example, acetic acid, the acid present in vinegar, is an organic acid that will react with water (the solvent) to produce a conjugate base called acetate. Acetates are used in some printing processes. For example, vinyl acetate is employed in the production of plastics, cellulose acetate is used in making photographic films and textiles. Acids produce protons (H^+) and therefore conjugate bases are negatively charged. The corresponding dissociation equilibrium is shown below:



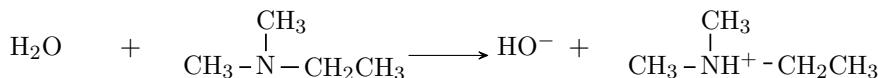
Amines are basic and they will react with water to produce a conjugate acid. Bases receive protons (H^+) from the solvent, hence the conjugate acid of a base is positively charged. An example is presented below.



Again, to review, we have that organic acids produce protons and generate negatively charged conjugate bases. At the same time, organic bases consume protons and generate a conjugate acid that is positively charged. To identify a conjugate acid-base pair we just need to look for a pair of molecules that resemble each other.

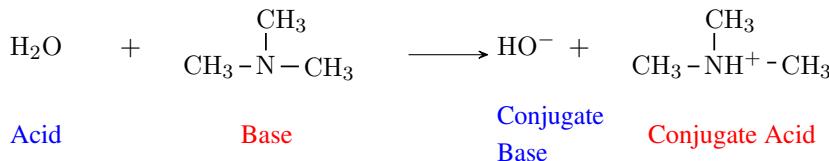
Sample Problem 59

Identify the acid, the base, the conjugate acid and the conjugate base in the reaction involving organic molecules:



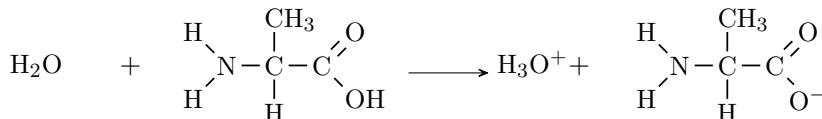
SOLUTION

We have that acids produce protons and bases receive those protons. In the reaction above, the second reactants received a proton from water and hence, it acts as a base. Hence water will be the acid and the amine, the second reactants, will be the base. The conjugate base would be HO^- and the conjugate acid the product on the right. These results make sense as amines are organic bases.



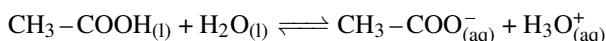
◆ STUDY CHECK

Identify the acid, the base, the conjugate acid and the conjugate base in the reaction:

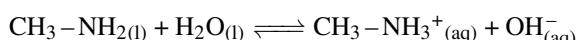


►Answer: B + A → CA + CB

Dissociating organic acids and bases Organic acids and bases often contain numerous hydrogen atoms in their molecular structure. It is critical to dissociate these molecules using the acid and basic centers and not others. For example, acetic acid $\text{CH}_3 - \text{COOH}$ contains a methyl group and a carboxylic group. When dissociation this molecule, we need to remove the proton only from the acidic group, hence its name:



Methylamine $\text{CH}_3 - \text{NH}_2$, on the other hand, is an organic base with a methyl and an amine group. Amine groups are basic per nature—they resemble ammonia—and hence when dissociation this base we need to attach an extra proton to the basic center:



**Sample Problem 60**

Write down the following dissociation or acid-base reaction involving one proton: $\text{H}_2\text{CO}_{3(\text{aq})} + \text{H}_2\text{O}_{(\text{aq})} \longrightarrow$

SOLUTION

As this is a dissociation reaction and carbonic acid is an acid, we will need the help of water. We will have that carbonic acid will lose one proton and water will gain that proton.



As carbonic acid loses a proton to become hydrogencarbonate, its charge becomes negative. Similarly, as water gains a proton to become the hydronium ion, its charge becomes positive so that overall the charge of the reaction is balanced.

❖ STUDY CHECK

Write down the following dissociation or acid-base reaction involving one proton: $\text{HCl}_{(\text{g})} + \text{NH}_3_{(\text{g})} \longrightarrow$

►Answer: $\text{HCl}_{(\text{g})} + \text{NH}_3_{(\text{g})} \longrightarrow \text{NH}_4\text{Cl}_{(\text{s})} + \text{H}_2\text{O}_{(\text{l})}$

5.3 Strength of acids and bases

At this point, we are familiar with acids and bases. Acids have a sour taste and produce protons in water. Differently, bases feel soupy to the touch and produce hydroxyls. Both acids and bases react together giving conjugate species. This section gains further insight into the strength of acids and bases. Some acids are weaker while others are stronger. The same idea can be applied to bases. Here we will also learn how to quantify the strength of an acid or base and how to compare the acidic or basic character of a chemical.

Review of acid-base strength Acids and bases are indeed electrolytes. Remember electrolytes can be weak or strong depending on the degree to which they dissociate. Strong acids are strong electrolytes that dissociate completely in water producing large quantities of protons H^+ . Strong bases are strong electrolytes that dissociate completely to produce this time large quantities of hydroxyls OH^- . Weak acids or weak bases dissociate only partially and hence they produce fewer protons or hydroxyls. Examples of strong electrolytes are: HCl , H_2SO_4 or HNO_3 . As they dissociate completely we use a single arrow to indicate they are strong electrolytes:



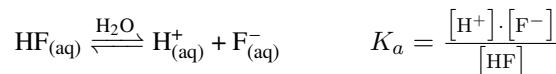
Weak acids or bases that only dissociate partially are represented by a double arrow as the reaction is indeed an equilibrium. Examples of weak acids or bases are NH_3 or HF .



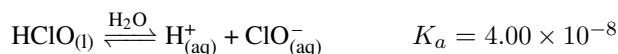
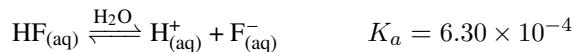
Strength of acids and bases How do we quantify the strength of an acid or base? Weak acids dissociate partially in the water, and the dissociation is equilibrated. This means that in the same container, the molecular form of the acid coexists with



its ionic-conjugate form. For this reason, we can employ an equilibrium constant called acidity constant K_a to characterize the degree of dissociation. The larger K_a the stronger the acid and hence the more protons will be produced in the solution. Let's consider the case of HF. We have that the expression of the acidity constant will be:

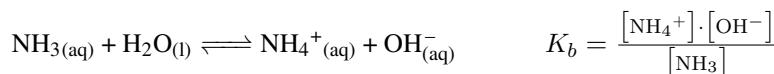


If we compare the acidity constant of two different acids, for example, hydrofluoric acid and hypochlorous acid

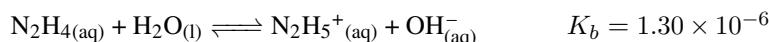
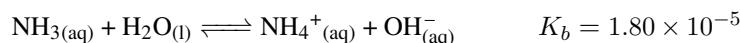


we can conclude that HF is stronger than HClO as its acidity constant is larger. Table 5.2 reports acidity constants for several acids and bases.

Basicity constant In a very similar way, bases also have what we call base dissociation constants: K_b . The bigger this value the stronger the base and the more hydroxyls will be produced. In the case of ammonia:



remember liquid water can not be part of an equilibrium constant. If we compare the basicity constant of two different bases, for example, ammonia and hydrazine



we can conclude that NH₃ is stronger than N₂H₄ as its basicity constant is larger.

K_a and K_b Acidity and basicity are related concepts. As such, there is a relationship between the acidity and basicity constants of an acid or base given by:

$$K_a \cdot K_b = 1.0 \cdot 10^{-14} \quad (5.1)$$

This relationship implies that all acids and bases have an acidity as well as basicity constants. For example, if the constant of acidity of a given acid is 1.5×10^{-5} , the basicity constant of the same species would be 6.6×10^{-10} . If K_a is large and the acid is strong K_b must be small and the basic character of a strong acid is very weak. Further in the chapter, Table 5.2 lists some acidity and basicity constants. In general, some simple rules predict the acid-base character of an acid-conjugate base pair. Strong acids in general produce weak conjugate bases. For example, HCl is a strong acid and its conjugate base (Cl⁻) is a weak base. Differently, HF is a weak acid and its conjugate base (F⁻) is a moderately strong base. Also, if pK_a is smaller than 7 we can consider that the chemical is more acidic than basic, and we call the chemical an acid. If pK_a is larger than 7 (and therefore pK_b is smaller than 7) we can consider that the chemical is more basic than acidic, and we call the chemical a base.

**Table 5.2 Acidity and basicity constants at 25°C**

Name	Formula	K_a	Name	Formula	K_a	
Increasing acidic strength	Hypoiodous acid	3.20×10^{-11}	Increasing acidic strength	:		
	Phenol	1.00×10^{-10}		Fluoroacetic acid	2.60×10^{-3}	
	Hydrocyanic acid	6.20×10^{-10}		Formic acid	1.80×10^{-4}	
	Hypobromous acid	2.80×10^{-9}		Bromoacetic acid	1.30×10^{-3}	
	Hypochlorous acid	4.00×10^{-8}		Chloroacetic acid	1.30×10^{-3}	
	Benzoic acid	6.25×10^{-5}		Dichloroacetic acid	4.50×10^{-2}	
	Hydrazoic acid	2.50×10^{-5}		Periodic acid	2.30×10^{-2}	
	Acetic acid	1.75×10^{-5}		Chlorous acid	1.10×10^{-2}	
	Iodoacetic acid	6.60×10^{-4}		Trichloroacetic acid	2.20×10^{-1}	
	Hydrofluoric acid	6.30×10^{-4}		Trifluoroacetic acid	3.00×10^{-1}	
	Nitrous acid	5.60×10^{-4}		Iodic acid	1.70×10^{-1}	
	Cyanic acid	3.50×10^{-4}		Chromic acid	1.80×10^{-1}	
	:					
Increasing basicity strength	Name	Formula	K_b	Name	Formula	K_b
	Aniline	$C_6H_5NH_2$	7.40×10^{-10}	Increasing basicity strength	:	
	Pyridine	C_5H_5N	1.70×10^{-9}		$C_4H_9NH_2$	4.00×10^{-4}
	Hydroxylamine	NH_2OH	8.70×10^{-9}		$C_2H_5NH_2$	4.50×10^{-4}
	Hydrazine	N_2H_4	1.30×10^{-6}		CH_3NH_2	4.60×10^{-4}
	Ammonia	NH_3	1.80×10^{-5}		$(CH_3)_3CNH_2$	4.80×10^{-4}
	Propylamine	$C_3H_7NH_2$	3.50×10^{-4}		$(CH_3)_2NH$	5.40×10^{-4}
	:					

Sample Problem 61

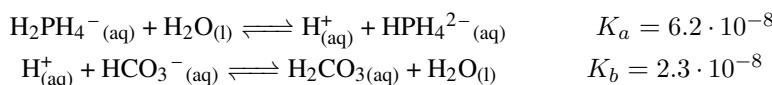
Indicate the strongest acid from:

**SOLUTION**

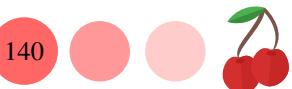
The acid dissociation constant tells how strong is the acid, hence the larger K_a the stronger the acid. Comparing both values: $K_a(HF) = 7.2 \cdot 10^{-4}$ and $K_a(HNO_2) = 4.5 \cdot 10^{-4}$, HF is the stronger of both.

◆ STUDY CHECK

Indicate the strongest of the following acids:

► Answer: H_2CO_3 is the strongest.

pK_a and pK_b As acidity and basicity constants tend to be very small numbers there is



a convenient form to deal with these values. By using logarithms one can transform a very tinny value into a larger digit. Specifically, if we use the negative value of a logarithm then we can convert a negative power of ten into a larger positive value. For example,

$$-\log(1 \times 10^{-5}) = 5$$

Using this mathematical trick, we define the pK_a and pK_b :

$$PK_a = -\log(K_a) \text{ and } PK_b = -\log(K_b) \quad (5.2)$$

For example, as the acidity constant of acetic acid is 1.75×10^{-5} its PK_a would be 4.74. Similarly, the basicity constant of aniline is 7.40×10^{-10} , and PK_b would be 9.13. We also use the following expression to convert pK_a and pK_b into K_a and K_b

$$K_a = 10^{-PK_a} \text{ and } K_b = 10^{-PK_b} \quad (5.3)$$

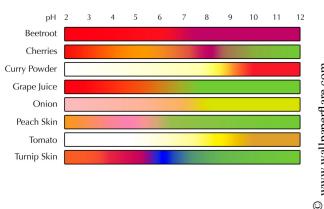
For example, as the PK_a of nitrous acid is 3.37, the acidity constant of this acid is 4.26×10^{-4} .

▼ A PH meter is used to measure the PH of solutions.



© www.wallpaperflare.com

▼ Color for different natural indicators depending on the pH.



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▼ Over breathing causes alkalosis and the PH of blood increases from 7.4. The CO₂ level in the blood raises after breathing from a plastic bag. CO₂ is an acid and decreases the PH of blood.



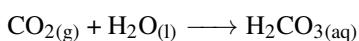
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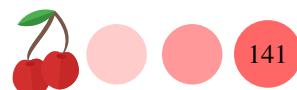
The conjugate seesaw The strength of an acid and its conjugate base are not independent. Strong acids produce conjugate bases that are moderately weak. Similarly, weak acids produce conjugate bases that are moderately strong. The same reasoning can be applied to bases. This idea is called the conjugate seesaw and helps predict why the conjugate salt of a weak base such as ammonia (NH₄Cl) gives a moderately strong acidic solution. This idea is summarized in the following relationship and we have that pK_a and pK_b are also related:

$$PK_a + PK_b = 14 \quad (5.4)$$

Acid-base properties of salts Remember that strong acids (bases) produce weak conjugate bases (acids). Similarly, weak acids (bases) produce strong conjugate bases (acids). For example, HF is a weak acid, and therefore its conjugate F⁻ acid would be fairly strong. Similarly, NaOH is a strong base and its conjugate acid (Na⁺) is therefore fairly weak. Now, let us think about the acid-base properties of NaF, a salt. Remember that salt is just a common name to refer to ionic compounds resulting from the combination of metallic and nonmetallic elements. Without doing any type of calculation we can predict that as Na⁺ is a weak acid and F⁻ a strong base. Therefore, a NaF solution would be basic. Similarly, we can predict that NH₄Cl would form an acidic solution, as ammonium (NH₄⁺) is the conjugate acid of ammonia (a weak base) and Cl⁻ is the conjugate base of a strong acid (HCl).

Acid-base properties of oxides Metallic oxides can be acidic, basic, or amphoteric. On one hand, acidic oxides react with water (or a base) forming its conjugate base. They tend to be covalent oxides, resulting from the combination of a nonmetal and oxygen. Examples of acidic oxides are CO₂, NO₂ or SO₂. For example, CO₂ can react with water forming carbonic acid:

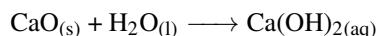




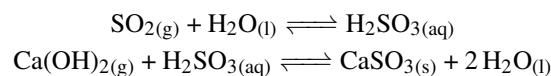
At the same time



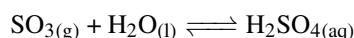
On the other hand, basic oxides react with water or acids to form a conjugate acid. They tend to be ionic compounds with metals from the first and second groups. Examples are MgO, K₂O or CaO. We have that calcium oxide reacts with water forming calcium hydroxide:



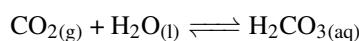
Calcium hydroxide is also known as slaked lime. This hydroxide is used for example in the scrubbing of stack gases from the exhaust of power plants and factories. When this compound reacts with sulfur trioxide the following set of reactions happens:



Group I hydroxides such as NaOH, LiOH or KOH are strong bases. Sodium and potassium hydroxides are common reagents, whereas lithium, rubidium, and cesium hydroxide are expensive and less used. Group II hydroxides such as Ca(OH)₂ or Ba(OH)₂ are also strong bases. However, these hydroxides tend to be insoluble, which can be convenient for some applications. For example, antacids are suspensions of metal hydroxides. The insoluble character helps protect the mouth and esophagus during their ingestion. Calcium hydroxide is called slaked lime and it is extensively used in water treatment plants to soften water—removing calcium and magnesium ions—and in the industry to scrub stack gases from exhaust pipes removing sulfur dioxide (and acidic gas). Calcium oxide—called lime—is also used in combination with soda ash (Na₂CO₃) in the softening go water involving the removal of calcium and magnesium ions in solutions. These ions hinder the action of detergents. Finally, amphoteric oxides can act as a basic or acidic oxides. We call this *amphotericism* and these oxides are *amphoteric*. They tend to be oxides containing elements on the line between metals and nonmetals (Be, Al, Ga, Ge, As, In, Sn, Sb, Pb, and Bi). Examples of amphoteric oxides are Al₂O₃ or BeO. Covalent oxides tend to be acidic. An example is sulfur trioxide that reacts with water to produce sulfuric acid—a reaction involved in acid rain:



Carbon dioxide produced carbonic acid in the presence of water:



5.4 The PH scale

This section describes the PH scale that simply transforms a concentration value—oftentimes a very small number—into a simple round value. In short, the PH value tells you how many protons are there in a solution so that the larger PH the fewer protons are there in the solution. It also informs about the hydroxyl concentration, as protons and hydroxyls are connected using the dissociation equilibrium of water.



Autoprotolysis of water and K_w Water is a weak electrolyte. The dissociation equilibrium of water is listed below:



This chemical equilibrium representing the dissociation of water is called the autoprotolysis of water. We have that water, as well as many other chemicals, that can act as a base or an acid, hence giving and receiving protons. We call these types of chemicals *amphiprotic*. Other examples of amphiprotic chemicals are HCO_3^- or HSO_4^- . The dissociation constant of water is called the ion-product of water K_w :

$$\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_{(\text{aq})}^+ + \text{OH}_{(\text{aq})}^- \quad [\text{H}^+] \cdot [\text{OH}^-] = 1.0 \cdot 10^{-14}$$

K_w is a constant that only depends on the temperature of the water being $1.0 \cdot 10^{-14}$ at 25°C . The ion product of water established a relationship between protons and hydroxyls in solution:

$$[\text{H}^+] \cdot [\text{OH}^-] = 1.0 \cdot 10^{-14} \quad (5.5)$$

Protons and Hydroxyls Acids and bases exist in solution with water. That means that as they produce protons or hydroxyls water receives these ions as it ionizes as well. Hence, the concentration of protons and hydroxyls in the solution is not independent. Indeed, the ion-product of water relates the concentration of protons ($[\text{H}^+]$) and the concentration of hydroxyls ($[\text{OH}^-]$):

$$[\text{H}^+] \cdot [\text{OH}^-] = 1.0 \times 10^{-14}$$

Water is neutral, which means that the concentration of protons ($[\text{H}^+]$) and the concentration of hydroxyls ($[\text{OH}^-]$) and both equal to $1.0 \cdot 10^{-7}\text{M}$. When we dissolve an acid or a base into the water, $[\text{OH}^-]$ and $[\text{H}^+]$ change drastically. When dissolving an acid, $[\text{H}^+]$ increases as acids produce protons, while $[\text{OH}^-]$ decreases. Differently, when dissolving a base, $[\text{OH}^-]$ increases, as bases produce hydroxyls, while $[\text{H}^+]$ decreases.

Sample Problem 62

The proton concentration in an acid solution is $7.0 \cdot 10^{-5}\text{M}$. Calculate $[\text{OH}^-]$.

SOLUTION

We will use Equation 5.5. The value given is $[\text{H}^+] = 7.0 \cdot 10^{-5}\text{M}$ and the problem ask $[\text{OH}^-]$. Solving for $[\text{OH}^-]$ we have:

$$7.0 \cdot 10^{-5} \cdot [\text{OH}^-] = 1.0 \cdot 10^{-14}$$

Hence $[\text{OH}^-] = 1.4 \cdot 10^{-10}\text{M}$.

◆ STUDY CHECK

The hydroxyl concentration in a basic solution is $2.3 \cdot 10^{-6}\text{M}$. Calculate the concentration of protons.

►Answer: $[\text{H}^+] = 4.3 \cdot 10^{-9}\text{M}$.

The PH scale The proton concentrations in aqueous solutions tend to be rather small. For example, the proton concentration in normal vinegar is $2 \cdot 10^{-3}\text{M}$. As it is

hard to work with these small concentrations, scientists developed the PH scale that transforms $[H^+]$ into a larger number (see Figure 5.1). The formula for the PH is:

$$PH = -\log[H^+] \quad (5.6)$$

The PH scale normally ranges from 0 to 14. PH values lower than 7 correspond to acidic solutions, whereas PH values larger than 7 correspond to basic solutions. Solutions with a PH of 7 are neutral. For example, the PH for vinegar is $-\log(2 \cdot 10^{-3})$ that is 2.69. However, it exists PH values out of the scale for very concentrated solutions. Examples of PH values and common chemicals are given in the figure below. An equivalent scale is also defined for the concentration of hydroxyls. The POH values are defined as:

$$POH = -\log[OH^-] \quad (5.7)$$

The POH scale also ranges from 0 to 14. POH values lower than 7 correspond to this time to basic solutions, whereas POH values larger than 7 correspond to acidic solutions. Solutions with a POH of 7 are neutral. The values of PH and POH are hence related by the following equation:

$$PH + POH = 14 \quad (5.8)$$

For example, if the PH of a solution is 4 therefore the POH will be 10. Both indications suggest that the solution would be acidic.

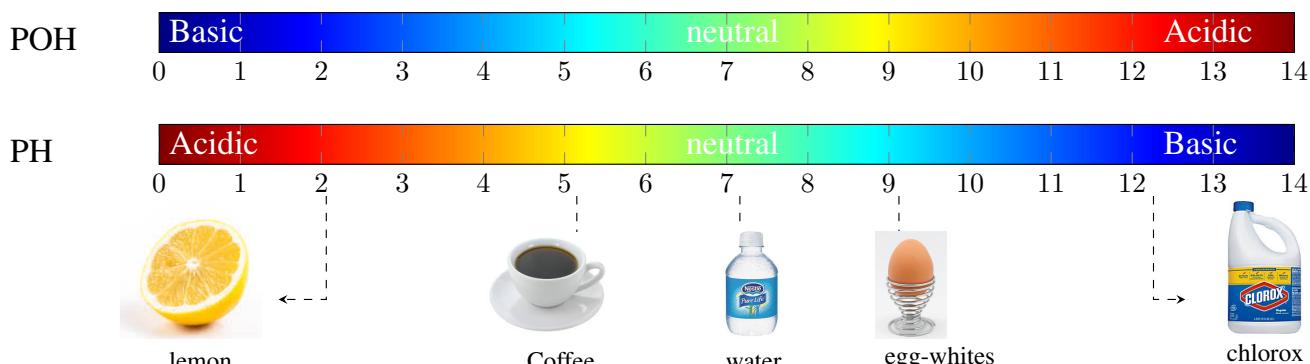


Figure 5.1 The PH scale

Sample Problem 63

Calculate the PH for: (a) an acid solution with proton concentration of $7.0 \cdot 10^{-5} M$ (b) a basic solution with a hydroxyl concentration of $7.0 \cdot 10^{-5} M$.

SOLUTION

(a) We will use Equation 5.6. Given is $[H^+] = 7.0 \cdot 10^{-5} M$ and the problem ask for the PH. Solving for PH we have:

$$PH = -\log(7.0 \cdot 10^{-5})$$

and the results is 4.15. This is an acidic PH. (b) We will also use Equation 5.6. However, before doing that, we need to compute the concentration of protons. In order to do this we will use Equation 5.5 given $[OH^-] = 8.0 \cdot 10^{-2} M$

$$[H^+] \cdot 8.0 \cdot 10^{-2} = 1.0 \cdot 10^{-14}$$

We have $[H^+] = 1.25 \cdot 10^{-13} M$. Now we can compute the PH. Solving for PH we have:

$$PH = -\log(1.25 \cdot 10^{-13})$$



and the results is 12.90. This is a basic PH.

◆ STUDY CHECK

Calculate the PH for: (a) a basic solution with proton concentration of $3.0 \cdot 10^{-8} M$ (b) a basic solution with a hydroxyl concentration of $2.0 \cdot 10^{-9} M$.

►Answer: 7.5; 5.3

From PH to proton concentration At this point, we know that the PH quantifies the proton concentration of a solution. So given $[H^+]$ we can calculate PH using the logarithm with the opposite sign. But what if we know the PH and we want to calculate the corresponding proton concentration? We can do this by using the formula:

$$[H^+] = 10^{-PH} \quad (5.9)$$

To use the previous formula you need to use the power key in your calculator. For example, if the PH is 3.3 and we need to calculate the proton concentration you will need to type: $10 \wedge -3.3$, and the result is $5.0 \cdot 10^{-4} M$. Mind that: (a) in some calculators, sometimes the power key looks like 10^x ; (b) you need to use the negative key and not the minus key. The minus sign is used for substations, the negative key is used for numbers. An equivalent relation exists between the concentration of hydroxyls and the POH:

$$[OH^-] = 10^{-POH} \quad (5.10)$$

The diagram in Figure 5.2 displays some of the most important equations involved in this section:

Sample Problem 64

The PH of a solution is 4.5. Calculate the proton concentration of that solution.

SOLUTION

We will use Equation 5.9, given PH and asking $[H^+]$.

$$[H^+] = 10^{-PH} = 10^{-4.5}$$

and the results is $3.16 \cdot 10^{-5} M$.

◆ STUDY CHECK

The PH of a solution is 9.5. Calculate the proton concentration of that solution.

►Answer: $3.16 \cdot 10^{-10} M$

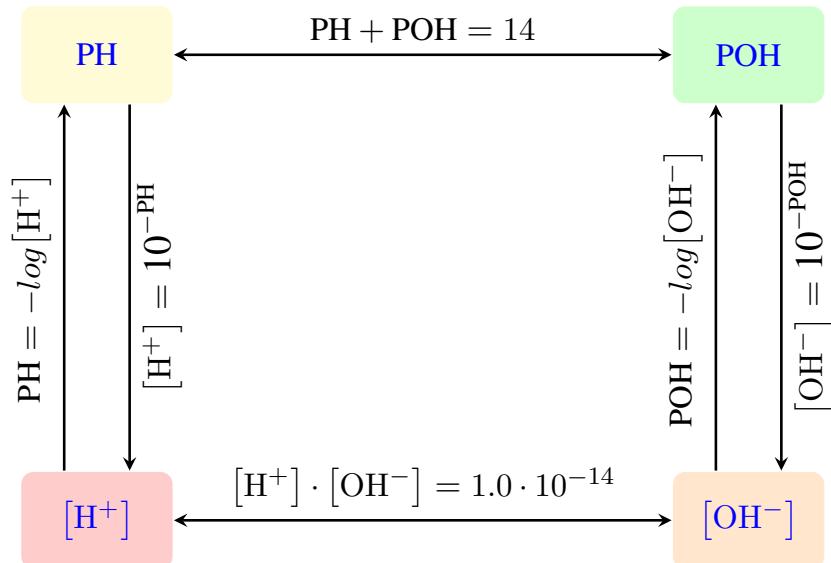
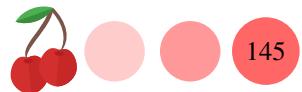


Figure 5.2 Diagram with formulas relating the PH, POH and the concentration of protons and hydroxyls in water.

5.5 PH of strong acid-base solutions

Imagine we prepare a strong acid solution and we want to estimate the PH of the resulting solution. The solution PH will depend on the molarity of the resulting solution:

$$PH = -\log(n_H \cdot c_a) \quad (5.11)$$

where:

n_H is the number of protons in the acid (e.g. H_3PO_4 has $n_H=3$)

c_a is the molarity of the acid solution

We have an equivalent formula for the POH of a strong base:

$$POH = -\log(n_{OH} \cdot c_b) \quad (5.12)$$

where:

n_{OH} is the number of hydroxyls in the base (e.g. $Ca(OH)_2$ has $n_{OH}=2$)

c_b is the molarity of the base solution

Mind these formulas only work for strong acids and bases, as their molarity is directly related to the concentration of protons and hydroxyls. The following example will demonstrate the use of these formulas.

Sample Problem 65

Calculate the PH of: (a) a 0.02M HNO_3 solution (b) a 0.02M $Ca(OH)_2$ solution.

SOLUTION

(a) We will use Equation 5.11 given that the molarity of the acid is 0.02M and the



acid only has a single proton:

$$PH = -\log(n_H \cdot c_a) = -\log(0.02) = 1.69$$

(b) We will use Equation 5.12 given that the molarity of the base is 0.02M and it has two hydroxyls ($n_{OH}=2$):

$$POH = -\log(n_{OH} \cdot c_b) = -\log(2 \cdot 0.02) = 1.39$$

Now, we will convert POH in PH using Equation 5.8:

$$PH = 14 - POH = 12.61$$

◆ STUDY CHECK

Calculate the PH of: (a) a 0.001M H_2SO_4 solution (b) a 0.001M NaOH solution.

►Answer: 2.7; 11

5.6 PH of weak acid-base solutions

The PH of solutions of weak electrolytes differs from that of stronger electrolytes. Weak electrolytes have effective concentrations that differ from their nominal ones. Not all the amount of substance you use to prepare the solution becomes ions, and those electrolytes have a percent dissociation different than 100%. Hence, the calculations involved in the PH calculation of weak acids and bases involved more complicated calculations. This section addresses the calculation of PH for solutions of weak acids and bases, as well as the PH of salt solutions.

PH of solutions of weak acids and bases Imagine we prepare a weak, acidic solution and we want to estimate its PH. The solution PH will depend on the molarity of the resulting solution. However, as weak acids and bases do not dissociate completely, the procedure and the formulas involved in the PH calculations differ from those of strong electrolytes, explained previously. In particular, for weak electrolytes, the calculation involves a quadratic equation. These equations can be solved either with the help of a graphic calculator or using a [quadratic equation solver link](#) that can be found in the internet. The resolution of quadratic formulas will lead to two different roots, a positive and a negative root. Only the positive root would make chemical sense. As such, you can directly toss the negative root.

The quadratic formula involved in the PH calculation for a weak acid is shown below:

$$[H^+]^2 + K_a \cdot [H^+] - K_a \cdot c_a = 0 \quad \text{with } [H^+] = x \quad (5.13)$$

where:

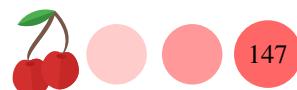
$[H^+] = x$ is concentration of protons in equilibrium

K_a is the acidity constant of the acid

c_a is the molarity of the acid solution

For example, the PH of a 0.1M HF solution, given that HF is a weak acid with $K_a = 6.3 \times 10^{-4}$, will be given by:

$$[H^+]^2 + 6.3 \times 10^{-4} \cdot [H^+] - 6.3 \times 10^{-5} = 0$$



Solving the quadratic equation, we obtain two roots: $[H^+] = 0.0076$ and $[H^+] = -0.0082$. Only the positive root will be valid and hence we have:

$$[H^+] = 0.0076$$

The PH of the solution will be 2.11. There is an equivalent formula involved in the calculation of the PH of a weak base:

$$[\text{OH}^-]^2 + K_b \cdot [\text{OH}^-] - K_b \cdot c_b = 0 \quad \text{with } [\text{OH}^-] = x \quad (5.14)$$

where:

$[\text{OH}^-] = x$ is concentration of hydroxyls in equilibrium

K_b is the basicity constant of the base

c_b is the molarity of the base solution

Mind that to calculate the PH or POH you will need to employ Equations 5.6 and 5.7. For example, the PH of a 0.1M NH₃ solution, given that ammonia is a weak base with $K_b = 1.8 \times 10^{-5}$, will be given by:

$$[\text{OH}^-]^2 + 1.8 \times 10^{-5} \cdot [\text{OH}^-] - 1.8 \times 10^{-6} = 0$$

Solving the quadratic equation, we obtain two roots: $[\text{OH}^-] = -0.0013$ and $[\text{OH}^-] = 0.0013$. Only the positive root will have chemical meaning and hence we have:

$$[\text{OH}^-] = 0.0013$$

The POH of the solution will be 2.88 and the PH will be 11.11. The following example will further demonstrate the use of these formulas.

Sample Problem 66

Calculate the PH of a 0.02M CH₂O₂ (formic acid) solution. $K_a = 1.8 \times 10^{-4}$

SOLUTION

As formic acid is a weak acid, we will have to use Equation 5.13 in order to calculate PH:

$$[H^+]^2 + K_A \cdot [H^+] - K_A \cdot c_a = 0$$

We have that $c_a = 0.02\text{M}$ and that $K_A = 1.8 \times 10^{-4}$. Therefore $-K_A \cdot c_a$ is -3.6×10^{-6} . Therefore, the quadratic formula that gives the PH is:

$$[H^+]^2 + 1.8 \times 10^{-4} \cdot [H^+] - 3.6 \times 10^{-6} = 0$$

Solving for $[H^+]$ and using only the positive root, we have $[H^+] = 1.8 \times 10^{-3}\text{M}$ and PH=2.74.

◆ STUDY CHECK

Calculate the PH of a 0.002M aniline solution. $K_b = 7.4 \times 10^{-10}$

►Answer: 8.08

PH of solutions of salt As well as hydracids or hydroxides, salts can exhibit acid or base character. For example, ammonium chloride (NH₄Cl) is an acidic salt, as ammonium is the conjugate acid of a weak base, and therefore has moderately strong character. Differently, chloride is the conjugate base of a strong acid (HCl) and has a weak character. Let us calculate the PH of a 0.1-M NH₄Cl solution. As the salt is



acidic, we will use Equation 5.13 given that $c_a=0.1\text{M}$ and $K_a = 5.5 \times 10^{-10}$ (mind for ammonia $K_b = 1.8 \times 10^{-5}$ and Equation 5.1 relates K_a and K_b):

$$[\text{H}^+]^2 + 5.5 \times 10^{-10} \cdot [\text{H}^+] - 5.5 \times 10^{-11} = 0$$

Solving for $[\text{H}^+]$ we have that $[\text{H}^+] = 7.4 \times 10^{-6}\text{M}$ and $\text{PH}=5.13$. As predicted, the PH of an ammonium chloride solution is acidic.

Sample Problem 67

Calculate the PH of a 0.02M HCOONa (sodium formate) solution. $K_a = 1.8 \times 10^{-4}$

SOLUTION

Formate is the conjugate base of a weak acid, therefore it will be moderately basic. We will use Equation 5.14 given that $K_b = 5.5 \times 10^{-11}$ and $c_b=0.02\text{M}$:

$$[\text{OH}^-]^2 + 5.5 \times 10^{-11} \cdot [\text{OH}^-] - 5.5 \times 10^{-12} = 0$$

Solving for $[\text{OH}^-]$ and using only the positive root, we have $[\text{OH}^-]=2.3 \times 10^{-6}\text{M}$ and $\text{POH}=5.63$. The final answer would be: $\text{PH}=8.36$.

◆ STUDY CHECK

Calculate the PH of a 0.01M sodium acetate (CH_3COONa). $K_a = 1.75 \times 10^{-5}$

► Answer: 8.38

Percent dissociation of weak acids and bases Weak acids (and bases) are indeed weak electrolytes, which means if we prepare a solution of a given concentration c_a they will dissociate giving a proton concentration ($[\text{H}^+]$) less than c_a . We define the percent dissociation α of an acid (or base) as:

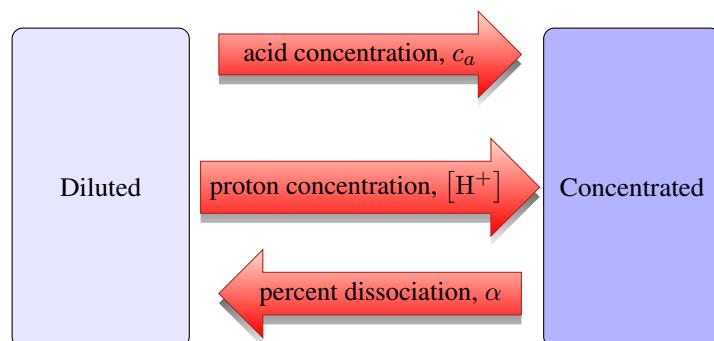
$$\alpha = \frac{\text{amount dissociated}}{\text{initial amount}} \times 100 = \frac{[\text{H}^+]}{c_a} \times 100 \quad (5.15)$$

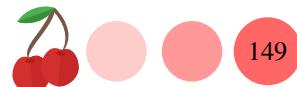
where:

$[\text{H}^+]$ is concentration of protons in equilibrium

c_a is the initial acid concentration

For example, a 0.2M HF solution has a proton concentration of 0.0076M . The percent dissociation of this acid at this concentration will be 3.8%. The percent dissociation changes with the acid (or base) concentration and more concentrated acids have in general a larger proton concentration than diluted acids. However, the percent dissociation of more concentrated acids is smaller than the one of less concentrated acids. The diagram below displays this concept.



**Sample Problem 68**

Calculate the percent dissociation of CH_2O_2 in 0.01M and 0.09M solutions.

$$K_a = 1.8 \times 10^{-4}$$

SOLUTION

We will first calculate $[\text{H}^+]$ for both solutions using Equation 5.13. For the most diluted $[\text{H}^+]$ will be given by:

$$[\text{H}^+]^2 + 1.8 \times 10^{-4} \cdot [\text{H}^+] - 1.8 \times 10^{-6} = 0$$

Solving and selecting the positive root, we have: $[\text{H}^+] = 1.25 \times 10^{-3}\text{M}$. For the most concentrated we have:

$$[\text{H}^+]^2 + 1.8 \times 10^{-4} \cdot [\text{H}^+] - 1.62 \times 10^{-5} = 0$$

Solving and selecting the positive root, we have: $[\text{H}^+] = 3.93 \times 10^{-3}\text{M}$. We can now calculate the degree of dissociation using Equation 5.15. For the most diluted we have:

$$\alpha = \frac{[\text{H}^+]}{c_a} \times 100 = \frac{1.25 \times 10^{-3}}{0.01} \times 100 = 12.5\%$$

For the most concentrated we have:

$$\alpha = \frac{3.93 \times 10^{-3}}{0.09} \times 100 = 4.36\%$$

We have that for more concentrated solutions of the same acid, the concentration of protons is larger than for more diluted solutions. In contrast, the degree of dissociation is larger for more diluted solutions.

◆ STUDY CHECK

Calculate the percent dissociation of a 0.05M methylamine CH_3NH_2 solution.

$$K_b = 4.4 \times 10^{-4}$$

►Answer: 9%

5.7 Math interlude: how to solve quadratic equations

Let's imagine we need to obtain the roots of a quadratic formula of the form:

$$ax^2 + bx + c = 0$$

Here, those roots would be called x_1 and x_2 . There are numerous ways to solve quadratic formulas. First, you can solve quadratic equations by simply applying the formula that gives you the roots

$$x_1 = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad \text{and} \quad x_2 = \frac{-b - \sqrt{b^2 - 4ac}}{2a}$$

Secondly, if you have access to the internet, you can also use web apps that give you the roots right away without having to do any calculations. For example, [E quadratic equation solver link](#). Finally, with a graphing calculator you can normally get the roots. This section addresses the use of the calculator to solve quadratic equations.

Solve quadratic equations You need a graphing calculator to solve quadratic equations and obtain their roots. Casio calculators are user-friendly, Texas calculators



are not. Here, I will show how to get the roots first using a Casio calculator and then using a Texas calculator. You need to follow the following steps to solve a quadratic formula in a Casio fx 9750GII:

- 1 **Step one:** Press **Menu** and 8.
- 2 **Step two:** Press the Poly (F2) menu. and select the degree: 2. Now enter the a, b, and c coefficients of the polynomial.
- 3 **Step three:** At this point, you will have the two roots

You need to follow the following steps to solve a quadratic formula in a Texas TI 84:

- 1 **Step one:** To open a new program: press **PRGM**, select New and type QUAD, the program name, using letter keys. Now, press **ENTER**
- 2 **Step two:** press **PRGM**, I/O, Prompt, press **ENTER**, type: **ALPHA**+A, then press the comma key, **ALPHA**+B and comma, **ALPHA**+C, press **ENTER**
- 3 **Step three:** Write the following equations using Alpha/Numeric keys:

$$(-B + \sqrt{B^2 - 4AC}) / (2A)$$

Now press **STO** X and **ENTER**

- 4 **Step four:** Write the following equations using Alpha/Numeric keys:

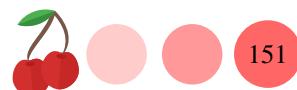
$$(-B - \sqrt{B^2 - 4AC}) / (2A)$$

Now press **STO** Y and **ENTER**

- 5 **Step five:** Press **PRGM**, I/O, Disp, type: "ROOTS EQUAL" (with quotes), press **,**, **ALPHA**+X, press **,**, and now, **ALPHA**+Y, press **ENTER**
- 6 **Step six:** Press **2nd** and **MODE** to quit and save.
- 7 **Step seven:** Press **PRGM** key, select QUAD, press **ENTER** twice to start program. It will then ask for A=?, B=?, and C=? Enter values for A, B, and C pressing **ENTER** after each value it will then display the two roots if they are real.

5.8 Buffer solutions

We have previously addressed the properties of acids and bases. Buffers are specific solutions able to accommodate acids or bases without changing their PH. Buffers play a key role for example in our blood where a buffer system absorbs small quantities of acids and bases produced during biological reactions while keeping its PH constant. This section covers the properties of buffers. You will learn what buffers are, what they are made of. You will also learn how to compute the PH of a buffer system and the PH of a buffer after an acid or a base it is been added.



Buffers Buffers are solutions of an acid and a base. But not any kind of acid or base. Buffers are solutions of a weak acid with its conjugate base, or weak bases and its conjugate acid. For example, a buffer would be a mixture of 0.1M NH₃ and 0.1M NH₄Cl. You can find acidic or basic buffers. For example, the previous example was a basic buffer, whereas a mixture of 0.1M CH₃COOH and 0.1M NaCH₃COO is an acidic buffer. Acidic buffers contain a mixture of a weak acid and its conjugate base. Basic buffers contain a mixture of a weak base and its conjugate acid. Buffer function thanks to the equilibrium that links the acid and base so that when small quantities of acid or base are added the conjugate species counteract this external action keeping the PH constant. Still, buffers have a limit of action, and if large quantities of external acid or bases are added the buffer equilibrium can be broken, losing their capacity to modulate the PH.

PH of a Buffer solution A buffer solution consists of a solution containing both a weak electrolyte and its conjugate counterpart in the same or different concentration. For example, the PH of a 0.01M CH₃COOH/0.1M NaCH₃COO ($K_a = 1.75 \times 10^{-5}$) acidic buffer can be computed using the following formula:

$$PH = PK_a + \log\left(\frac{c_b}{c_a}\right) \quad (5.16)$$

where:

PK_a is the PK of the acid in the buffer

c_a is the acid concentration in the buffer

c_b is the base concentration in the buffer

This formula is called the Henderson-Hasselbalch equation. Using the data above, we have that: $PH = 4.76 + \log\left(\frac{0.1}{0.01}\right) = 5.75$. The following example will further demonstrate how to calculate the PH of buffer solutions.

Sample Problem 69

Calculate the PH of 20mL of a 0.1M NH₄Cl/0.2M NH₃ ($K_b = 1.80 \times 10^{-5}$).

SOLUTION

This is a basic buffer and the main equilibrium involves ammonia, a weak base. In order to calculate the PH we need the concentration of the acid and base counter parts. The buffer volume is not important as it will be canceled out in the Henderson-Hasselbalch equation. We would also need K_a , as we have K_b we can easily compute K_a , giving 5.5×10^{-10} . The final PH will be:

$$PH = 9.25 + \log\left(\frac{20 \cdot 0.2}{20 \cdot 0.1}\right) = 9.56$$

❖ STUDY CHECK

Calculate the PH of a 0.2M HF/0.3M KF ($K_a = 6.30 \times 10^{-4}$).

►Answer: 3.36

PH of Buffer solution mixed with acids or bases This section covers the PH calculation of buffers when external acids or bases different than the ones involved in the buffer equilibrium, are added to the solution. For example, the PH



of 5mL of a 0.01M CH₃COOH/0.1M NaCH₃COO ($K_a = 1.75 \times 10^{-5}$) after adding 1mL of NaOH 3M would be calculated with the following formula:

$$PH = PK_a + \log\left(\frac{V_b \cdot c_b + (V_b \cdot c_b)^{\text{added}} - (V_a \cdot c_a)^{\text{added}}}{V_a \cdot c_a + (V_a \cdot c_a)^{\text{added}} - (V_b \cdot c_b)^{\text{added}}}\right) \quad (5.17)$$

where most of the symbols of Equation 5.17 are the same as in Equation 5.17:

$(V_b \cdot c_b)^{\text{added}}$ is volume and molarity of the added base

$(V_a \cdot c_a)^{\text{added}}$ is volume and molarity of the added acid

The following example illustrates how to use Equation 5.16.

Sample Problem 70

Calculate the PH of 20mL of a 0.1M NH₄Cl/0.2M NH₃ ($K_b = 1.80 \times 10^{-5}$) after adding 1mL of HCl 0.3M.

SOLUTION

In this example, we are adding an acid to a basic buffer. We have that $PK_a = 9.25$, $V_a = V_b = 20\text{mL}$, $c_a = 0.1\text{M}$ and $c_b = 0.2\text{M}$. As we are adding an acid we have $(V_b \cdot c_b)^{\text{added}} = 0$ and $(V_a \cdot c_a)^{\text{added}} = 1 \cdot 0.3 = 0.3\text{mM}$. Using Equation 5.17:

$$PH = 9.25 + \log\left(\frac{20 \cdot 0.2 - (1 \cdot 0.3)^{\text{added}}}{20 \cdot 0.1 + (1 \cdot 0.3)^{\text{added}}}\right) = 9.46$$

We have that the original PH of the buffer is 9.56. After adding an acid, the new PH (9.46) remains close to the original buffer PH.

◆ STUDY CHECK

Calculate the PH of 5mL of a 0.2M HF/0.3M KF ($K_a = 6.30 \times 10^{-4}$) after adding 1mL of HCl 0.2M.

►Answer: 3.23

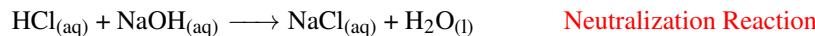
5.9 Titrations

A titration is a chemical technique used to calculate the unknown molarity of an acid or base. It is based on the principle that acids neutralize bases and we can figure out the molarity of the unknown chemical (the titrate) by knowing the reacting amounts. A titration uses chemical equipment: a burette, Erlenmeyer, and an indicator (see Figure 5.4). The unknown chemical is called the titrate and the known chemical is called the titrant. The goal of a titration is to calculate the volume of titrant needed to neutralize the titrate. We reach the endpoint of a titration when the titrant and titrate completely neutralize. At the end point, the mixture of titrant and titrate has a specific PH. Even though the chemical procedure in the lab is similar when titrating strong or weak acids or bases, the calculations needed to calculate the PH at the endpoint differ. This section will cover the principles and calculations involved in titrations.

Neutralization Reactions Titrations involve a neutralization reaction in which an acid neutralizes a base. Acids produce protons H⁺ and bases hydroxyls OH⁻ that neutralize each other forming water, H₂O. More importantly, they react in very specific



ratios. Let us take a look at the reaction of hydrochloric acid with sodium hydroxide to produce water and sodium chloride:



In this reaction, one mole of HCl reacts with one mole of NaOH. The fact that one more reacts with one more can be used as a principle for acid-base titration. We will have to use the stoichiometry of the reaction to calculate the volume of titrant needed to neutralize the titrate. Imagine you have an unknown sample of HCl and you need to determine the amount of acid in the solution. If you know that this sample reacts with a specific amount of NaOH as you know that they react in a one-2-one ratio then you would know the acidic content. This is the idea behind titration: a laboratory procedure in which an unknown sample is neutralized with a known solution. A chemical *indicator*, which changes color depending on the acidity of the medium, is used to visually reveal the moment in which the acid and the base are completely neutralized. The point at which the indicator changes color is called the *endpoint*. At the endpoint, the acid and the base are neutralized.

Endpoint formula At the *equivalence point*, also called the *stoichiometric point*, the moles of acid and the moles of the base are the same. A simple formula is extensively used to calculate the unknown acid concentration in a titration:

$$n_H \cdot c_a \cdot V_a = n_{OH} \cdot c_b \cdot V_b \quad (5.18)$$

where:

$n_H \cdot c_a \cdot V_a$ and $n_{OH} \cdot c_b \cdot V_b$ are moles of protons and hydroxyls, respectively

c_a and V_a are acid concentration and volume respectively

c_b and V_b are base concentration and volume respectively

n_H and n_{OH} are the number of protons of the acid and hydroxyls of the base

The units on this formula need to be consistent and for example, if the units of V_a are mL then the units of V_b should also be mL . This formula can be used when we titrate a known acid with a known base and we need to calculate the volume of titrant needed to reach the endpoint.

Equation 5.18 can also be used to identify if we have passed the endpoint in a titration. Imagine we titrate 2mL of 3M H_2SO_4 (titrant) with 2mL of 1M NaOH (titrate) and we want to know if we are before, after, or at the endpoint. Using Equation 5.18 we have:

$$2 \cdot 3\text{M} \cdot 2\text{mL} = 1 \cdot 1\text{M} \cdot V_b$$

That is, we would need 12 mL of the base. Therefore, as we only used 2mL we would be before the endpoint and we would have not reached the endpoint.

Sample Problem 71

A 50mL sample of an unknown acid is neutralized with 25 mL of a NaOH 3M solution. Calculate the molarity of the unknown acid.

SOLUTION



We will use Equation 5.18, given: $c_b = 3\text{M}$, $V_b = 25\text{mL}$ and $V_a = 50\text{mL}$.

$$c_a \cdot 50\text{mL} = 3\text{M} \cdot 25\text{mL}$$

and the results is 1.5M.

◆ STUDY CHECK

A 15mL sample of an unknown acid is neutralized with 45 mL of a NaOH 1M solution. Calculate the molarity of the unknown acid.

►Answer: 3M

The mid-point In titrations, there is another important point called the mid-point. The mid-point is reached at half the equivalency point. For example, the end-point of the titration of 10 mL of 0.1M HCl by 10 mL of 0.1M NaOH happens when we add 10 mL of the base. The mid-point hence will happen when we add 5mL of the base. We have that the volumes of the end (V_{EP}) and the midpoint (V_{MP}) are related by the formula below:

$$V_{MP} = \frac{V_{EP}}{2} \quad (5.19)$$

The midpoint is also used to compute the acidity or basicity constant of weak electrolytes. We have that if we titrate a weak acid, at the midpoint, the concentration of the acid and the conjugate base are the same at the midpoint. Hence, for a weak acid at the midpoint, we have:

$$PH = PK_a \text{ (at the midpoint)} \quad (5.20)$$

There is an equivalent equation for the titration of a weak base at the midpoint, this time leading to PK_b . As you can see titration curves are also useful to understand the nature of acids or bases involved.

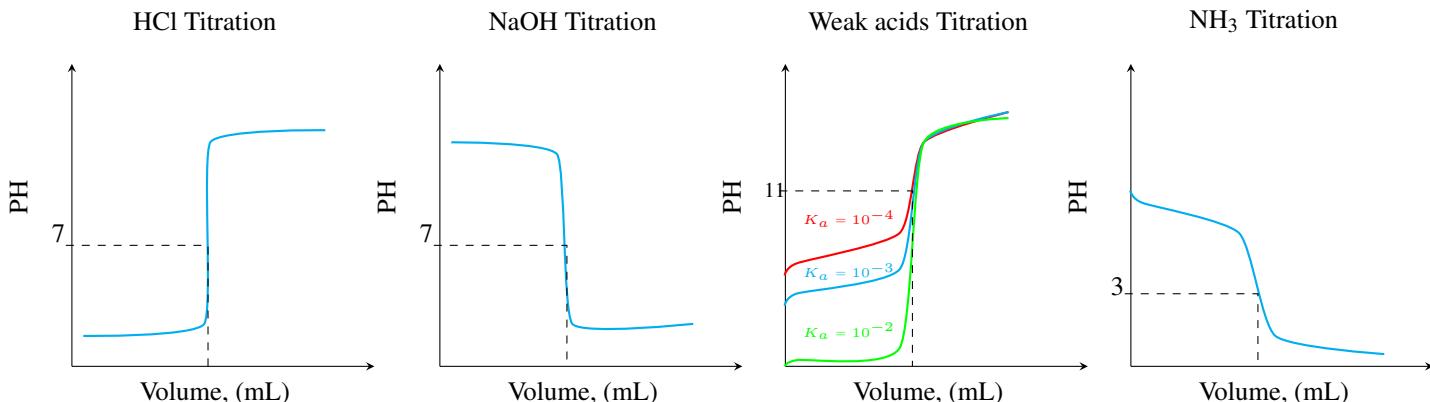
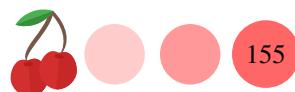


Figure 5.3 Different shapes of titration curves. Plateaus are flat for the PH curves of strong acids and bases, while being inclined for weak electrolytes. For weak electrolytes, plateaus are referred to as buffer areas.

5.10 Titrations curves

A titration plot or PH curve represents the change in the PH during titration as the volume of the titrant increases. In the vertical axis, it represents PH, in the horizontal axis, it represents volume. The species present in the titrate change as the titration proceed. For example, in the case of the titration of a weak acid with a strong base, before it starts, the major



species in solution is the weak acid HA. When the titration proceeds and before reaching the endpoint, the major species in solution are the weak acid and the conjugate base (A^- and HA), as the titrant neutralizes some of the acids. At the endpoint, the major species present is the conjugate base A^- . After the endpoint, the pH is given by the excess of the titrant.

Titration curve differences Titration curves look slightly different depending on the nature of the chemical to be titrated as shown in Figure 5.3. When titrating a strong acid, the curve starts at an acidic pH and near the endpoint, pH rises sharply until reaching a plateau at a basic pH. The pH at the endpoint is neutral. When titrating a strong base, the curve starts at a basic pH, and near the endpoint, pH decreases sharply until reaching a plateau at an acidic pH. The pH at the endpoint is also neutral. The titration ends with a strong basic pH. When titrating a weak acid, the curve starts at a high acidic pH, and near the endpoint, pH rises smoothly and not sharply until reaching a plateau at a low basic pH. The pH at the endpoint is basic and the difference between the initial and final plateaus is small. Finally, when titrating a weak base, the curve starts at a basic pH, and near the endpoint, pH decreases smoothly and not sharply until reaching a plateau at an acidic pH. The pH at the endpoint is basic and the difference between the initial and final plateaus is small. For weak acids and bases, the location of the starting plateau depends on the equilibrium constant. For the titration of a weak acid, the plateau lowers as the acidity constant increases. In other words, stronger acids have a lower starting plateau, and stronger bases have a higher starting plateau. Still, the equivalence point does not depend on the nature of the acid but on the stoichiometry. Overall, we have that the main difference between acid and base titration curves is the starting pH, whereas the difference between strong and weak titration curves is the pH at the equivalency point, being basic for weak acids and acidic for weak bases. For weak acids and bases, the plateaus are called buffer areas, and in this pH range, both the acid and conjugate base coexist. At the same time, and also for weak electrolytes, the pH in the half-point corresponds to the pK value of the acid or base.

Table 5.3 pH Titration formulas

Titrate	Before the EndPoint	At the MidPoint	At the EndPoint	After the EndPoint
Strong Acid	$[H^+] = c_R$		pH=7	$[OH^-] = c_R$
Strong Base	$[OH^-] = c_R$		pH=7	$[H^+] = c_R$
Weak Acid	$[H^+] = \frac{c_R}{c_F} \cdot K_a$	$pH = PK_a$	$[OH^-]^2 + K_b \cdot [OH^-] - K_b \cdot c_F = 0$	$[OH^-] = c_R$
Weak Base	$[OH^-] = \frac{c_R}{c_F} \cdot K_b$	$POH = PK_b$	$[H^+]^2 + K_a \cdot [H^+] - K_a \cdot c_F = 0$	$[H^+] = c_R$

5.11 Quantitative analysis of a titration



We spoke at this point about the idea behind titrations, its most important points, and how to graphically represent the PH changes that happen. Now we will focus on calculating the PH value at different points along a titration. The formula involved behind titration can be complex and often involves quadratic formulas. In particular, the formulas to be used depends on the nature of the titrate and the titrant.

Titration PH formulas The goal of this section is to quantify—calculate the value—the PH at the equivalency point when titrating an acid or a base with a strong chemical. For example, we will have a weak acid that will be titrated with a strong base and we will have to determine the PH at the equivalency point. There is a series of formulas to calculate the PH at the equivalency point. The formulas are given in Table 5.3 and the formula to use will depend on the nature of the substance to be titrated. If we titrate a strong acid or base, the formulas are relatively simple. Differently, if we titrate a weak acid or base, the formulas are quadratic equations. Also, independently of the nature of the titrate, there are certain concentrations c_R and c_F that appear in most of the formulas. In the following, we will address the meaning of these concentrations.

c_R and c_F First, c_R is the concentration of protons or hydroxyls remaining in the solution. The formula for c_R is:

$$c_R = \frac{|n_H \cdot c_a \cdot V_a - n_{OH} \cdot c_b \cdot V_b|}{V_a + V_b} \quad (5.21)$$

where all variables refer to Equation 5.18. For example, if we titrate 1mL of NaOH 3M with 4mL of HCl 2M, C_R would be:

$$c_R = \frac{|1 \cdot 2 \cdot 4 - 1 \cdot 3 \cdot 1|}{4 + 1} = 1M$$

Second, c_F is the concentration of the conjugate species formed in the solution. The formula for c_F is:

$$c_F = \frac{\min(n_H \cdot c_a \cdot V_a, n_{OH} \cdot c_b \cdot V_b)}{V_a + V_b} \quad (5.22)$$

where all variable refer to 5.18. Let us calculate c_F when mixing 1mL of NaOH 3M with 4mL of HCl 2M. We will have to compute $n_H \cdot c_a \cdot V_a$ and $n_{OH} \cdot c_b \cdot V_b$, and choose the smallest value. We have that $n_H \cdot c_a \cdot V_a = 8\text{mmol}$ and $n_{OH} \cdot c_b \cdot V_b = 3\text{mmol}$. The smallest value is 3mmol, therefore $c_F = 0.6M$.

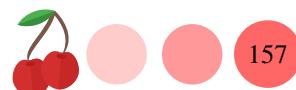
The following example demonstrates how to select the appropriate PH formula to calculate PH during a titration. They key is to identify the location in terms of the endpoint (before, at, or after) and the nature of the titrate (strong, weak, acid or base).

Sample Problem 72

A 25mL sample of 3M HCl is titrated by 25 mL of a NaOH 2M solution.
 (a) identify the titrate and titrant, and indicate whether you are before, after or at the endpoint
 (b) indicate whether the titrate is an acid or a base, and a weak or a strong electrolyte
 (c) indicate the formula that would need to be used from Table 5.3 to calculate the PH
 (d) calculate the PH

SOLUTION

As they say HCl is titrated with NaOH, therefore hydrochloric acid is the titrate (the one that is being titrated) and sodium hydroxide is the titrant—the one used to titrate. The titrant is a strong acid. In order to find out whether we are before,



at or after the endpoint, we will have to use Equation 5.18 and calculate the volume of titrant needed to neutralize the titrate. If the volume of titrant we have used is less than the endpoint volume then we will be before the end point. If the titrant volume is larger then we will be beyond the end point. We will be at the endpoint if the volume of titrant used is the same as the endpoint volume. We have that $c_a = 3\text{M}$, $V_a = 25\text{mL}$, and $n_H = 1$. We also have that $c_b = 2\text{M}$, and $n_{OH} = 1$. We will calculate V_b that fulfills Equation 5.18:

$$1 \cdot 3 \cdot 25 = 1 \cdot 2 \cdot V_b$$

Therefore, $V_b = 37.5\text{mL}$. As we have used only 25mL of base, we would be before the endpoint and the formula to use for the endpoint PH would be: $[\text{H}^+] = c_R$. We can calculate c_R :

$$c_R = \frac{|n_H \cdot c_a \cdot V_a - n_{OH} \cdot c_b \cdot V_b|}{V_a + V_b} = \frac{|1 \cdot 3\text{M} \cdot 25\text{mL} - 1 \cdot 2\text{M} \cdot 25\text{mL}|}{(25 + 25)\text{mL}} = \\ = 0.5\text{M}$$

We have that $\text{PH} = -\log c_R = 0.30$.

STUDY CHECK

A 5mL sample of 2M H_2SO_4 is titrated by 25 mL of a NaOH 1M solution. (a) indicate whether you are before, after or at the endpoint (b) indicate whether the titrate is an acid or a base, and a weak or a strong electrolyte (c) indicate the formula that would need to be used to calculate the PH (d) calculate the PH

►Answer: after, strong acid; $[\text{OH}^-] = c_R$; 13.22

PH at the midpoint The PH at the midpoint depends on the type of acid or base that is being titrated. For strong electrolytes, the PH at the midpoint will be given by the molarity of the initial solution. For example, when titrating a 0.1M HCl solution with 0.1M NaOH, the PH at the midpoint will be close to 1. Differently, the PH at the midpoint for weak electrolytes is given by the acidity or basicity constant of the acid. Specifically, it corresponds to the PK of the acid or base. For example, when titrating a 0.1M HAc (acetic acid, $K_a = 1.8 \times 10^{-5}$) solution with 0.1M NaOH, the PH at the midpoint will be close to 4.7.

The following examples will cover titration in which the titrate is a weak electrolyte, acid or base. For these case, the corresponding PH formula involves a quadratic equation that will lead to the calculation to the concentration of protons or hydroxyles. Afterwards, the PH would need to be calculated using the regular logarithmic formulas (Equations 5.6-5.8)

Sample Problem 73

A 1mL sample of 2M acetic acid (CH_3COOH , $K_a = 1.75 \times 10^{-5}$) is titrated by 0.66 mL of a NaOH 3M solution. (a) indicate whether you are before, after or at the endpoint (b) indicate whether the titrate is an acid or a base, and a weak or a strong electrolyte (c) indicate the formula that would need to be used from Table 5.3 to calculate the PH (d) calculate the PH

SOLUTION

We have that CH_3COOH is the titrant and NaOH is the titrate. This is because the question indicates that you titrate CH_3COOH and therefore the chemical to



be titrated is the titrant. The titrant is a weak acid. In order to find out whether we are before, at or after the endpoint, we will have to use Equation 5.18 and calculate the volume of titrant needed to neutralize the titrate. If the volume of titrant we have used is less than the endpoint volume then we will be before the end point. If it is larger then we will be beyond the end point. We will be at the endpoint if the volume of titrant used is the same as the endpoint volume. We have that $c_a = 2\text{M}$, $V_a = 1\text{mL}$, and $n_H = 1$. We also have that $c_b = 3\text{M}$, and $n_{OH} = 1$. We will calculate V_b that fulfills 5.18:

$$1 \cdot 2 \cdot 1 = 1 \cdot 3 \cdot V_b$$

Therefore, $V_b = 0.66\text{mL}$. Therefore, we are at the endpoint and the PH is given by:

$$[\text{OH}^-]^2 + K_b \cdot [\text{OH}^-] - K_b \cdot c_f = 0$$

as we have that $K_a = 1.75 \times 10^{-5}$ and therefore $K_b = 1.33 \times 10^{-9}$, and $c_f = 2/0.66 = 1.2\text{M}$:

$$[\text{OH}^-]^2 + 1.33 \times 10^{-9} \cdot [\text{OH}^-] - 1.59 \times 10^{-9} = 0$$

Solving for $[\text{OH}^-]$ we have $[\text{OH}^-] = 3.98 \times 10^{-5}\text{M}$ and therefore $\text{POH}=4.4$ and $\text{PH}=9.59$.

❖ STUDY CHECK

A 1mL sample of 2M NH_3 ($K_b=1.80 \times 10^{-5}$) is titrated by 2 mL of a HCl 1M solution. (a) indicate whether you are before, after or at the endpoint (b) indicate whether the titrate is an acid or a base, and a weak or a strong electrolyte (c) indicate the formula that would need to be used to calculate the PH (d) calculate the PH

Answer: at the EP, weak base; $[\text{H}^+]^2 + K_a \cdot [\text{H}^+] - K_a \cdot c_f = 0$; 4.71

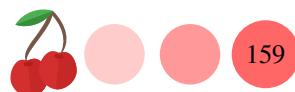


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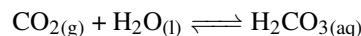
Figure 5.4 An acid base titration using phenolphthalein as indicator. From left to right, before, at and after the end point.

5.12 Blood as a buffer

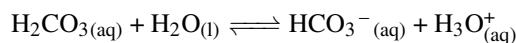
Carbon dioxide acts as a buffer in the blood, hence regulating its PH. Here, we will discuss some chemical aspects that impact its role as buffer.



Carbon dioxide is an acid Carbon dioxide is an acidic gas. When it dissolved reversibly in water it produces carbonic acid:



At the same time H_2CO_3 partially dissociates in water as a weak acid producing bicarbonate—also known as hydrogen carbonate:



As a result, the dissolution of carbon dioxide in the blood produced a buffer containing carbonic acid and bicarbonate—the conjugate base of carbonic acid. This buffer system keeps the PH of blood constant to a value of 7.4 which is slightly above the neutral value of 7.

The dangerous change in blood PH Most biological molecules are very sensitive to PH changes. Small deviations in PH can be dangerous or even fatal. If the blood PH falls below 7.34 it becomes more acidic causing a clinical condition called *acidosis*. On the other hand, if the PH rises above 7.45, the blood becomes more basic causing a condition called *alkalosis*. Changes in PH below 6.8 or above 8.0 can cause death. Figure 5.5 displays the PH range that leads to acidosis and alkalosis.

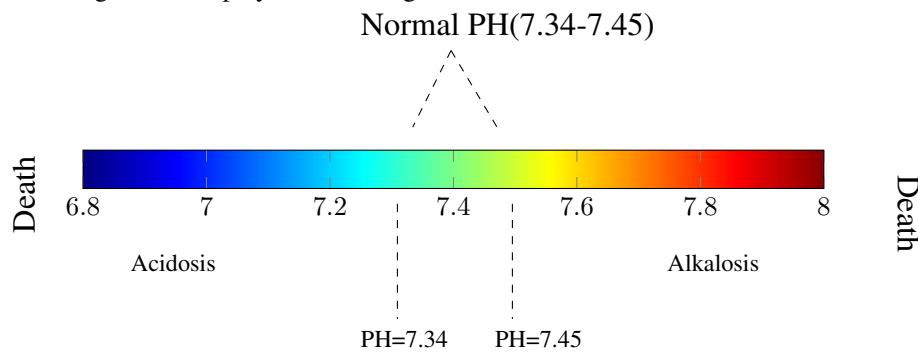


Figure 5.5 PH range that leads to acidosis and alkalosis

Alkalosis and carbon dioxide Our body needs oxygen to function properly. When you inhale, you introduce oxygen into the lungs. When you exhale, you release carbon dioxide, which is a waste product. Normally, the respiratory system keeps these two gases in balance. Respiratory alkalosis occurs when you breathe too fast or too deep. This hyperventilation—also known as over-breathing—causes carbon dioxide levels to drop too low. This means there is not enough CO_2 in the blood and that causes the PH to increase becoming too alkaline. Treating the condition is a matter of raising carbon dioxide levels in the blood. You can do this by breathing from a plastic bag. Respiratory acidosis occurs when too much CO_2 builds up in the body. Normally, the lungs remove CO_2 while you breathe. However, sometimes your body is unable to get rid of enough CO_2 . Treatments for this condition are usually designed to help your lungs. For example, you may be given drugs to dilate your airway. You might also be given oxygen or a continuous positive airway pressure (CPAP) device. The CPAP device can help you breathe if you have an obstructed airway or muscle weakness.

Sample Problem 74

Explain why CO_2 decreases the PH of blood.

SOLUTION

CO_2 is an acid and when dissolved in water it generates protons, H^+ . Increasing



the amount of protons decreases PH as PH is a measure the concentration of protons in solution.

STUDY CHECK

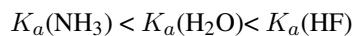
The PH of a patient's blood sample is 7.3. Indicate whether the patient suffers alkalosis, acidosis, or perhaps none of the afflictions. Can the PH level cause death?

►Answer: acidosis, is not deadly.

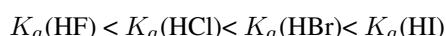
5.13 Molecular mechanisms behind acid-base strength

Why are some acids stronger than others? There is not simple answer to this question. The strength of a given acid depends not only on its molecular structure but also on energetic and electronic arguments. In this section, we will explore the mechanisms responsible for acidity in three different families of chemicals: binary acids (e.g. HCl), oxoacids (e.g. HClO), and carboxylic acids (e.g. CH₃COOH).

Binary acids Binary acids result from the combination of an element (e.g. N, O, F) with hydrogen: NH₃, H₂O, HF, HCl, HBr, and HI. Mind that ammonia and even methane are indeed very weak acids. Here we will compare the acidity of well-known acids (e.g. HCl) as well as other hydrogen-based chemicals (e.g. NH₃). We find two different acidity trends across periods and groups of the periodic table. On one hand, we have that across a period from left to right acidity increases



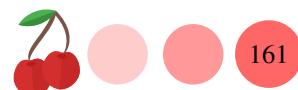
For this set of acids, the dominant contribution to acidity is the electronegativity character of the central atom: the larger the electronegativity of the central atom the larger the tendency of this atom to withdraw electron density from hydrogen and hence the bond becomes weaker (*acidity factor 1*). The less electron density localized in the bond the larger acidity—the easier would be to break this bond. On the other hand, across a group, acidity increases when going from HF to HI, that is from top to bottom of the periodic table. We have that across a group



This trend corresponds with an increase in the atomic weight of the central atom and an increase in the capacity of the corresponding anion to stabilize the negative charger. Acid dissociation necessarily implies the formation of an anion (e.g. Cl⁻ or even NH₂⁻). The more stable this anion the stronger its acidity. Heavier atoms are more capable to stabilize negative charges and hence they are more stable. Therefore, the larger the atomic weight of the central atom the stronger acidity (*acidity factor 2*). At this point, we saw two different factors that contribute to acidity.

These factors play a key role as well in other types of acids as we will see in the following.

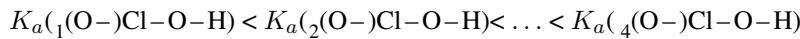
Oxoacids Oxoacids contain a central halogen atom bonded to one or more oxygen atoms as well as hydrogen. These acids normally have the following general structure: $n(\text{O}^-)\text{Cl}-\text{O}-\text{H}$. For example, Cl-O-H is called hypochlorous acid (HClO), and



$\text{Cl}(\text{O}-)_{3}\text{O}-\text{H}$ is called perchloric acid (HClO_4). We will first address the changes in acidity with the nature of the central halogen and then address the changes in acidity with the number of oxygen atoms in the molecule. When comparing the acidity of hypochlorous acid, hypobromous acid, and hypoiodous acid, we find that

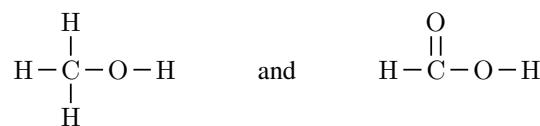


In other words, acidity increases from bottom to top across a group. That is the greater the electronegativity of the halogen the stronger the acid character. This trend is indeed opposite to the one found in binary acids. As the electronegativity of the halogen increases more electron density is withdrawn towards the $\text{X}-\text{O}$ bond and less electronic density is available for the $\text{O}-\text{H}$. As a consequence, the $\text{O}-\text{H}$ bond becomes weaker due to the indirect changes of the $\text{O}-\text{X}$ bond as acidity increases. Hence, we have a new factor that controls acidity: the larger the electronegative of the central halogen in an oxoacid the stronger acidity (*Acidity factor 3*). When comparing the acidity of hypochlorous acid, chlorous acid, chloric acid, and perchloric acid, we find that



In other words, acidity increases as the number of oxygen atoms connected to the central halogen increases. As the number of electronegative oxygen atoms connected to the central halogen atoms increases, more electron density will be withdrawn from the central Cl. This will also impact the oxygen connected to the acidic hydrogen weakening the $\text{O}-\text{H}$ bond and increasing acidity. The more oxygens are connected to the central halogen the stronger acidity (*Acidity factor 4*). To summarize, two different factors impact the acid character of oxoacids: the electronegativity of the central halogen and the number of oxygens connected to the central halogen.

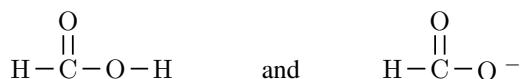
Carboxylic acids We can start by comparing the acidity of two different organic compounds, methanol, the simplest of all alcohols, and formic acid, the simplest carboxylic acid. The structure of both molecules is presented below:



Methanol

Formic acid

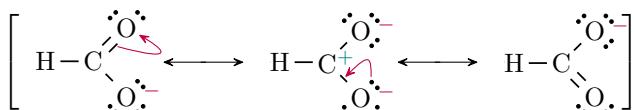
Indeed, methanol, as well as other alcohols, are not acidic whereas carboxylic acids and in particular formic acid are in general weak acids. We can understand this trend through two factors. On one hand, following *acidity factor 4* carboxylic acids have two oxygen atoms connected to the central carbon. Both withdraw electron density from carbon hence weakening the $\text{O}-\text{H}$ bond and increasing acidity. There is a new acidity factor that contributes to the acidity of carboxylic acids. The result of dissociating a carboxylic acid is a negatively charged carboxylate ion



Formic acid

Formate ion

The negative charge in the oxygen is stabilized by resonance, that is, it is not localized on a single oxygen but distributed between the two oxygen atoms as shown below. Hence carboxylates are stabilized by resonance and this contributes to the acidity of the carboxylic acids *acidity factor 5*.



Molecular mechanisms behind acid-base strength: a review

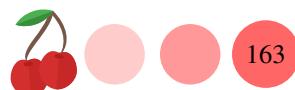
Five different factors contribute to the acidity of a chemical.

- 1 **First Factor:** the larger the electronegativity of the atom directly connected to hydrogen the stronger acidity.
- 2 **Second Factor:** the heavier the atom connected to hydrogen the stronger acidity.
- 3 **Third Factor:** the larger the electronegativity of an atom secondarily connected to hydrogen the stronger acidity.
- 4 **Fourth Factor:** the larger the number of electronegative atoms indirectly connected to hydrogen the stronger acidity.
- 5 **Fifth Factor:** a possible stabilization of the corresponding anion generated by the dissociation of acid increases acidity strength.

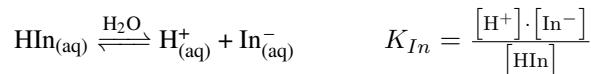
5.14 Indicators

There are several techniques to locate the endpoint during titration. On one hand, we can use a PH meter and measure the PH during a titration. The endpoint locates between the initial and final plateau. We can also use an automatic titrator, a machine that automatically mixes the acid and the base while displaying the PH. Another technique uses an indicator that changes color when the PH changes from acidic to basic or the opposite.

How do indicators function? Acid-base indicators are water-soluble organic dyes that have a different color depending on PH. Halochromism is the effect of changing color due to changes in an external force such as PH. Many flowers or plants exhibit this quality. For example, the french hydrangea is a plant that changes color depending on the acidity of the soil. Turmeric is a specie that turns from yellow to brown when the PH increases. Indicator can be extracted from many plants and fruits such as red cabbage, geranium, poppy, rose petals, or blueberries. Indeed, indicators are weak acids that exist in a conjugate base form as well. Both the acid (the indicator form with the hydrogen attached) and the conjugate base have different colors due to differences in their electronic structure that transform into differences in absorbing light.



For example, phenolphthalein is a common acid-base indicator that is transparent when the PH is acidic and pink when the PH is basic. The equivalency point of a titration (when acid and base are neutralized) is not necessarily the endpoint (when the indicator changes color). However, if both points are close enough chemical indicators are an accurate way to visually locate the equivalency point during a titration. As indicators are weak acids, each particular indicator is characterized by a constant of acidity referred to as K_{In} so that



The color change is considered to happen when the difference between the acidic and basic form of the indicator is an order or magnitude—ten times—different. This is the ten times rule. For this difference, we have that

$$PH = PK_{In} \pm 1$$

We can always use a different value for the difference (Δ) between the acid and basic form of an indicator so that the PH range will be given by

$$PH = PK_{In} \pm \log(\Delta)$$

This expression helps with the selection of the indicator for a given titration. For example, if we want to select an indicator that changes color when the difference between acid and base form is 5 times ($\Delta = 5$), then the OH range would be: $PH = PK_{In} \pm 0.7$

Selecting an indicator A good indicator will turn into a different color within the transition between acid and basic PH during titration. For example, for the titration of hydrochloric acid with sodium hydroxide, the PH changes from 5 before the equivalency point to 8 after. Any indicator with PK_{In} between 5 and 8 would be able to accurately indicate the stoichiometric point. Examples are bromothymol blue, m-nitrophenol, and even phenolphthalein which transition color at 8. For the titration of a weak acid and a strong base, the selection of an indicator is more difficult as the difference between the acidic and basic plateaus during the titration is less pronounced. We must choose an indicator that changes color more closely to the endpoint. Table 5.4 reports numerous acid-base indicators and their colors.

Litmus paper Litmus paper is an indicator heavily used for quick PH testing in labs. It contains a mixture of dyes that were extracted originally from lichens. There are two main types of litmus paper, red and blue litmus. Light blue litmus paper turns red when the medium is acidic, whereas red litmus paper turns blue in basic mediums. By wetting a piece of litmus paper one can also test for the acidity of gases, for example, ammonia vapor would turn blue on a piece of wet red litmus paper.

Sample Problem 75

When titrating hydrochloric acid with sodium chloride using p-Nitrophenol ($K_a = 6.3 \times 10^{-8}$), indicate the PH at which the ratio between the acid and base form of the indicator is 10%.

SOLUTION

We have that the PH at which an indicator changes color depends on the pK_a of the indicator. pK_a for p-Nitrophenol is 7.2, hence the PH for color transition



will be $7.2 \pm \log(\Delta)$, given that Δ is the difference in concentration between acid and basic form. For a 10% difference, we have that $7.2 \pm \log(0.1)$ and the color change will start at 6.2 and finish at 8.2

❖ **STUDY CHECK**

When titrating an acid with a strong base using Methyl orange ($K_a = 3.9 \times 10^{-4}$), indicate the pH at which the concentration of the acid form of the indicator is four times the one of the base base.

►Answer: 2.8.

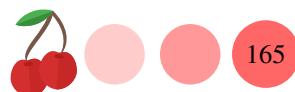


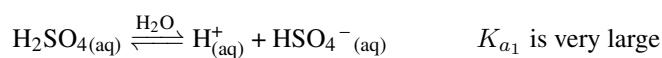
Table 5.4 Acid-base indicators showing ample representations of their colors

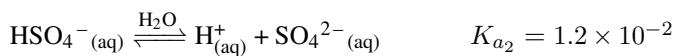
Name	PH Range	Color acid form	Color basic form
Thymol Blue	1.2-2.8	red	yellow
Pentamethoxy red	1.2-2.3	red-violet	colorless
Methyl yellow	2.9-4.0	red	yellow
Methyl orange	3.1-4.4	red	orange
Bromophenol blue	3.0-4.6	yellow	blue-violet
Tetrabromophenol blue	3.0-4.6	yellow	blue
Alizarin sodium sulfonate	3.7-5.2	yellow	violet
α -Naphthyl red	3.7-5.0	red	yellow
p-Ethoxychrysoidine	3.5-5.5	red	yellow
Bromocresol green	4.0-5.6	yellow	blue
Methyl red	4.4-6.2	red	yellow
Bromocresol purple	5.2-6.8	yellow	purple
Bromophenol blue	6.2-7.6	yellow	blue
Azolitmin	5.0-8.0	red	blue
Phenol red	6.4-8.0	yellow	red
Neutral red	6.8-8.0	red	yellow
Rosolic acid	6.8-8.0	yellow	red
Cresol red	7.2-8.8	yellow	red
α -Naphtholphthalein	7.3-8.7	rose	green
Tropeolin	7.6-8.9	yellow	rose-red
Thymol blue	8.0-9.6	yellow	blue
Phenolphthalein	8.0-10.0	colorless	red
α -Naphtholbenzein	9.0-11.0	yellow	blue
Thymolphthalein	9.4-10.6	colorless	blue
Nile blue	10.1-11.1	blue	red
Diazo violet	10.1-12.0	yellow	violet
Tropeolin	11.0-13.0	yellow	orange-brown
Nitramine	11.0-13.0	colorless	orange-brown
Trinitrobenzoic acid	12.0-13.4	colorless	orange-red

5.15 Titrations of polyprotic acids

Monoprotic acids contain a single proton. Examples are hydrochloric acid (HCl) and nitric acid (HNO₃). Polyprotic acids contain more than one proton. Examples are sulfuric acid (H₂SO₄), a diprotic acid, and phosphoric acid, (H₃PO₄). When titrating an acid, the number of protons determines the number of endpoints observed. Monoprotic acids go through a single endpoint, whereas diprotic acids go through two different end points.

PH curves of polyprotic acids The principles that control the shape of PH curves of monoprotic acids also apply to polyprotic acids. PH curves of strong acids have well-defined plateaus, whereas PH curves of weak acids or bases have shorter PH transitions and inclined plateaus. For polyprotic acids, these principles are applied to each endpoint in the PH curve. For example, sulfuric acid (H₂SO₄) can give away two protons as shown in Figure 5.6. The first proton dissociation equilibrium is characterized by a very large K_a , whereas the second dissociation corresponds to a weak acid dissociation:





The PH curve of this acid should reflect these facts and the first transition is well-defined, whereas the second one is shorter. For weak electrolytes, the plateaus represent buffer areas where the acid and conjugate bases exist. At the half-point, the PH is the same as the pK of each dissociation.

End points of polyprotic acids We can also employ the endpoint formula to locate the volume of titrant needed to reach each of the end points during the titration. For example, when titrating a 10mL sample of 0.1M phosphoric acid with 0.1M-NaOH, we would need 10mL to reach the first end point, 20mL to reach the second end point, and a total of 30mL to reach the third and last end point, completely neutralizing the acid.

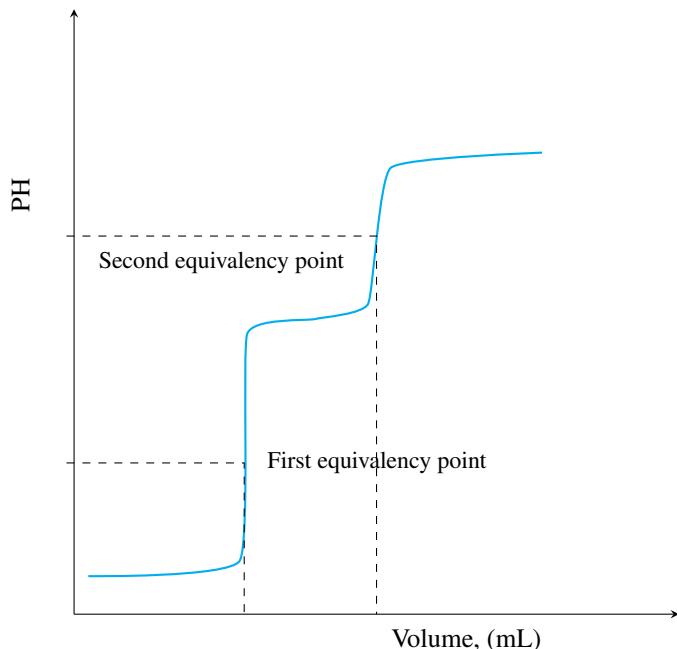
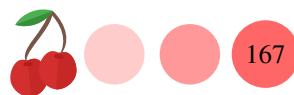


Figure 5.6 PH curve for a diprotic acid showing two equivalency points



CHAPTER 5

THE NATURE OF ACIDS AND BASES

5.1 Classify the following species as Arrhenius acids, or bases: (a) H_2SO_4 (b) NaOH (c) HNO_3 (d) HCl (e) $\text{Ca}(\text{OH})_2$

5.2 Classify the following species as Arrhenius acids, or bases: (a) KOH (b) H_3PO_4 (c) HI (d) $\text{Mg}(\text{OH})_2$

5.3 Classify the following species as Brönsted-Lowry acids, bases or both: (a) H_2O (b) OH^- (c) NH_3 (d) NO_2^-

5.4 Classify the following species as Brönsted-Lowry acids, bases or both: (a) HCO_3^- (b) HI (c) HCN (d) HSO_4^- (e) HCOONa

5.5 Classify the following species as Lewis acids or bases: (a) CO_2 (b) NH_3 (c) F^-

5.6 Classify the following species as Lewis acids or bases: (a) SO_2 (b) BCl_3 (c) I^-

DISSOCIATIONS OF ACIDS & BASES

5.7 From the following pairs, select the strongest acid:
 (a) HIO_3 ($K_a = 1.6 \cdot 10^{-1}$) or H_2SO_3 ($K_a = 1.5 \cdot 10^{-2}$)
 (b) HN_3 ($K_a = 1.9 \cdot 10^{-5}$) or H_2CO_3 ($K_a = 4.3 \cdot 10^{-7}$)

5.8 From the following pairs, select the strongest base:
 (a) CN^- ($K_a = 6.2 \cdot 10^{-10}$) or H_2O ($K_a = 1.0 \cdot 10^{-7}$)
 (b) $\text{H}_2\text{C}_6\text{H}_5\text{O}^-$ ($K_a = 1.8 \cdot 10^{-5}$) or HCOOH ($K_a = 1.7 \cdot 10^{-4}$)

5.9 Write down the formula of the conjugate bases:
 (a) H_2O (b) HCl (c) HNO_3 (d) H_2SO_4

5.10 Write down the formula of the conjugate bases:
 (a) HSO_4^- (b) H_2S (c) HCOOH (d) H_2PO_4^-

5.11 Write down the formula of the conjugate acids:
 (a) NH_4^+ (b) CH_3COO^- (c) HS^- (d) CN^-

5.12 Identify the conjugate acid-base pairs: (a) $\text{HCl}_{(g)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{Cl}_{(aq)}^- + \text{H}_3\text{O}_{(aq)}^+$ (b) $\text{CH}_3\text{COO}_{(l)}^- + \text{HCl}_{(g)} \rightleftharpoons \text{Cl}_{(aq)}^- + \text{CH}_3\text{COOH}_{(aq)}$ (c) $\text{CO}_3^{2-}_{(aq)} + \text{HCN}_{(g)} \rightleftharpoons \text{CN}_{(aq)}^- + \text{HCO}_3^-_{(aq)}$ (d) $\text{HNO}_3_{(aq)} + \text{OH}_{(aq)}^- \rightleftharpoons \text{NO}_3^-_{(aq)} + \text{H}_2\text{O}_{(aq)}$

5.13 Write down the following dissociation or acid-base reaction involving the exchange of one proton:
 (a) $\text{HNO}_3_{(l)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons$ (b) $\text{H}_2\text{SO}_4_{(l)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons$
 (c) $\text{HCl}_{(g)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons$ (d) $\text{NH}_3_{(g)} + \text{H}_3\text{O}_{(aq)}^+ \rightleftharpoons$

5.14 Write down the following dissociation or acid-base reaction involving the exchange of one proton:
 (a) $\text{CO}_3^{2-}_{(aq)} + \text{HCN}_{(g)} \rightleftharpoons$ (b) $\text{HCO}_3^-_{(aq)} + \text{HCN}_{(g)} \rightleftharpoons$
 (c) $\text{HCO}_3^-_{(aq)} + \text{OH}_{(aq)}^- \rightleftharpoons$

THE PH SCALE

5.15 Answer the following questions: (a) The proton concentration of a solution is $3 \times 10^{-3}\text{M}$. Calculate the hydroxyl concentration in the same solution (b) The hydroxyl concentration of a solution is $8 \times 10^{-6}\text{M}$. Calculate the proton concentration in the same solution.

5.16 Answer the following questions: (a) The proton concentration of a solution is $1 \times 10^{-10}\text{M}$. Calculate the hydroxyl concentration in the same solution (b) The hydroxyl concentration of a solution is $3 \times 10^{-5}\text{M}$. Calculate the proton concentration in the same solution.

5.17 Answer the following questions: (a) The PH of a solution is 1.34. Calculate the POH of the same solution (b) The POH of a solution is 12. Calculate the PH of the same solution.

5.18 Answer the following questions: (a) The PH of a solution is 3. Calculate the POH of the same solution (b) The POH of a solution is 13. Calculate the PH of the same solution.

5.19 Answer the following questions: (a) The PH of a solution is 1.56. Calculate the concentration of protons. (b) The POH of a solution is 10.34. Calculate the hydroxyl concentration in the same solution. (c) The PH of



a solution is 12.4. Calculate the hydroxyl concentration in the same solution.

5.20 Fill the table below:

[H ⁺]	[OH ⁻]	Acidic/Basic/Neutral?
1.5 × 10 ⁻⁴	6.6 × 10 ⁻¹¹	(a)
4.9 × 10 ⁻¹²	2.0 × 10 ⁻³	(b)
1.9 × 10 ⁻⁶	5.3 × 10 ⁻⁹	(c)
1.0 × 10 ⁻⁷	1.0 × 10 ⁻⁷	(d)

5.21 Fill the table below:

[H ⁺]	[OH ⁻]	PH	POH
4.5 × 10 ⁻³		–	–
	3.2 × 10 ⁻⁷	–	–
–	–	5.1	
–	–		6.9

5.22 Fill the table below:

[H ⁺]	[OH ⁻]	PH	POH
3.5 × 10 ⁻¹	–	–	–
–	–	–	2

PH OF STRONG ACID-BASE SOLUTIONS

5.23 Answer the following questions: (a) Calculate the PH of a 0.34M HCl solution (b) Calculate the PH of a 0.04M HNO₃ solution (c) Calculate the PH of a 0.08M NaOH solution

5.24 Answer the following questions: (a) Calculate the PH of a 0.27M H₂SO₄ solution (b) Calculate the PH of a 0.03M Ba(OH)₂ solution

PH OF WEAK ACID-BASE SOLUTIONS

5.25 Solve the following quadratic equation and select the positive root: $x^2 + 6.6 \times 10^{-5} \cdot x - 6.60 \times 10^{-7} = 0$

5.26 Solve the following quadratic equation and select the positive root: $x^2 + 6.6 \times 10^{-5} \cdot x - 1.32 \times 10^{-5} = 0$

5.27 Answer the following questions: (a) Calculate the PH of a 0.23M C₆H₅COOH (benzoic acid, $K_a = 6.25 \times 10^{-5}$) solution. (b) Calculate the PH of a 0.08M C₆H₅NH₂ (Aniline, $K_b = 7.40 \times 10^{-10}$) solution.

5.28 Answer the following questions: (a) Calculate the PH of a 0.05M C₆H₅OH (phenol, $K_a = 1.00 \times 10^{-10}$) solution. (b) Calculate the PH of a 0.09M C₅H₅N (pyridine, $K_b = 1.70 \times 10^{-9}$) solution.

5.29 Calculate the PH of the following solutions:

- (a) 0.2M-CH₃COOH solution ($K_a = 1.8 \times 10^{-5}$)
- (b) 0.2M-CH₃COOH and 0.1M-NaCH₃COO solution ($K_a = 1.8 \times 10^{-5}$)

5.30 Calculate the PH of the following solutions:

- (a) 0.4M-NH₃ solution ($K_b = 1.8 \times 10^{-5}$)
- (b) 0.4M-NH₃ and 0.3M-NH₄Cl solution ($K_b = 1.8 \times 10^{-5}$)

BUFFER SOLUTIONS

5.31 Indicate if the following mixtures of solutions can act as a buffer: (a) 0.1M-H₂SO₄/0.1M-Na(SO₄)₂ (b) 0.01M-NH₃/0.01M-NH₄Cl (c) 0.2M-HNO₂/0.2M-NaNO₂

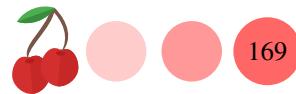
5.32 Indicate if the following mixtures of solutions can act as a buffer: (a) 0.4M-H₂SO₃/0.1M-NaHSO₃ (b) 0.23M-HCl/0.20M-KCl (c) 0.56M-HCN/0.22M-NaCN

5.33 Indicate if the following mixtures of solutions can act as a buffer: (a) KCl/HCl (b) H₂SO₄/NaHSO₄ (c) Na₂SO₄/NaHSO₄

5.34 Indicate if the following mixtures of solutions can act as a buffer: (a) H₃PO₄/NaH₂PO₃ (b) Na₃PO₄/Na₂HPO₃ (c) HNO₂/NaNO₂

5.35 Which of the following substances can be mixed together to prepare a buffer: (a) CH₃COOH (b) CH₃COONa (c) NaOH (d) HCl (e) NaCl

5.36 Which of the following substances can be mixed together to prepare a buffer: (a) NH₃ (b) NH₄Cl (c) Na₂SO₄ (d) H₂SO₄ (e) NaCl (f) HCl



5.37 Calculate the PH of the following buffers: (a) 0.15 M-HCN/0.35M-NaCN, $K_a = 6.20 \times 10^{-10}$ (b) 0.15 M-HCN/0.15M-NaCN, $K_a = 6.20 \times 10^{-10}$ (c) 0.25 M-HCN/0.15M-NaCN, $K_a = 6.20 \times 10^{-10}$

5.38 Calculate the PH of the following buffers: (a) 0.25 M-NH₃/0.45M-NH₄Cl, $K_b = 1.80 \times 10^{-5}$ (b) 0.15 M-HNO₂/0.05M-NaNO₂, $K_a = 5.60 \times 10^{-4}$

5.39 Calculate the PH of the following buffers: (a) 0.02 M-C₆H₅NH₂/0.05M-C₆H₅NHCl, $K_b = 7.40 \times 10^{-10}$ (b) 0.4 M-HCNO/0.5M-NaCNO, $K_a = 3.50 \times 10^{-4}$

5.40 The PH of a C₆H₅NH₂/C₆H₅NHCl ($K_b = 7.40 \times 10^{-10}$) buffer is 4.0. Calculate the ratio of [C₆H₅NH₂]/[C₆H₅NHCl].

5.41 Calculate the PH for the following scenarios: (a) A 0.3 M-HCNO/0.4M-NaCNO, $K_a = 3.50 \times 10^{-4}$ buffer (b) A 0.3 M-HCNO/0.4M-NaCNO, $K_a = 3.50 \times 10^{-4}$ buffer after adding 3mL of 0.1M HCl into 5mL of the buffer

5.42 Calculate the PH for the following scenarios: (a) A 0.3 M-HCNO/0.4M-NaCNO, $K_a = 3.50 \times 10^{-4}$ buffer after adding 3mL of 0.1M NaOH into 5mL of the buffer (b) A 0.3 M-HCNO/0.4M-NaCNO, $K_a = 3.50 \times 10^{-4}$ buffer after adding 1mL of 0.1M NaOH into 5mL of the buffer

5.43 Calculate the PH for the following scenarios: (a) A 0.8 M-HF/0.1M-NaF, $K_a = 6.30 \times 10^{-4}$ buffer (b) A 0.8 M-HF/0.1M-NaF, $K_a = 6.30 \times 10^{-4}$ buffer after adding 1mL of 0.1M HCl into 2mL of the buffer (c) A 0.8 M-HF/0.1M-NaF, $K_a = 6.30 \times 10^{-4}$ buffer after adding 1mL of 0.1M NaOH into 2mL of the buffer (d) Is the buffer more resistant to acids or bases, and why?

5.44 Calculate the PH for the following scenarios: (a) A 0.1 M-HF/0.9M-NaF, $K_a = 6.30 \times 10^{-4}$ buffer (b) A 0.1 M-HF/0.9M-NaF, $K_a = 6.30 \times 10^{-4}$ buffer after adding 1mL of 0.1M HCl into 2mL of the buffer (c) A 0.1 M-HF/0.9M-NaF, $K_a = 6.30 \times 10^{-4}$ buffer after adding 1mL of 0.1M NaOH into 2mL of the buffer (d) Is the buffer more resistant to acids or bases, and why?

5.45 Calculate the PH of the following buffer solutions: (a) 0.02 M-NH₃/0.02M-NH₄Cl solution ($K_b = 1.8 \times 10^{-5}$) (b) 0.2 M-NH₃/0.2M-NH₄Cl solution ($K_b = 1.8 \times 10^{-5}$) (c) Which of the buffers is more effective?

5.46 Calculate the PH of the following buffer solutions: (a) 0.02 M-CH₃CO₂H/0.02M-NaCH₃CO₂ solution ($K_a = 1.7 \times 10^{-5}$) (b) 0.2 M-CH₃CO₂H/0.2M-NaCH₃CO₂ solution ($K_a = 1.7 \times 10^{-5}$) (c) Which of the buffers is more effective?

5.47 Calculate the ratio of carbonic acid and bicarbonate in a H₂CO₃/NaHCO₃ buffer solution with PH=5 ($K_{a_1} = 4.5 \times 10^{-7}$).

5.48 Calculate the ratio of ammonia and ammonium chloride in a NH₃/NH₄Cl buffer solution with PH=9 ($K_b = 1.8 \times 10^{-5}$).

TITRATIONS

5.49 Solve the following titration scenarios: (a) In a titration experiment, 13.5 mL of 0.34 M HCl neutralizes 34.3 mL of KOH. What is the concentration of the KOH solution? (b) In a titration experiment, 20.4 mL of 0.10 M HCl neutralizes 12.4 mL of Ca(OH)₂. What is the concentration of the base solution?

5.50 Solve the following titration scenarios: (a) In a titration experiment, 10.4 mL of 0.20 M H₂SO₄ neutralizes 8.4 mL of Ca(OH)₂. What is the concentration of the base solution? (b) In a titration experiment, 12.5 mL of 0.23 M H₃PO₄ neutralizes 4.8 mL of Ca(OH)₂. What is the concentration of the base solution?

5.51 A 5mL sample of a monoprotic acid neutralizes 10mL of a 0.01M-KOH solution. Calculate the molarity of the acid.

5.52 A 10mL sample of a monoprotic acid neutralizes 5mL of a 0.2M-Ca(OH)₂ solution. Calculate the molarity of the acid.

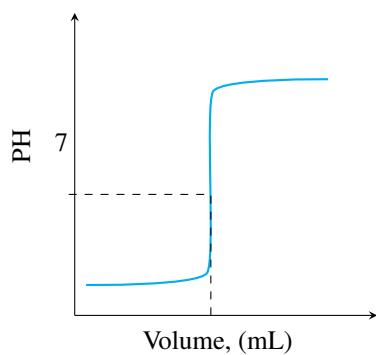
5.53 A 5 grams sample of an acid neutralizes 30mL of a 0.5M-NaOH solution. Calculate the molar mass of the acid.



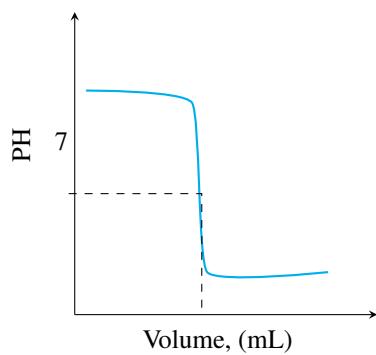
5.54 You prepare a base solution by dissolving 3-g of the base into 250mL of solution. Five milliliters of this solution neutralizes 5mL of a 0.3M H_2SO_4 solution. Calculate the molar mass of the base.

TITRATION CURVES

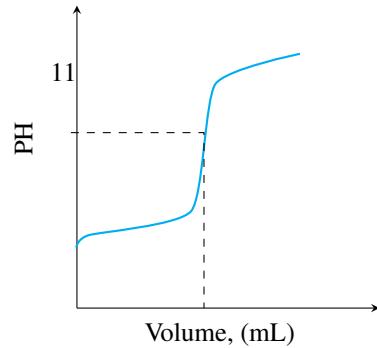
5.55 Consider the titration curve below. Answer the following questions: (a) Is the titrate an acid or a base? (b) Is the titrate weak or strong? (c) Indicate the endpoint (d) Indicate the midpoint



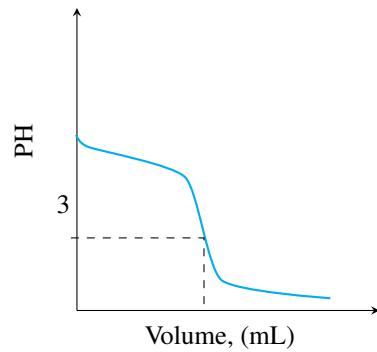
5.56 Consider the titration curve below. Answer the following questions: (a) Is the titrate an acid or a base? (b) Is the titrate weak or strong? (c) Indicate the endpoint (d) Indicate the midpoint



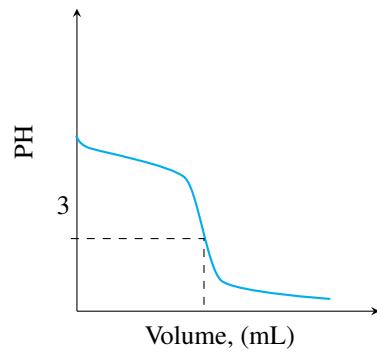
5.57 Consider the titration curve below. Answer the following questions: (a) Is the titrate an acid or a base? (b) Is the titrate weak or strong? (c) Indicate the endpoint (d) Indicate the midpoint



5.58 Consider the titration curve below. Answer the following questions: (a) Is the titrate an acid or a base? (b) Is the titrate weak or strong? (c) Indicate the endpoint (d) Indicate the midpoint

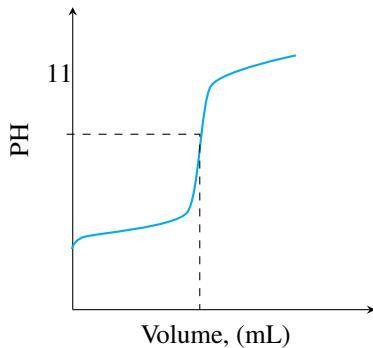


5.59 Consider the titration curve below for the titration of a weak base. On the curve indicate the points that correspond to: (a) $\text{PH}=\text{PK}_a$? (b) The region of maximum buffering? (c) The PH depends only on B (d) The PH depends only on BH^+ (e) The PH depends on the excess titrant



5.60 Consider the titration curve below for the titration of a weak acid. On the curve indicate the points that correspond to: (a) $\text{PH}=\text{PK}_a$? (b) The region of maximum buffering? (c) The PH depends only on HA (d) The PH

depends only on A^- (e) The pH depends on the excess titrant



QUANTITATIVE ANALYSIS OF A TITRATION

5.61 A 15 mL solution of 0.2 M HCl is titrated with a 0.3 M KOH solution. Calculate the pH after the following additions of the base solution: (a) 0mL (b) 5mL (c) 10mL (d) 15mL

5.62 A 25 mL solution of 0.1 M HNO_2 ($K_a = 5.60 \times 10^{-4}$) is titrated with a 0.05 M KOH solution. Calculate the pH after the following additions of the base solution: (a) 0mL (b) 25mL (c) 50mL (d) 65mL

5.63 A 20 mL solution of 0.1 M KOH is titrated with a 0.5 M HCl solution. Calculate the pH after the following additions of the acid solution: (a) 0mL (b) 2mL (c) 4mL (d) 5mL

5.64 A 10 mL solution of 0.2 M NH_3 ($K_b = 2.50 \times 10^{-5}$) is titrated with a 0.1 M HCl solution. Calculate the pH after the following additions of the base solution: (a) 0mL (b) 10mL (c) 20mL (d) 30mL

5.65 A 20 mL solution of 0.1 M HCl is titrated with a 0.1 M KOH solution. Calculate: (a) the pH at the endpoint (b) the pH at the midpoint

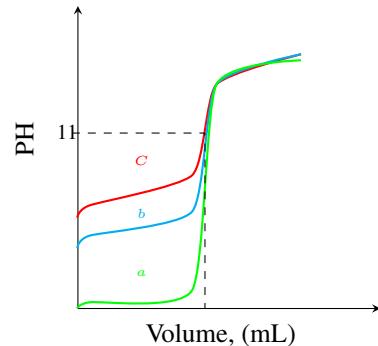
5.66 A 25 mL solution of 0.3 M HNO_2 ($K_a = 5.60 \times 10^{-4}$) is titrated with a 0.1 M KOH solution. Calculate: (a) the pH at the endpoint (b) the pH at the midpoint

5.67 A 50 mL solution of an 0.5 M acid is titrated with 125mL of 0.2 M NaOH solution giving a pH of 11.47. Calculate the acidity constant of the acid.

5.68 A 25 mL solution of a 0.1 M base is titrated with 0.2 M HCl solution. The pH at the equivalence point is 3.20. Calculate the basicity constant of the base.

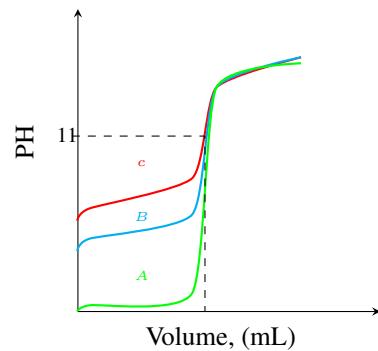
5.69 The following plot show the pH curves for the titration of three weak acids with a strong base. (a) Which pH curve is the weakest acid? (b) Which pH curve is the strongest?

Weak acids Titration



5.70 The following plot show the pH curves for the titration of three weak acids with a strong base. (a) True or false: the acid (A) is stronger than (B) (b) True or false: the acid (B) is stronger than (C) (c) True or false: the acid (C) is stronger than (A)

Weak acids Titration



MOLECULAR MECHANISMS BEHIND ACID-BASE STRENGTH

5.71 Compare the acidity of the following pairs and justify the mechanism responsible for your choice: (a) H_2O and H_2S (b) SiH_4 and PH_3 (c) CH_3COOH and CH_2FCOOH (d) CH_2ClCOOH and CH_2FCOOH



5.72 Compare the acidity of the following pairs and justify the mechanism responsible for your choice:
 (a) H₂S and HCl (b) SiH₄ and GeH₄ (c) CH₃CH₂OH and CH₃COOH (d) CH₃CH₂OH and CH₃CHFOH

INDICATORS

5.73 We titrate 10mL of a 0.1M-HCl solution with 0.05M-NaOH using an indicator with $K_{In} = 1 \times 10^{-7}$ that is blue on its acid form and red on its basic form. Answer the following questions: (a) What is the initial color of the solution (b) After adding 20mL of NaOH, indicate the color of the solution (c) After adding 30mL of NaOH, indicate the color of the solution (d) What is the PH of the equivalency point (e) At what PH will the color transition occur using the 10% rule

5.74 We titrate 10mL a 0.1M-CH₃COOH ($K_a = 1.8 \times 10^{-5}$) solution with 0.01M-NaOH using methyl red ($K_{In} = 9 \times 10^{-6}$) that is yellow on its acid form and orange on its basic form. Answer the following questions: (a) What is the initial color of the solution (b) After adding 50mL of NaOH, indicate the color of the solution (c) After adding 150mL of NaOH, indicate the color of the solution (d) What is the PH of the equivalency point (e) At what PH will the color transition occur using the 10% rule

5.75 Which of the following indicators can be used in the titration of a 20mL sample of 0.01M-NH₃ with 0.1M-HCl: (a) Thymol blue ($pK_{In} = 8.9$) (b) Phenolphthalein ($pK_{In} = 9.4$) (c) Bromophenol blue ($pK_{In} = 3.8$) (d) Cresol red ($pK_{In} = 1.0$)

5.76 Which of the following indicators can be used in the titration of a 20mL sample of 0.1M-CH₃COOH ($K_a = .18 \times 10^{-5}$) with 0.1M-KOH: (a) Thymol blue ($pK_{In} = 8.9$) (b) Phenolphthalein ($pK_{In} = 9.4$) (c) Bromophenol blue ($pK_{In} = 3.8$) (d) Cresol red ($pK_{In} = 1.0$)

5.77 An indicator with $pK_{In} = 5$ has a color transition that becomes noticeable when 3% of its acid form has been converted into a base. Indicate the PH at which the color transition starts to happen.

5.78 A solution is buffered to PH=3. Indicate the color of the following indicators: (a) Thymol blue ($pK_{In} =$

8.9, Y-B) (b) Phenolphthalein ($pK_{In} = 9.4$, Colorless-R)(c) Bromophenol blue ($pK_{In} = 3.8$, Y-B)(d) Cresol red ($pK_{In} = 1.0$, R-Y)

TITRATIONS OF POLYPROTIC ACIDS

5.79 We titrate a diprotic acid, H₂A with KOH. The first equivalence point is reached after adding 20mL of base. Given that the protons of a polyprotic acid are removed one at a time, answer the questions below: (a) What volume of base is needed to reach the second equivalence point? (b) List the most important specie present after adding 0mL of base (c) List the most important specie present after adding 10mL of base (d) List the most important specie present after adding 20mL of base (e) List the most important specie present after adding 30mL of base (f) List the most important specie present after adding 40mL of base (g) Calculate K_{a1} and K_{a2} given that the PH after adding 10mL of base is 1.9, and after 30mL is 7.1

5.80 Oxalic acid HO₂C–CO₂H is the simplest dicarboxylic acid ($PK_{a1} = 1.2$ and $PK_{a2} = 4.2$). It is a white crystalline solid that forms a colorless solution in water. We titrate 50mL of 0.1M HO₂C–CO₂H solution with 0.1M NaOH. Answer the questions below: (a) Calculate the PH after adding 25mL of base (b) Calculate the PH after adding 50mL of base (c) Calculate the PH after adding 75mL of base (d) Calculate the PH after adding 100mL of base (e) Calculate the PH after adding 150mL of base



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Ch. 6. Solubility equilibria

INSOLUBLE compounds and the solubility of solid chemicals in water is critical in fields such as engineering, medicine, and dentistry. For example, the presence of acids in the saliva enables tooth decay as they enhance the solubility of tooth enamel made of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. On a similar note, barium sulfate BaSO_4 , an insoluble compound, is opaque to x-rays and helps reveal digestive track issues. This chapter applies concepts of chemical equilibrium to the study of insoluble compounds. We will learn how to compute chemical solubilities using the equilibrium constant associated with the solubility equilibrium, and to assess the effect on the solubility of a common ion in solution.

6.1 Solubility

The solubility of an insoluble solute is the concentration of a saturated solution. A solution is saturated when no more solute can dissolve on it. One can express solubility in two different ways, with respect to the solution and with respect to the solvent. If we refer to solubility to the solution, we have two different solubility units: molar or mass-based solubility. Molar solubility is the molarity of a saturated solution, whereas mass-based solubility—or simply solubility—is the concentration in grams per liter of a saturated solution. Both types of solubilities—molar and mass-based—are related. If we refer to solubility with respect to the solvent, the solubility values are often expressed in g/100mL units, where mL refers to the volume of water.

Solubility Molar solubility or simply solubility s is defined as the moles of solute dissolved in 1L of a saturated solution. For example, the solubility of silver iodide (AgI) at 25°C is 9.0×10^{-9} mol/L. This means that 9.0×10^{-9} moles of silver iodide will dissolve in one liter of a saturated solution.

Mass-based solubility Mass-based solubility \bar{s} is defined as the number of grams of solute dissolved in a liter of a saturated solution. For example, the solubility of silver iodide (AgI) at 25° is 2.1×10^{-6} g/L. This means that 2.1×10^{-6} grams of silver iodide will dissolve in one liter of a saturated solution.

Relating solubility and mass-based solubility We can convert solubility values in terms of mass into solubility values in terms of moles by means of the molar mass of the insoluble solute

$$\bar{s} = s \cdot MW \quad (6.1)$$

where:



s is solubility in mol/L

\bar{s} is solubility in g/L

MW the molar weight of the insoluble compound

Sample Problem 76

How many grams of AgCl will dissolve in 5mL of a AgCl saturated solution, given that $s=1.33 \times 10^{-5}\text{M}$?

SOLUTION

As we have the molar solubility, we will convert this value into g/mol:

$$1.33 \times 10^{-5} \frac{\text{mol}}{\text{L}} \times \frac{143\text{g}}{\text{mol}} = 1.90 \times 10^{-3} \frac{\text{g}}{\text{L}}$$

In order to calculate the number of grams of solute in 5mL, we can do:

$$1.90 \times 10^{-3} \frac{\text{g}}{\text{L}} \times 0.005\text{L} = 9.51 \times 10^{-5}\text{g}$$

◆ STUDY CHECK

How many mL of solution contains 1ng of solute in a saturated ScF₃ solution, given $s=2.41 \times 10^{-12}\text{M}$. The molar mass of is ScF₃ 101.9g/mol.

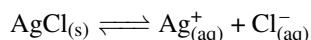
►Answer: 4072mL

Solubility based on water volume Often we will find solubility expressed in terms of 100mL of water. For example, the solubility of Aluminium chloride is 45.8 g/100 mL at 20°. This unit is defined with respect to the volume of water and ultimately is useful to find out the amount of solute that will dissolve in a given volume of water. For AlCl₃, we have that 45.8 grams of solute will dissolve in 100 mL of solvent.

6.2 Solubility equilibrium

When insoluble compounds dissolve in water an equilibrium between the solid and the dissolved ions establishes. Based on the stoichiometry of the compound we will obtain a different number of moles of ions in solution.

Solubility equilibrium Insoluble compounds dissolve in small amounts in water. Solubility equilibrium is the equilibrium that describes the dissolution of an insoluble compound to produce an aqueous solution of ions. For example, for the case of silver chloride, we have:



The solubility equilibrium above represents the dissolution of the insoluble salt—a solid—to produce ions, silver and chloride in solution. In general terms, solubility equilibria start with a solid and generate ions in solution. In order to break down the insoluble compound into ions, we just need to take into account the stoichiometry of the compound. For example, for the case of Cobalt(II) phosphate, we have:

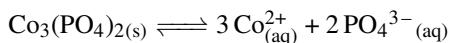
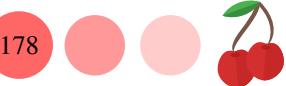


Table 6.1 Solubility product constants on water at 25°C

Name	Formula	K_{sp}	Name	Formula	K_{sp}
Aluminium hydroxide	$\text{Al}(\text{OH})_3$	3.00×10^{-34}	Magnesium phosphate	$\text{Mg}_3(\text{PO}_4)_2$	1.04×10^{-24}
Aluminium phosphate	AlPO_4	9.84×10^{-21}	Manganese(II) carbonate	MnCO_3	2.24×10^{-11}
Barium bromate	$\text{Ba}(\text{BrO}_3)_2$	2.43×10^{-4}	Manganese(II) hydroxide	$\text{Mn}(\text{OH})_2$	2.00×10^{-13}
Barium carbonate	BaCO_3	2.58×10^{-9}	Manganese(II) iodate	$\text{Mn}(\text{IO}_3)_2$	4.37×10^{-7}
Barium chromate	BaCrO_4	1.17×10^{-10}	Manganese(II) sulfide (green)	MnS	3.00×10^{-14}
Barium fluoride	BaF_2	1.84×10^{-7}	Manganese(II) sulfide (pink)	MnS	3.00×10^{-11}
Barium hydroxide octahydrate	$\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$	2.55×10^{-4}	Mercury(I) bromide	Hg_2Br_2	6.40×10^{-23}
Barium iodate	$\text{Ba}(\text{IO}_3)_2$	4.01×10^{-9}	Mercury(I) carbonate	Hg_2CO_3	3.6×10^{-17}
Barium iodate monohydrate	$\text{Ba}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$	1.67×10^{-9}	Mercury(I) chloride	Hg_2Cl_2	1.43×10^{-18}
Barium molybdate	BaMoO_4	3.54×10^{-8}	Mercury(I) fluoride	Hg_2F_2	3.10×10^{-6}
Barium nitrate	$\text{Ba}(\text{NO}_3)_2$	4.64×10^{-3}	Mercury(I) iodide	Hg_2I_2	5.20×10^{-29}
Barium selenate	BaSeO_4	3.40×10^{-8}	Mercury(I) oxalate	$\text{Hg}_2\text{C}_2\text{O}_4$	1.75×10^{-13}
Barium sulfate	BaSO_4	1.08×10^{-10}	Mercury(I) sulfate	Hg_2SO_4	6.50×10^{-7}
Barium sulfite	BaSO_3	5.00×10^{-10}	Mercury(I) thiocyanate	$\text{Hg}_2(\text{SCN})_2$	3.20×10^{-20}
Beryllium hydroxide	$\text{Be}(\text{OH})_2$	6.92×10^{-22}	Mercury(II) bromide	HgBr_2	6.20×10^{-20}
Cadmium arsenate	$\text{Cd}_3(\text{AsO}_4)_2$	2.20×10^{-33}	Mercury(II) hydroxide	HgO	3.60×10^{-26}
Cadmium carbonate	CdCO_3	1.00×10^{-12}	Mercury(II) iodide	HgI_2	2.90×10^{-29}
Cadmium fluoride	CdF_2	6.44×10^{-3}	Mercury(II) sulfide (black)	HgS	2.00×10^{-53}
Cadmium hydroxide	$\text{Cd}(\text{OH})_2$	7.20×10^{-15}	Mercury(II) sulfide (red)	HgS	2.00×10^{-54}
Cadmium iodate	$\text{Cd}(\text{IO}_3)_2$	2.50×10^{-8}	Neodymium carbonate	$\text{Nd}_2(\text{CO}_3)_3$	1.08×10^{-33}
Cadmium phosphate	$\text{Cd}_3(\text{PO}_4)_2$	2.53×10^{-33}	Nickel(II) carbonate	NiCO_3	1.42×10^{-7}
Cadmium sulfide	CdS	1.00×10^{-27}	Nickel(II) hydroxide	$\text{Ni}(\text{OH})_2$	5.48×10^{-16}
Calcium carbonate (calcite)	CaCO_3	3.36×10^{-9}	Nickel(II) iodate	$\text{Ni}(\text{IO}_3)_2$	4.71×10^{-5}
Calcium fluoride	CaF_2	3.45×10^{-11}	Nickel(II) phosphate	$\text{Ni}_3(\text{PO}_4)_2$	4.74×10^{-32}
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	5.02×10^{-6}	Nickel(II) sulfide (alpha)	NiS	4.00×10^{-20}
Calcium iodate	$\text{Ca}(\text{IO}_3)_2$	6.47×10^{-6}	Nickel(II) sulfide (beta)	NiS	1.30×10^{-25}
Calcium molybdate	CaMoO_4	1.46×10^{-8}	Potassium hexachloroplatinate	K_2PtCl_6	7.48×10^{-6}
Calcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$	2.07×10^{-33}	Potassium perchlorate	KClO_4	1.05×10^{-2}
Calcium sulfate	CaSO_4	4.93×10^{-5}	Potassium periodate	KIO_4	3.71×10^{-4}
Cobalt(II) arsenate	$\text{Co}_3(\text{AsO}_4)_2$	6.80×10^{-29}	Praseodymium hydroxide	$\text{Pr}(\text{OH})_3$	3.39×10^{-24}
Cobalt(II) carbonate	CoCO_3	1.00×10^{-10}	Radium iodate	$\text{Ra}(\text{IO}_3)_2$	1.16×10^{-9}
Cobalt(II) phosphate	$\text{Co}_3(\text{PO}_4)_2$	2.05×10^{-35}	Radium sulfate	RaSO_4	3.66×10^{-11}
Copper(I) bromide	CuBr	6.27×10^{-9}	Rubidium perchlorate	RuClO_4	3.00×10^{-3}
Copper(I) chloride	CuCl	1.72×10^{-7}	Scandium fluoride	ScF_3	5.81×10^{-24}
Copper(I) cyanide	CuCN	3.47×10^{-20}	Scandium hydroxide	$\text{Sc}(\text{OH})_3$	2.22×10^{-31}
Copper(I) hydroxide	Cu_2O	2.00×10^{-15}	Silver(I) acetate	AgCH_3COO	1.94×10^{-3}
Copper(I) iodide	CuI	1.27×10^{-12}	Silver(I) arsenate	Ag_3AsO_4	1.03×10^{-22}
Copper(I) thiocyanate	CuSCN	1.77×10^{-13}	Silver(I) bromate	AgBrO_3	5.38×10^{-5}
Copper(II) arsenate	$\text{Cu}_3(\text{AsO}_4)_2$	7.95×10^{-36}	Silver(I) bromide	AgBr	5.35×10^{-13}
Copper(II) hydroxide	$\text{Cu}(\text{OH})_2$	4.80×10^{-20}	Silver(I) carbonate	Ag_2CO_3	8.46×10^{-12}
Copper(II) iodate monohydrate	$\text{Cu}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$	6.94×10^{-8}	Silver(I) chloride	AgCl	1.77×10^{-10}
Copper(II) oxalate	CuC_2O_4	4.43×10^{-10}	Silver(I) chromate	Ag_2CrO_4	1.12×10^{-12}
Copper(II) phosphate	$\text{Cu}_3(\text{PO}_4)_2$	1.40×10^{-37}	Silver(I) cyanide	AgCN	5.97×10^{-17}
Copper(II) sulfide	CuS	8.00×10^{-37}	Silver(I) iodate	AgIO_3	3.17×10^{-8}
Iron(II) carbonate	FeCO_3	3.13×10^{-11}	Silver(I) iodide	AgI	8.52×10^{-17}
Iron(II) fluoride	FeF_2	2.36×10^{-6}	Silver(I) oxalate	$\text{Ag}_2\text{C}_2\text{O}_4$	5.40×10^{-12}
Iron(II) hydroxide	$\text{Fe}(\text{OH})_2$	4.87×10^{-17}	Silver(I) phosphate	Ag_3PO_4	8.89×10^{-17}

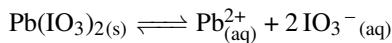


Sample Problem 77

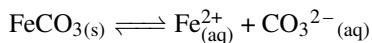
Write down the solubility equilibrium for: Lead(II) iodate, and FeCO_3 .

SOLUTION

The first insoluble compound, Lead(II) iodate, with formula $\text{Pb}(\text{IO}_3)_2$, contains cation lead(II) Pb^{2+} and anion IO_3^{2-} (iodate). The solubility equilibrium will be given by:



The solubility equilibrium for the second insoluble compound iron(II) carbonate will be:

**◆ STUDY CHECK**

Write down the solubility equilibrium for: Copper(II) phosphate, and CuCN .

►Answer: $\text{Co}_3(\text{PO}_4)_{2(s)} \rightleftharpoons 3 \text{Co}_{(\text{aq})}^{2+} + 2 \text{PO}_{4(\text{aq})}^{3-}$;
 $\text{CuCN}_{(\text{s})} \rightleftharpoons \text{Cu}_{(\text{aq})}^+ + \text{CN}_{(\text{aq})}^-$

6.3 Solubility product

When an insoluble solid dissolves in liquid a solubility equilibrium is established between the solid and the dissolved solid, and this equilibrium has associated an equilibrium constant. This equilibrium constant informs about the amount of solid that dissolves, which in general is small. Unless otherwise stated, all solutions in this chapter are water-based solutions at 25°C —remember equilibrium constants are temperature and solvent-dependent.

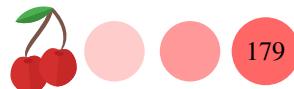
Solubility product in terms of molarities, K_{sp} Silver chloride, AgCl is an insoluble compound in water which means this compound will not fully dissolve in water. Still, small quantities of the salt will indeed dissolve leading to a small amount of silver and chlorine ions. As this compound is insoluble the ion concentration will be very small. The dissociation equilibrium involved in the dissolution, indicate below, is characterized by an equilibrium constant K_{sp} called *solubility product constant* or simply *solubility product*:



As pure solids are not included in any equilibrium constant, the formula above does not include $\text{AgCl}_{(\text{s})}$. Hence, all solubility products simply result from the product of the molarities of the ions involved in the dissociation with the corresponding powers based on the stoichiometry of the salt. This is why the term *product* is included on its name. K_{sp} will have a different explicit expression depending on the formula of the insoluble compound—depending on its stoichiometry. For example, K_{sp} for calcium fluoride—a 1:2 compound—would be:



Solubility products are related to the solubility of chemicals. However, the relation is not one-on-one. In other words, a larger K_{sp} does not necessarily imply a larger



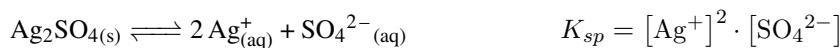
solubility. For example, K_{sp} for PbBr_2 is $6.6 \times 10^{-3}\text{M}$ whereas K_{sp} for MgCO_3 is $4.0 \times 10^{-5}\text{M}$. We have that K_{sp} for PbBr_2 is smaller than K_{sp} for MgCO_3 . However, the solubility of PbBr_2 is indeed larger than the solubility of MgCO_3 . Table 6.1 reports numerous solubility product constant values.

Sample Problem 78

Write down the expression of K_{sp} in terms of the ion concentration for the following compounds: Ag_2SO_4 , $\text{Mg}(\text{OH})_2$, and MgCO_3 .

SOLUTION

The solubility equilibrium for first compound, silver sulfate, is



The solubility product depends on the square concentration of silver ions. For magnesium hydroxide:



Finally, for magnesium carbonate:



◆ STUDY CHECK

Write down the expression of K_{sp} in terms of the ion concentration for the following compounds: PbCl_2 , and manganese(II) sulfide.

►Answer: $[\text{Pb}^{2+}] \cdot [\text{Cl}^-]^2; [\text{Mn}^{2+}] \cdot [\text{S}^{2-}]$

Relating solubility to the concentration of ions We have that insoluble compounds dissolve to produce small amounts of ions in solutions. The concentration of these ions is directly related to solubility s by means of the stoichiometry of the compound. For example, for silver chloride—a salt with a 1:1 stoichiometry—we have that solubility is has a 1 and 1 relationship with the concentration of ions:

$$[\text{Ag}^+] = s \text{ and } [\text{Cl}^-] = s$$

Similarly, for barium sulfate we have that solubility has a 1:1 relationship with the concentration of ions:

$$[\text{Ba}^{2+}] = s \text{ and } [\text{SO}_4^{2-}] = s$$

When the stoichiometry of the compound is not 1:1 we need to include the stoichiometry coefficients in the relationship between solubility and ion concentration. For example, for Ag_2SO_4 —a compound with 2:1 stoichiometry, we have that

$$[\text{Ag}^+] = 2 \cdot s \text{ and } [\text{SO}_4^{2-}] = s$$

This is because for every mole of silver sulfate we produce two moles of silver—and hence the factor two—and one mole of sulfate in solution. Similarly, for $\text{Nd}_2(\text{CO}_3)_3$ we have

$$[\text{Nd}^{3+}] = 2 \cdot s \text{ and } [\text{CO}_3^{2-}] = 3 \cdot s$$

6.4 Predicting precipitation



At this point, we have used the solubility product to calculate the concentration of ions in a saturated solution of a solid. Imagine we have a solution containing a mixture of two different ions given that the ions in the solution can combine to form a precipitate. The question is, will a solid precipitate? Similar to the solubility product, we can use a construct called the concentration product to predict whether a mixture of ions will precipitate.

Predicting precipitation: an introduction The values of the solubility product constant can be used to predict the precipitation of a salt when mixing two reagents. Imagine for example that we have a 0.1M Cu^+ solution and you gradually add a solution containing I^- . Given that CuI is an insoluble compound with a K_{sp} of 1.27×10^{-12} , the goal would be to compute the I^- concentration that would make CuI precipitate. We will answer this question by obtaining first the expression for K_{sp} :

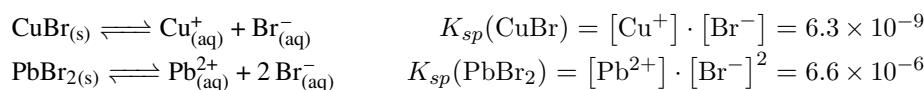


As we know the concentration of Cu^+ , and we have that the concentration of both ions is related by means of the solubility products constant, hence we can solve for the critical $[\text{I}^-]_c$ that would make CuI precipitate:

$$K_{sp} = [\text{Cu}^+] \cdot [\text{I}^-]_c = (0.1) \cdot [\text{I}^-]_c = 1.27 \times 10^{-12}$$

We have that $[\text{I}^-]_c = 1.27 \times 10^{-11}\text{M}$. Hence, Copper(I) iodide will precipitate when its concentration is larger than $1.27 \times 10^{-11}\text{M}$.

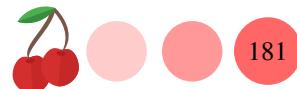
Selective precipitation When we have a mixture of different ions that form insoluble precipitates (e.g. Pb^{2+} and Cu^+ both form insoluble bromides) we can use the principles of selective precipitation to separate the ions. We know that PbBr_2 and CuBr are insoluble compounds. Let us say we have a mixture of both ions with 0.01M concentration, and we add a solution containing Br^- . As two different precipitates will form (CuBr and PbBr_2) the question is: are we going to be able to separate both compounds? Or the precipitation of both will overlap? If the concentration needed to precipitate both insoluble compounds is ten times different we will be able to selectively precipitate both compounds. Here we assume that the addition of the cation will not modify the volume of the mixture. We will calculate the amount solution added needed to precipitate each of the solids. Let us first address the expressions for the solubility product for each solid:



We will calculate the critical concentration of bromide $[\text{Br}^-]_c$ needed to precipitate each of the solids, first Copper(I) bromide:

$$K_{sp}(\text{CuBr}) = [\text{Cu}^+] \cdot [\text{Br}^-] = (0.01) \cdot [\text{Br}^-]_{c,\text{CuBr}} = 6.3 \times 10^{-9}$$

Solving for $[\text{Br}^-]_{c,\text{CuBr}}$ we have: $[\text{Br}^-]_{c,\text{CuBr}} = 6.3 \times 10^{-9} / 0.01 = 6.3 \times 10^{-7}\text{M}$ for the precipitation of CuBr . Now, we calculate the concentration of bromide needed to precipitate Lead(II) bromide: $[\text{Br}^-]_{c,\text{PbBr}_2}^2 = \frac{6.6 \times 10^{-6}}{0.01}$ hence $[\text{Br}^-]_{c,\text{PbBr}_2} = (\frac{6.6 \times 10^{-6}}{0.01})^{\frac{1}{2}} = 2.5 \times 10^{-2}\text{M}$ for PbBr_2 . Comparing both concentrations we have that the values are different enough so it would be feasible to separate both ions in solution. We will have to add $6.3 \times 10^{-3}\text{mL}$ of the solution to precipitate Copper(I) bromide and $2.5 \times 10^{-2}\text{mL}$ to precipitate Lead(II) bromide.



6.5 Solubility and K_{sp}

The solubility product is the equilibrium constant associated to the solubility equilibrium. At the same time, the solubility product constant is related to the solubility of the insoluble compound and the relationship is not direct. This section will cover how to express K_{sp} in terms of solubility, and at the same time, how to express solubility in terms of K_{sp} . Before that, we will start by addressing the idea of solubility.

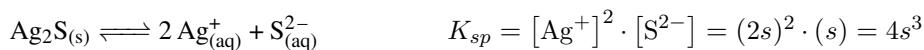
K_{sp} in terms of molar solubility The solubility product is directly related to molar solubility s . We will demonstrate how to obtain this relationship by means of three examples. First, the solubility product of AgCl is:



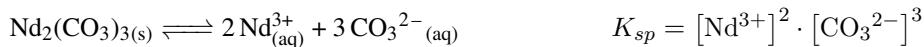
As the concentration of each ion, Ag^+ and Cl^- , is related to the molar solubility of the salt, we have

$$K_{sp} = [\text{Ag}^+] \cdot [\text{Cl}^-] = (s) \cdot (s) = s^2$$

Second, for silver sulfide, an insoluble compound with a more complex stoichiometry, we have:



Third, the solubility equilibrium and K_{sp} expression for $\text{Nd}_2(\text{CO}_3)_3$ is



As the ion concentrations are related to solubility, we have

$$K_{sp} = (2s)^2 \cdot (3s)^3 = 108s^5$$

K_{sp} in terms of molar solubility: general formula For any insoluble salt A_xB_y , we have that K_{sp} is related to s by means of a general formula:

$$K_{sp} = a \cdot s^b \quad (6.2)$$

where:

a is $x^x \cdot y^y$

b is $x + y$

For example, for Ba_1F_2 the constant a would be $1^1 \cdot 2^2$, that is four, whereas the constant b will be $1 + 2$ that equals to three. As such, the expression of K_{sp} in terms of s would be: $K_{sp} = 4s^3$. This approach is useful when we need to compute the solubility product constant given the molar solubility.

Sample Problem 79

Write down the relationship between K_{sp} and s for the following salts:
 $\text{Co}_3(\text{PO}_4)_2$ and HgS .

SOLUTION



We will use Equation 6.2. For the first salt, we have:

$$K_{sp}(\text{Co}_3(\text{PO}_4)_2) = (3^3 \cdot 2^2) \cdot s^{3+2} = 108 \cdot s^5$$

For the second salt:

$$K_{sp}(\text{HgS}) = (1^1 \cdot 1^1) \cdot s^{1+1} = s^2$$

◆ STUDY CHECK

Write down the relationship between K_{sp} and s for the following salts: Ag_2CO_3 and $\text{Fe}(\text{OH})_3$.

►Answer: $4s^3; 27s^4$

Molar solubility in terms of K_{sp} : general formula We previously explored the relationship between K_{sp} and molar solubility. Here we will explore the relationship between molar solubility and K_{sp} , simply solving for s in Equation 6.2. Again, for any insoluble salt A_xB_y , we have:

$$s = \left(\frac{K_{sp}}{a} \right)^{\frac{1}{b}} \quad (6.3)$$

where:

a is $x^x \cdot y^y$

b is $x + y$

For example, for Ba_1F_2 the constant a would be $1^1 \cdot 2^2$, that is four, whereas the constant b will be $1 + 2$ that equals to three. As such, the expression of s in terms of K_{sp} would be: $s = \left(\frac{K_{sp}}{4} \right)^{\frac{1}{3}}$. This approach is useful when the solubility product constant is given and we need to calculate the molar solubility. As the relation between molar solubility and K_{sp} is not a one-to-one relationship, K_{sp} are not directly related to solubility. For salts with a similar stoichiometry, it would be safe to compare solubilities in terms of K_{sp} . For example:

CuS	$K_{sp}=8 \times 10^{-37}$	$s = 6 \times 10^{-19}$
PbS	$K_{sp}=3 \times 10^{-28}$	$s = 1 \times 10^{-14}$
LiF	$K_{sp}=2 \times 10^{-3}$	$s = 3 \times 10^{-2}$

and we have that the lower K_{sp} the lower solubility. When the salt stoichiometry differs

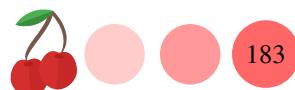
MgF_2	$K_{sp}=5 \times 10^{-11}$	$s = 2 \times 10^{-4}$
Li_3PO_4	$K_{sp}=2 \times 10^{-4}$	$s = 7 \times 10^{-2}$
Li_2CO_3	$K_{sp}=8 \times 10^{-4}$	$s = 6 \times 10^{-2}$

then an increase in K_{sp} does not necessarily follows an increase in solubility.

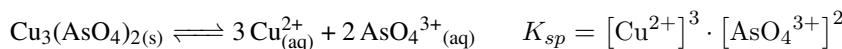
Sample Problem 80

The solubility product of Copper(II) arsenate $\text{Cu}_3(\text{AsO}_4)_2$ is 7.95×10^{-36} . Calculate the molar solubility of the salt.

SOLUTION



In order to calculate solubility, we will first break the salt down into its ions. Copper(II) arsenate contains Cu^{2+} ions and arsenate ions AsO_4^{3-} . The solubility dissociation is given by:



The molar concentration of copper and arsenate are related to solubility, taking into account the stoichiometric coefficients:

$$K_{sp} = [\text{Cu}^{2+}]^3 \cdot [\text{AsO}_4^{3-}]^2 = (3s)^3 \cdot (2s)^2 = 108s^5$$

As we know the value of the solubility product, we can solve for s :

$$7.95 \times 10^{-36} = 108s^5$$

Solving for s we have:

$$s^5 = \frac{7.95 \times 10^{-36}}{108} \text{ and } s = \sqrt[5]{\frac{7.95 \times 10^{-36}}{108}} = \left(\frac{7.95 \times 10^{-36}}{108}\right)^{\frac{1}{5}} = 3.7 \times 10^{-8} M$$

STUDY CHECK

The solubility product of Nickel(II) phosphate $\text{Ni}_3(\text{PO}_4)_2$ is 4.74×10^{-32} .

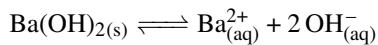
Calculate the molar solubility of the salt.

►Answer: $2.13 \times 10^{-7} M$

6.6 Solubility , PH and common ion effect

The solubility value of an insoluble compound refers to the amount of ions produced by an insoluble compound when dissolved in clean water. Instead of clean water, we can think of a solution containing ions. If the ions have no relation with the solubility equilibrium, the value of solubility in pure water and a solution with ions will be the same. Differently, if the solution contains ions involved in the equilibrium, those will impact solubility. In particular, solubility will be reduced. This effect is referred to as the common ion effect. For example, the solubility of PbCl_2 in pure water is $1.6 \times 10^{-2} M$. In contrast, the solubility in a $0.1M$ NaCl solution—a solution containing chloride a common ion—is $1.5 \times 10^{-3} M$. Similarly, the solubility in a $0.5M$ NaCl solution is $6.4 \times 10^{-5} M$. Some insoluble compounds have acid-base properties. For example, Mg(OH)_2 is an insoluble compound with basic character. This means that its solubility will be related to the OH^- of the solution. In acidic solutions, its solubility will increase, whereas in basic solutions its solubility will be reduced. For these types of chemicals, it is important to establish a relationship between PH and solubility.

Solubility and PH Some insoluble salts have acid-base character. For example, Ba(OH)_2 is an insoluble salt with basic character—since OH^- is a base—and FeF_2 is also a basic salt, as F^- is a moderately strong base resulting from the dissociation of HF, a weak acid. Therefore, for these salts, solubility is related to the PH. Only salts that result from weak acids or bases would have an acid-base character. For example, CaCO_3 or CuCN are all basic insoluble salts as carbonic acid and hydrocyanic acid are both weak acids. Let us calculate the PH of a Ba(OH)_2 solution. We have that the solubility equilibrium is given by



and K_{sp} is related to solubility s by means the following formula

$$K_{sp} = 4s^3$$

As the solubility product of Ba(OH)_2 is 2.5×10^{-4} we have that the solubility of the hydroxide is 0.04M. We have that the concentration of the ions in solution is related to solubility by

$$[\text{Ba}^{2+}] = s$$

$$[\text{OH}^-] = 2s$$

Hence we have that the PH is directly related to solubility

$$POH = -\log([\text{OH}^-]) = -\log(2s) = 1.09$$

and PH will be 12.9. For insoluble compounds with acid-base properties, PH affects solubility is affected by PH. In the example above, as Ba(OH)_2 is a basic compound, increasing PH towards even more basic values would impede the salt dissociation and hence decrease its solubility. Differently, decreasing PH would increase solubility as the amount of hydroxyls in solution would decrease and more hydroxyls would need to be formed.

Common ion effect Insoluble compounds dissociate to produce ions in solution. For example, a saturated AgCl solution will contain $1.3 \times 10^{-5}\text{M}$ - Ag^+ and Cl^- . By adding a chemical with a common ion (e.g. NaCl) into the solution we can decrease solubility as common ions will decrease the salt dissociation. Let us work on a problem: we want to calculate the solubility of AgCl in a 0.1M- NaCl solution given that $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$. In order to do this, we will first display the solubility equilibriu of the salt



The concentration of the different ions in solution are related to the salt solubility. However, as we now have a common ion (Cl^-), we should add this new concentration to the original solubility of the salt

$$[\text{Ag}^+] = s$$

$$[\text{Cl}^-] = 0.1 + s$$

Solving for s we have:

$$K_{sp} = [\text{Ag}^+] \cdot [\text{Cl}^-] = (s) \cdot (0.1 + s) = 1.8 \times 10^{-10}$$

that leads to a polynomial

$$s^2 + 0.1s - 1.8 \times 10^{-10} = 0$$

The new solubility value would be $1.8 \times 10^{-9}\text{M}$, lower than $1.8 \times 10^{-10}\text{M}$, the solubility for the salt in water.

6.7 Predicting precipitation from mixtures and solutions

At this point, we have used the solubility product to calculate the concentration of ions in a saturated solution of a solid. Imagine we have a solution containing a mixture of two different ions given that the ions in the solution can combine to form a precipitate. The question is, will a solid precipitate? Similar to the solubility product, we can use a construct called the concentration product to predict whether a mixture of ions will precipitate.



Predicting precipitation in ion mixtures: concentration product

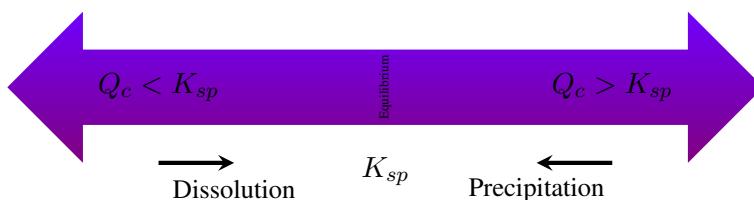
Let us analyze a situation in which we dissolve in water an insoluble compound such as lead(II) fluoride. The solubility products constant K_{sp} is just an equilibrium constant that describes the process of solubility, that is the dissolution of a solid. K_{sp} depends on the equilibrium concentration of the ions in solution. With equilibrium, we mean that the concentrations were measured after a long long time, so that the system has reached equilibrium. For example, K_{sp} for lead(II) fluoride is 3.3×10^{-8} and its mathematical expression is presented below



In the expression above, $[\text{Pb}^{2+}]$ represents the equilibrium concentration of ions Lead(II) and $[\text{F}^{-}]$ is the equilibrium concentration of fluoride. These concentrations result from dissolving the insoluble chemical in water. Let us now analyze a situation in which we have a mixture of ions containing 0.1M-Pb^{2+} ions and 0.1M-F^{-} . We want to assess if a precipitate will form, given that both ions can combine to produce lead(II) fluoride. To predict precipitation, we will use the reaction concentration product Q_c , and we will compare this product with the solubility product constant K_{sp} :

$$Q_c = [\text{Products}]_{\text{noneq}} \quad \text{concentration product} \quad (6.4)$$

A precipitate will appear only the computed Q_c value is larger than K_{sp} . In other words, mixtures of solutions more concentrated than the compound's solubility will precipitate, whereas less concentrated mixtures will not.



You might have noticed that K_{sp} and Q_c have a very similar formula. The difference beholds on the nature of the concentrations included in each of the formulas. K_{sp} includes *equilibrium* concentration, that is concentrations resulting of the slow dissolution of an insoluble compound measured after a long time, whereas Q_c includes *nonequilibrium* concentrations resulting of artificially preparing and quickly mixing ion solutions. For the example we are considering, after mixing a 0.1M-Pb^{2+} solution and a 0.1M-F^{-} solution, we have that Q_c is larger than K_{sp} and therefore a precipitate will form:

$$Q_c = [\text{Pb}^{2+}]_{\text{noneq}} \cdot [\text{F}^{-}]_{\text{noneq}}^2 = 0.1 \cdot 0.1^2 = 1 \times 10^{-3} > K_{sp} = 3.3 \times 10^{-8}$$

hence (\downarrow)

Imaging that we mix now a 10^{-3}M-Pb^{2+} solution and a 10^{-3}M-F^{-} solution. For this case, we have that Q_c is smaller than K_{sp} and therefore no precipitate will form:

$$Q_c = [\text{Pb}^{2+}]_{\text{noneq}} \cdot [\text{F}^{-}]_{\text{noneq}}^2 = 10^{-3} \cdot (10^{-3})^2 = 10^{-9} < K_{sp} = 3.3 \times 10^{-8}$$

hence ($\cancel{\downarrow}$)



Sample Problem 81

Predict if a precipitate will form in any of the following mixtures: (a) $[Cu^+] = 10^{-6} M$ and $[I^-] = 10^{-7} M$ given that $K_{sp}(CuI) = 1.27 \times 10^{-12} M$
 (b) $[Cd^{2+}] = 0.5 M$ and $[F^-] = 0.5 M$ given that $K_{sp}(CdF_2) = 6.44 \times 10^{-3} M$

SOLUTION

We will calculate Q_c for each of the mixtures and we will compare the value with K_{sp} . Q_c values larger than K_{sp} will produce a precipitate, whereas Q_c values smaller than K_{sp} will not produce a precipitate. For the first mixture, we have that:

$$Q_c(CuI) = [Cu^+]_{noneq} \cdot [I^-]_{noneq} = (10^{-6}) \cdot (10^{-7}) = 10^{-13} < K_{sp}(CuI)$$

Therefore in the first mixture no precipitate will form. For the second mixture:

$$Q_c(CdF_2) = [Cd^{2+}]_{noneq} \cdot [F^-]_{noneq}^2 = (0.5) \cdot (0.5)^2 = 3.1 \times 10^{-2} > K_{sp}(CdF_2)$$

Therefore in the second mixture a precipitate will form.

◆ STUDY CHECK

Predict if a precipitate will form in a mixtures of $[Li^+] = 10^{-1} M$ and $[CO_3^{2-}] = 10^{-1} M$ given that $K_{sp}(Li_2CO_3) = 8.15 \times 10^{-4} M$

►Answer: yes

Predicting precipitation from mixing solutions Let us now analyze a situation in which we mix two different solutions, 5mL of a solution containing 0.1M $Pb(NO_3)_2$ and 6mL of a solution containing 0.01M NaF. Assuming that liquid volume can be added, we would like to know whether lead(II) fluoride would precipitate. To answer this question, we need to calculate the concentration of lead(II) and of fluoride in the resulting mixture. With this information, we could compute the ion product and compare this value with the solubility product (3.3×10^{-8}). We will first calculate the concentration of lead(II) produced from $Pb(NO_3)_2$, given that the salt dissociates giving one lead cation and two nitrate anions:

$$[Pb^{2+}] = \frac{0.1M \cdot 5mL}{11mL} = 4.5 \times 10^{-2} M$$

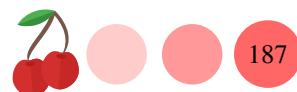
and then calculate the fluoride concentration produced from NaF, given that the salt dissociates giving one sodium cation and one fluoride anion:

$$[F^-] = \frac{0.01M \cdot 6mL}{11mL} = 5.4 \times 10^{-3} M$$

With these two concentrations, we can compute the ion product Q_c and compare it with K_{sp} :

$$\begin{aligned} Q_c &= [Pb^{2+}]_{noneq} \cdot [F^-]_{noneq}^2 = (4.5 \times 10^{-2}) \cdot (5.4 \times 10^{-3})^2 = \\ &= 1.3 \times 10^{-6} > K_{sp} = 3.3 \times 10^{-8} \text{ hence } (\downarrow) \end{aligned}$$

Based on this comparison, we can predict that after mixing the two solutions PbF_2 will precipitate.



Sample Problem 82

Predict if a $\text{Cu}_3(\text{AsO}_4)_2$ precipitate will form after mixing 10mL of a 10^{-9}M Na_3AsO_4 with 10mL of a 10^{-10}M CuCl_2 , given that $K_{sp}(\text{Cu}_3(\text{AsO}_4)_2)=8 \times 10^{-36}$.

SOLUTION

We will first calculate the concentration of Cu^{2+} resulting from mixing 10mL of a 10^{-10}M CuCl_2 with 10mL of another solution:

$$[\text{Cu}^{2+}] = \frac{10^{-10}\text{M} \cdot 10\text{mL}}{20\text{mL}} = 5 \times 10^{-11}\text{M}$$

and then calculate the concentration of AsO_4^{3-} resulting from mixing 10mL of a 10^{-9}M Na_3AsO_4 with 10mL of another solution:

$$[\text{AsO}_4^{3-}] = \frac{10^{-9}\text{M} \cdot 10\text{mL}}{20\text{mL}} = 5 \times 10^{-10}\text{M}$$

We can now calculate the ion product and compare it with the solubility product:

$$\begin{aligned} Q_c &= [\text{Cu}^{2+}]_{noneq}^3 \cdot [\text{AsO}_4^{3-}]_{noneq}^2 = (5 \times 10^{-11})^3 \cdot (5 \times 10^{-10})^2 = \\ &= 3.3 \times 10^{-50} < K_{sp} = 8 \times 10^{-36} \text{ hence } (\downarrow) \end{aligned}$$

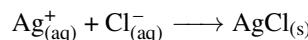
The insoluble salt will not precipitate.

◆ STUDY CHECK

Predict if a FeCO_3 precipitate will form after mixing 4mL of a 10^{-6}M FeSO_4 with 5mL of a 10^{-6}M Na_2CO_3 , given that $K_{sp}(\text{FeCO}_3)=3 \times 10^{-11}$.

►Answer: no precipitate

Predicting the amount of precipitate formed A precipitate can form when mixing two solutions containing specific ions. For example, AgCl is an insoluble compound. A precipitate will form if you mix solutions of AgNO_3 and NaCl . In these chemicals, Ag^+ and Cl^- are directly involved in the precipitate formation, whereas NO_3^- and Na^+ are spectators. In this section, we will cover how to compute the amount of precipitate formed and the concentration of the leftover ions that will contribute to reduce the solubility of the solid, in comparison to plain water. We will leave aside the spectator ions knowing that they will remain in solution and we will focus mainly on the ions involved in the precipitate. Let us consider the situation in which we mix 5mL of 0.01M- AgNO_3 with 6mL of 0.005M- NaCl . In order to determine the amount of precipitate formed, we will first set up the precipitation reaction:



Then, we will identify the limiting reactant by comparing the moles of ions reacting. We will calculate the moles of Ag^+ by computing the moles of silver(I) coming from AgNO_3 —when multiplying volume by molarity we obtain milimoles:

$$n^{\text{Ag}^+} = 5\text{mL} \cdot 0.01\text{M} = 5 \times 10^{-2}\text{mmol}$$

We will now calculate the number of moles of chloride:

$$n^{\text{Cl}^-} = 6\text{mL} \cdot 0.005\text{M} = 3 \times 10^{-2}\text{mmol}$$



We have that in order to react with the amount of Ag^+ in the mixture, we would need $n^{\text{Cl}^-} = 5 \times 10^{-2}$ mmol and we only have 3×10^{-2} mmol of chloride, hence chloride is the limiting reagent and the leftovers will be:

$$n_{\text{left}}^{\text{Ag}^+} = 5 \times 10^{-2} - 3 \times 10^{-2} = 2 \times 10^{-2} \text{ mmol}$$

The number of moles of precipitate formed will be given by:

$$n^{\text{AgCl}} = 3 \times 10^{-2} \text{ mmol of Cl}^- \times \frac{1 \text{ mol of AgCl}}{1 \text{ mol of Cl}^-} = 3 \times 10^{-2} \text{ mmol of AgCl}$$

When AgCl forms at the same time there will be silver(I) ion leftovers. We will finally calculate the concentration of the leftover ion simply by dividing the leftover moles by the overall volume of the mixture—mind we mix two different volumes assuming liquid volumes can be added:

$$c_{\text{left}}^{\text{Ag}^+} = \frac{n_{\text{left}}^{\text{Ag}^+}}{V} = \frac{2 \times 10^{-2} \text{ mmol}}{(5 + 6) \text{ mL}} = 1.8 \times 10^{-3} \text{ M}$$

The ions Silver(I) is a common ion that will affect the solubility of silver chloride, in fact reducing its value:

$$K_{sp} = [\text{Ag}^+] \cdot [\text{Cl}^-] = (s + c_{\text{left}}^{\text{Ag}^+}) \cdot (s) = 1.8 \times 10^{-10}$$

that leads to a polynomial

$$s^2 + c_{\text{left}}^{\text{Ag}^+} \cdot s - 1.8 \times 10^{-10} = 0$$

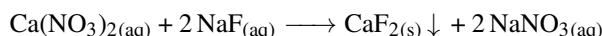
Solving for s given that $c_{\text{left}}^{\text{Ag}^+} = 1.8 \times 10^{-3} \text{ M}$ we have that $s = 1.0 \times 10^{-7} \text{ M}$, lower than the solubility of silver chloride in water ($1.3 \times 10^{-5} \text{ M}$).

Sample Problem 83

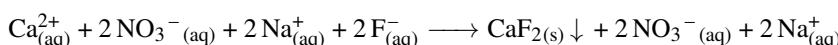
A mixture is prepared by adding 100mL of 0.01M- CaNO_3 with 50mL of 0.02M- NaF . Calculate the number of moles of CaF_2 that precipitate— CaF_2 is insoluble—and the concentration of the leftover ion in solution.

SOLUTION

The following reaction takes place:



Given that CaF_2 precipitates, we will have the following ions in the solution:



The spectators will be NO_3^- and Na^+ , whereas Ca^{2+} and F^- are involved in the precipitation reaction. We will first calculate the number of moles the ions involved in the precipitation

$$n^{\text{Ca}^{2+}} = 100 \text{ mL} \cdot 0.01 \text{ M} = 1 \text{ mmol} \quad \text{and} \quad n^{\text{F}^-} = 50 \text{ mL} \cdot 0.02 \text{ M} = 1 \text{ mmol}$$

to then identify the limiting reagent, calculating the number of moles needed to react with 1mmol of Ca^{2+}

$$n_{\text{needed}}^{\text{F}^-} = 1 \text{ mmol of Ca}^{2+} \times \frac{2 \text{ mol of F}^-}{1 \text{ mol of Ca}^{2+}} = 2 \text{ mmol of F}^-$$

As we will need 2-mmol of F^- but we only have 1-mmol, F^- will limit the precipitation whereas Ca^{2+} will be in excess. We will base our calculations on



F^- to predict the moles of precipitate formed

$$n^{\text{CaF}_2} = 1\text{mmol of F}^- \times \frac{1\text{mol of CaF}_2}{2\text{mol of F}^-} = 0.5\text{mmol of CaF}_2$$

and the leftover moles of Ca^{2+} , given that we have 1mmol of Ca^{2+} and we need

$$n^{\text{Ca}^{2+}}_{\text{needed}} = 1\text{mmol of F}^- \times \frac{1\text{mol of Ca}^{2+}}{2\text{mol of F}^-} = 0.5\text{mmol of Ca}^{2+}$$

the leftovers will be 0.5mmol. Finally, we can calculate the concentration of leftover ions by doing

$$[\text{Ca}^{2+}] = \frac{n^{\text{Ag}^+}_{\text{left}}}{V} = \frac{0.5\text{mmol}}{(50 + 100)\text{mL}} = 3.3 \times 10^{-3}\text{M}$$

The solubility of CaF_2 in the solution with leftover calcium would be 0.11M, lower than the one in water (0.12M). **STUDY CHECK**

A mixture is prepared by adding 50mL of 0.03M- GaCl_3 with 75mL of 0.05M- NaOH . Calculate the number of moles of Ga(OH)_3 that precipitate and the concentration of the leftover ion in solution.

►Answer: 1.25mmol; $2 \times 10^{-3}\text{M}$



CHAPTER 6

SOLUBILITY

6.1 The solubility of AlNO_3 is 82 g/100mL at 30°C expressed with respect to the solvent. Calculate the grams of solute that can be dissolved in 5mL of water.

6.2 The solubility of ammonium chlorate NH_4ClO_4 is 96 g/100mL at 50°C expressed with respect to the solvent. Calculate the liters of water needed to dissolve 1 gram of ammonium chlorate.

6.3 The solubility of an insoluble solute is 25 g/L at 25°C expressed with respect to the solution. Calculate the milliliters of solution needed to dissolve 5 grams of solute.

6.4 The solubility of an insoluble solute is 100 g/L at 20°C expressed with respect to the solution. Calculate the milliliters of solution needed to dissolve 10 grams of solute.

6.5 The solubility of an insoluble solute is 4mol/L at a given temperature expressed with respect to the solution. Calculate the moles of solute dissolved in 100mL of solution.

6.6 The molar solubility of silver carbonate is $1.3 \times 10^{-4}\text{mol/L}$ at 20°C . Calculate the moles of solute dissolved in 25mL of solution.

6.7 The molar solubility of zinc hydroxide ($\text{MW}=99.4\text{g/mol}$) is $4.6 \times 10^{-6}\text{mol/L}$ at 20°C . Express this value in grams per liter.

6.8 The molar solubility of lead(II) fluoride ($\text{MW}=254.2\text{g/mol}$) is 0.56g/L at 20°C . Express this value in moles per liter.

SOLUBILITY EQUILIBRIUM

6.9 Write down the solubility equilibrium for the following chemicals: (a) CuCl (b) Iron(II) sulfide (c) CuS

6.10 Write down the solubility equilibrium for the following chemicals: (a) Mercury(II) sulfide (b) AlPO_4 (c) Manganese(II) sulfide

6.11 Write down the solubility equilibrium for the following chemicals: (a) Beryllium hydroxide (b) $\text{Ba}(\text{BrO}_3)_2$ (c) Lead(II) iodide

6.12 Write down the solubility equilibrium for the following chemicals: (a) SrSO_4 (b) Silver(I) chromate (c) $\text{Sr}(\text{IO}_3)_2$

6.13 Write down the relationship between solubility s and the ionic concentration for the following insoluble compounds: (a) NiCO_3 (b) $\text{Ra}(\text{IO}_3)_2$ (c) FeF_2

6.14 Write down the relationship between solubility s and the ionic concentration for the following insoluble compounds: (a) $\text{Al}(\text{OH})_3$ (b) $\text{Mn}(\text{IO}_3)_2$ (c) BaMoO_4

SOLUBILITY PRODUCT

6.15 Write down the solubility product in terms of the molarities of the ions in solution for the following chemicals: (a) CuCl (b) FeS (c) MnS

6.16 Write down the solubility product in terms of the molarities of the ions in solution for the following chemicals: (a) MgCO_3 (b) PbCrO_4 (c) TlBr

6.17 Write down the solubility product in terms of the molarities of the ions in solution for the following chemicals: (a) ScF_3 (b) NiS (c) HgI_2

6.18 Write down the solubility product in terms of the molarities of the ions in solution for the following chemicals: (a) $\text{Co}_3(\text{PO}_4)_2$ (b) Fe(OH)_3

PREDICTING PRECIPITATION

6.19 A solution has a 0.1M concentration of Na_2CO_3 . Calculate the concentration of a $\text{Ba}(\text{NO}_3)_2$ solution needed to precipitate BaCO_3 . $K_{sp}(\text{BaCO}_3) = 2.6 \times 10^{-9}$.



6.20 A solution has a 0.001M concentration of $\text{Mn}(\text{NO}_3)_2$. Calculate the concentration of a Na_2CO_3 solution needed to precipitate MnCO_3 . $K_{sp}(\text{MnCO}_3) = 2.2 \times 10^{-11}$.

6.21 We have a mixture of $\text{Cd}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ containing a 0.01M concentration of both compounds. We gradually add a 0.01M Na_3PO_4 solution. Indicate if we would be able to separate both cations using fractional precipitation. $K_{sp}(\text{Cd}_3(\text{PO}_4)_3) = 2.5 \times 10^{-33}$ and $K_{sp}(\text{Ca}_3(\text{PO}_4)_3) = 2.1 \times 10^{-33}$.

6.22 We have a mixture of $\text{Ba}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ containing a 0.001M concentration of both compounds. We gradually add a 0.01M Na_2SO_4 solution. Indicate if we would be able to separate both cations using fractional precipitation. $K_{sp}(\text{Ba}_2(\text{SO}_4)_3) = 1.1 \times 10^{-10}$ and $K_{sp}(\text{Ca}_2(\text{SO}_4)_3) = 2.1 \times 10^{-33}$.

SOLUBILITY AND K_{sp}

6.23 For the following compounds, indicate the expression of K_{sp} in terms of solubility: (a) BaCO_3 (b) Calcium fluoride (c) Fe(OH)_3 (d) Cobalt(II) arsenate (e) CdS

6.24 For the following compounds, indicate the expression of K_{sp} in terms of solubility: (a) MnCO_3 (b) Scandium(III) hydroxide (c) Copper(I) oxide (d) PbF_2 (e) Iron(II) fluoride

6.25 For the following compounds, indicate the expression of K_{sp} in terms of solubility: (a) $\text{Cd}_3(\text{PO}_4)_2$ (b) Mercury(II) sulfide (c) Calcium phosphate

6.26 For the following compounds, indicate the expression of K_{sp} in terms of solubility: (a) Al(OH)_3 (b) Scandium(III) fluoride (c) $\text{Cd}_3(\text{AsO}_4)_2$

6.27 For the following compounds, calculate s using the given information: (a) CdS given that its $K_{sp} = 1.00 \times 10^{-27}$ (b) Cobalt(II) carbonate given that its $K_{sp} = 1.00 \times 10^{-10}$ (c) CuCN given that its $K_{sp} = 3.47 \times 10^{-20}$ (d) Copper(II) sulfide given that its $K_{sp} = 8.00 \times 10^{-37}$

6.28 For the following compounds, calculate s using the given information: (a) FeS given that its $K_{sp} = 8.00 \times 10^{-19}$ (b) Lead(II) carbonate given that its $K_{sp} =$

3×10^{-13} (c) PbSO_4 given that its $K_{sp} = 2.53 \times 10^{-8}$ (d) Magnesium carbonate given that its $K_{sp} = 6.82 \times 10^{-6}$

6.29 Calculate K_{sp} the following compounds:

(a) BaSeO_4 given that $s = 1.84 \times 10^{-04}$ (b) CdF_2 given that $s = 1.10 \times 10^{-01}$ (c) BaCO_3 given that $s = 5.01 \times 10^{-05}$

6.30 Calculate K_{sp} the following compounds:

(a) Ag_2CO_3 given that $s = 1.28 \times 10^{-04}$ (b) AlPO_4 given that $s = 9.92 \times 10^{-11}$ (c) Ag_2S given that $s = 1.26 \times 10^{-17}$

SOLUBILITY , PH AND COMMON ION EFFECT

6.31 Calculate the PH of a saturated solution of the following compounds: (a) Al(OH)_3 given that $K_{sp} = 3.0 \times 10^{-34}$. (b) Be(OH)_2 given that $K_{sp} = 6.92 \times 10^{-22}$. (c) Cd(OH)_2 given that $K_{sp} = 7.20 \times 10^{-15}$.

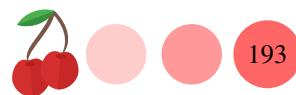
6.32 Calculate the PH of a saturated solution of the following compounds: (a) Ca(OH)_2 given that $K_{sp} = 5.02 \times 10^{-6}$. (b) Cu(OH)_2 given that $K_{sp} = 4.80 \times 10^{-20}$. (c) Fe(OH)_2 given that $K_{sp} = 4.87 \times 10^{-17}$.

6.33 Calculate the solubility of a saturated solution of the following compounds: (a) Fe(OH)_3 buffered at PH=6.00, given that $K_{sp} = 2.79 \times 10^{-39}$. (b) Pb(OH)_2 buffered at PH=8.00, given that $K_{sp} = 1.43 \times 10^{-20}$. (c) Mg(OH)_2 buffered at PH=5.00, given that $K_{sp} = 5.61 \times 10^{-12}$.

6.34 Calculate the solubility of a saturated solution of the following compounds: (a) Zn(OH)_2 buffered at PH=7.00, given that $K_{sp} = 3 \times 10^{-17}$. (b) Sn(OH)_2 buffered at PH=8.50, given that $K_{sp} = 5.45 \times 10^{-27}$. (c) Ni(OH)_2 buffered at PH=6.50, given that $K_{sp} = 5.48 \times 10^{-16}$.

6.35 Indicate if the solubility of the following compounds will be affected by the PH (a) BaCO_3 (b) BaSO_4 (c) CuCN (d) MnS

6.36 Indicate if the solubility of the following compounds will be affected by the PH (a) Zn(OH)_2 (b) Al(OH)_3 (c) AlCl_3 (d) AgF



6.37 Calculate the solubility for the following conditions: (a) a saturated solution of FeCO_3 on water given that $K_{sp} = 3.13 \times 10^{-11}$ (b) a saturated solution of FeCO_3 on a Na_2CO_3 0.1M solution given that $K_{sp} = 3.13 \times 10^{-11}$ (c) a saturated solution of FeCO_3 on a $\text{Fe}(\text{NO}_3)_2$ 0.1M solution given that $K_{sp} = 3.13 \times 10^{-11}$

6.38 Calculate the solubility for the following conditions: (a) a saturated solution of PbBr_2 on water given that $K_{sp} = 6.60 \times 10^{-6}$ (b) a saturated solution of PbBr_2 on a $\text{Pb}(\text{NO}_3)_2$ 0.1M solution given that $K_{sp} = 6.60 \times 10^{-6}$ (c) a saturated solution of PbBr_2 on a NaBr 0.1M solution given that $K_{sp} = 6.60 \times 10^{-6}$

6.39 Calculate the solubility for the following conditions: (a) a saturated solution of AgI on water given that $K_{sp} = 8.52 \times 10^{-17}$ (b) a saturated solution of AgI on a AgNO_3 0.2M solution given that $K_{sp} = 8.52 \times 10^{-17}$ (c) a saturated solution of AgI on a NaCl 0.3M solution given that $K_{sp} = 8.52 \times 10^{-17}$

6.40 Calculate the solubility for the following conditions: (a) a saturated solution of AgCl on water given that $K_{sp} = 1.77 \times 10^{-10}$ (b) a saturated solution of AgCl on a AgNO_3 0.1M solution given that $K_{sp} = 1.77 \times 10^{-10}$ (c) a saturated solution of AgCl on a NaCl 0.5M solution given that $K_{sp} = 1.77 \times 10^{-10}$

PREDICTING PRECIPITATION FROM MIXTURES AND SOLUTIONS

6.41 Predict whether CdF_2 will precipitate in the following mixtures given that $K_{sp} = 6.44 \times 10^{-3}$: (a) A mixture containing $[\text{Cd}^{2+}] = 1 \times 10^{-1}\text{M}$ and $[\text{F}^-] = 1 \times 10^{-1}\text{M}$ (b) A mixture containing $[\text{Cd}^{2+}] = 1 \times 10^{-1}\text{M}$ and $[\text{F}^-] = 1 \times 10^{-2}\text{M}$ (c) A mixture containing $[\text{Cd}^{2+}] = 1 \times 10^{-2}\text{M}$ and $[\text{F}^-] = 1 \times 10^{-2}\text{M}$

6.42 Predict whether CuCl will precipitate in the following mixtures given that $K_{sp} = 1.7 \times 10^{-7}$: (a) A mixture containing $[\text{Cu}^+] = 1 \times 10^{-3}\text{M}$ and $[\text{Cl}^-] = 1 \times 10^{-3}\text{M}$ (b) A mixture containing $[\text{Cu}^+] = 1 \times 10^{-4}\text{M}$ and $[\text{Cl}^-] = 1 \times 10^{-4}\text{M}$ (c) A mixture containing $[\text{Cu}^+] = 1 \times 10^{-5}\text{M}$ and $[\text{Cl}^-] = 1 \times 10^{-3}\text{M}$

6.43 Indicate whether a precipitation will form when mixing the following solutions given that K_{sp} for $\text{Ni}(\text{IO}_3)_2$ is 4.7×10^{-5} : (a) 10mL of a 0.1M-NiCl so-

lution and 10mL of a 0.1M- NaIO_3 solution (b) 10mL of a 0.1M-NiCl solution and 20mL of a 0.1M- NaIO_3 solution (c) 10mL of a 0.01M-NiCl solution and 20mL of a 0.01M- NaIO_3 solution

6.44 Indicate whether a precipitation will form when mixing the following solutions given that K_{sp} for FeF_2 is 2.4×10^{-6} : (a) 1mL of a 0.1M- $\text{Fe}(\text{NO}_3)_2$ solution and 1mL of a 0.1M-NaF solution (b) 1mL of a 0.01M- $\text{Fe}(\text{NO}_3)_2$ solution and 1mL of a 0.1M-NaF solution (c) 1mL of a 0.01M- $\text{Fe}(\text{NO}_3)_2$ solution and 1mL of a 0.01M-NaF solution

6.45 Answer the following questions: (a) Compute the concentration of AgNO_3 needed to precipitate AgCl in a 0.01M NaCl solution given that $K_{sp} = 1.77 \times 10^{-10}$ (b) Compute the concentration of Na_2CO_3 needed to precipitate Ag_2CO_3 in a 0.001M AgNO_3 solution given that $K_{sp} = 8.46 \times 10^{-12}$

6.46 Answer the following questions: (a) Compute the concentration of NaOH needed to precipitate $\text{Sc}(\text{OH})_3$ in a 0.02M $\text{Sc}(\text{NO}_3)_3$ solution given that $K_{sp} = 2.22 \times 10^{-31}$ (b) Compute the concentration of $\text{Mg}(\text{NO}_3)_2$ needed to precipitate $\text{Mg}_3(\text{PO}_4)_2$ in a 0.0001M K_3PO_4 solution given that $K_{sp} = 1.04 \times 10^{-24}$

6.47 We add 5mL of a 0.01M AgNO_3 solution to 15mL of a 0.01M KI solution and a precipitate form. Indicate the equilibrium concentration of silver and iodide ions given $K_{sp}(\text{AgI}) = 8.52 \times 10^{-17}$.

6.48 We add 50mL of a 0.02M $\text{Ni}(\text{NO}_3)_2$ solution to 15mL of a 0.01M KIO_3 solution and a precipitate form. Indicate the leftover concentration of ions and the equilibrium concentration of nickel(II) and iodate ions given $K_{sp}(\text{Ni}(\text{IO}_3)_2) = 4.71 \times 10^{-5}$.



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Ch. 7. Entropy and free energy

It is common sense that some natural phenomena happen spontaneously in nature, without any help, in nature whereas others do not. For example, one would expect a ball on a hill to roll down instead of rolling up. How does common sense apply in chemistry? Why some reactions happen spontaneously whereas others do not. For example, methane (CH_4) spontaneously burns with oxygen (O_2), producing carbon dioxide, and water. Differently, if we mix water and carbon dioxide, CH_4 is not spontaneously produced. Thermodynamics helps make sense of spontaneity in physics and chemistry. In particular, three thermodynamic properties—enthalpy, entropy, and Gibbs free energy—are commonly used to predict different aspects of spontaneity. At the same time, spontaneity in chemistry is indeed related to equilibrium and these properties can be translated into equilibrium constants.

7.1 Spontaneity

Chemical kinetics is a discipline that deals with the pace of chemical reactions by using activation energies, concentrations, and temperatures. It also deals with the different pathways of reaction. However, chemical kinetics does not provide information about the reasons why chemical reactions happen. Thermodynamics informs about the direction in which a chemical reaction occurs spontaneously and the reasons for this reaction to happen, without informing about the speed at which the process occurs. It uses thermodynamic functions—enthalpies, entropies, and Gibbs free energies—to understand the factors that favor the spontaneity of a reaction. Overall, kinetics and thermodynamics are complementary disciplines in chemistry as it is convenient to gain insight into the pace and spontaneity of chemical reactions.

Spontaneity A spontaneous process happens naturally, without any help or external input. For example, ice spontaneously melts at room temperature, without any help. Still, spontaneity happens under a certain set of conditions. For example, ice melts at room temperature but does not melt at -5°C , as the process in these conditions is not spontaneous. Other spontaneous processes are the rusting of iron at room temperature, or the freezing of water below 0°C . Spontaneous processes have a natural tendency to occur. Still, this tendency might not be actualized in practice. At the same time, this natural tendency to occur is not linked in any way to the speed or rate of the process. For example, diamonds have a natural tendency to become graphite. Still, the rate of this change is so slow that in human years it does never occur. Remember that thermodynamics addresses spontaneity whereas kinetics address the rate of occurrence of a process.



7.2 Entropy

Entropy, represented with an S , refers to the spreading of energy and composition of a system. Energy and matter have the tendency to spread and this spreading is represented by entropy. Think about a glass full of hot water and how water is going to spontaneously cool down, as the energy spreads between the glass and its environment. Similarly, think about a gas container opened in vacuum, and how gas molecules spontaneously will leave the container and spread out. Overall, entropy has a macroscopic and microscopic description, with these two descriptions converging into a cohesive concept.

The meaning of Entropy, S Entropy is represented with the letter S . Qualitatively, it is a measure of the spreading in space of the energy of a system, or simply the system. For example, in a glass full of hot water, the energy is concentrated in the glass as the water molecules initially have high thermal energy. With time, the system evolves naturally so that heat spreads between the room and the container. The initial state (glass with hot water) has lower entropy than the final state (glass with thermalized water). Another example, think about a concentrated solution separated from a more diluted system by means of a membrane. Initially, the entropy of the system is low, as one side of the container has a high density of molecules whereas the other side has a lower density. As the molecules diffuse and the concentration equalizes. In this case, the entropy of the initial state (a concentrated and a diluted solution) is lower than the entropy of the final system (two solutions of equal concentration). These two examples represent how energy and matter spread as entropy increases in spontaneous processes. On one hand, entropy, just like enthalpy, is a *state function* in thermodynamics which means that the change of entropy of a system when going from an initial into a final state is independent of the path taken to arrive from the initial into the final state. On the other hand, entropy is an *extensive property* that depends on the size of the system and for example the entropy change when heating 2 moles of gas is larger than when heating 1 mole of gas.

A macroscopic description of entropy Overall an entropy change is associated with the flow of heat. The change of entropy associated with the heat flow, at constant temperature, can be computed using the expression below, called generalized Clausius relation:

$$\Delta S = \frac{q}{T} \quad (7.1)$$

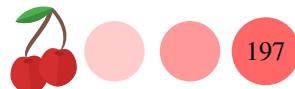
where:

ΔS is the entropy change

q is the reversible heat transferred

T is the absolute temperature (in K)

This expression refers to q that is the heat enhanced reversibly, exchanging heat in very tinny bits so that the temperature does not change significantly. The larger the heat exchanges the larger the entropy change. At the same time, a larger entropy change will be associated with the heat exchange at low temperatures than at high temperatures. The entropy change resulting from a heat flow can be referred to as *thermal entropy*. Formula 7.1 is one of the ways to mathematically describe the *second law of thermodynamics* that says that a system and its surroundings—an isolated system—evolve spontaneously increasing its overall entropy.



Sample Problem 84

We warm up a cup of vegetable oil in the microwave, at low power and for a long time, giving 40KJ of heat to the oil. Calculate the entropy change experienced by the oil at 30°C.

SOLUTION

We will calculate the thermal entropy by means of Clausius' relation given that the heat is 40000J and the fixed temperature is $30 + 273 = 303\text{K}$. Remember as the oil (this is the system under study) receives heat the numerical value of heat of positive and also we need absolute temperature in Clausius' relation. We finally have that:

$$\Delta S = \frac{q}{T} = \frac{40000}{303} = 132\text{J/K}$$

As a final comment, mind that the heat exchange has happened reversibly as they point the microwave functions at a low power and for a low time.

◆ STUDY CHECK

We cool down a cup of vegetable oil with a water bath, so that the oil releases 20KJ of heat to the bath. Calculate the entropy change experienced by the oil at 40°C.

►Answer: 63.9J/K

A microscopic description of entropy A mathematical or molecular level description of entropy was suggested by Ludwig Boltzmann. Entropy depends on the number of energetically equivalent microstates, that is, the number of different ways in which a system existing in a given state can be arranged. The Boltzmann formula for entropy is:

$$S = k_B \ln(W) \quad (7.2)$$

where:

S is the entropy of a system

k_B is the Boltzmann constant ($1.381 \times 10^{-23} \text{ J/K}$)

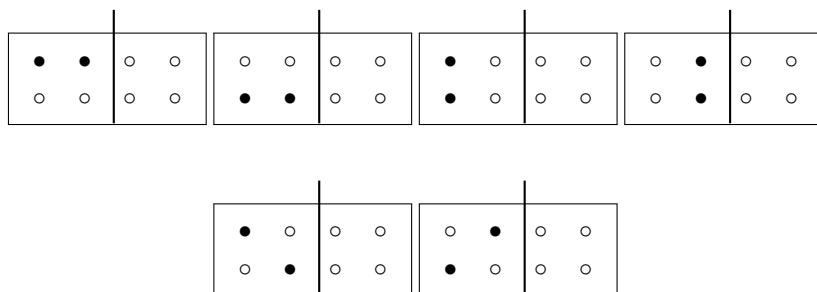
W is the number of microstates

The Boltzmann's constant results from statistical thermodynamics–probabilistic thermodynamics–being related to the ideal gas constant through $R = N_A \cdot k_B$, with N_A Avogadro's number. At the same time, W is the number of microstates of the system that is the number of different ways in which the particles of a system can be differently arranged for a given energy. Hence the molecular-level description of entropy is closely related to probability and we may imagine that the system exists in numerous microstates of short existence. When measuring the system we are indeed measuring a time average of the properties of the different microstates. The larger the number of microstates—the more ways a particular state can be achieved—the most probable the configuration—the greater is the likelihood of finding that state.

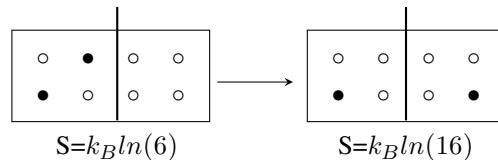
Let us analyze an example to describe the meaning of microstate and the use of Boltzmann entropy. Imagine a box with two identical ideal-gas particles and two compartments. In each compartment, the particles can occupy four different locations, with two locations on the top part of the compartment and two locations on the bottom part. Each of the particle arrangements would be a microstate. Let us now analyze the



number of equivalent microstates when the box is closed so that the particles cannot jump into the other compartment. Below are all possible microstates for this scenario:



The number of different arrangements represented above is $X=6$, and the entropy associated with this system would be $k_B \ln(6)$ that is 2.5×10^{23} J/K. Now, if we open the separation between the two compartments so that the molecules can freely move from one compartment to the other, the number of microstates increases considerably. We would have three different scenarios: (1) the scenario in which the particles stay in the left compartment, (2) the scenario in which the particles stay in the right compartment, (3) the scenario in which the particles are spread between both compartments. What situation do you think is more feasible? In particular, we have a set of six configurations in which both particles populate the left compartment and a set of six configurations in which both particles populate the right compartment. The entropy for these two scenarios is $k_B \ln(6)$. We would also have a set of 16 configurations in which each particle populates a different compartment. The entropy for these two scenarios is $k_B \ln(16)$. The Boltzmann formula suggests that the most feasible scenario, the scenario with higher entropy, corresponds to the spreading of particles between both compartments. As we will see along the chapter, the situation in which each particle populates a different compartment has larger entropy and hence it would be the most probable scenario.



The calculation of different microstates come from the close study of the situation in hand. In the scenario described above, we had two compartments and four possible locations. Each molecule had a single state or orientation. One can also find the case that the molecules have several states. For example, CO molecules can be found in two different orientations when an external field is applied. In the case of multiple molecular arrangements it is convenient to use the formula below:

$$W = A^N \quad (7.3)$$

where:

A is the number of molecular states

W is the number of microstates

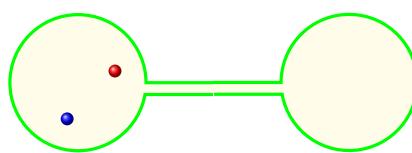
For example for the scenario of two molecules with two different orientations we will have 2^2 microstates.



The type of probability related to the number of configurations in space is called *positional probability* and the entropy resulting from positional probability is called *positional entropy*. Positional probability can be used to understand phenomena such as the change of state of the dissolution of solids in liquids. When a solid becomes liquid the number of possible microstates increases and hence entropy increases as well. Similarly, when dissolving a solute into a liquid, the number of microstates and entropy increases. However, computing the number of microstates to estimate positional entropy is not practical for large systems with numerous configurations. The number of microstates increases exponentially with the number of particles to the point that, for large systems, is not practical to compute entropy using Equation 7.2.

Sample Problem 85

The image below represents two different ideal gas-molecules in a two-bulb container. The molecules are able to travel from one side to the other.



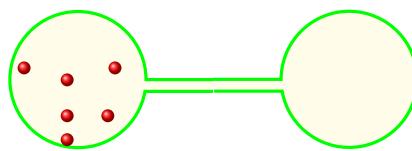
Answer the following questions: (a) What is the total number of microstates in this system (b) What is the most likely arrangement of the molecules (c) What is the least likely arrangement of the molecules (d) What is the probability of finding the system in the most likely arrangement of the molecules

SOLUTION

Overall we have three different scenarios. We can find all the molecules in the left container, all the molecules in the right container, or one molecule in the left and the other in the right. As the molecules are different, we only have one microstate in which both are in a single container. Differently, we have two different microstates in which the particles are distributed. Overall we have 4 microstates, the probability of finding the particles on both sides would be $2/4 \times 100=50\%$.

◆ STUDY CHECK

The image below represents six ideal gas-molecules in a two-bulb container. The molecules are able to travel from one side to the other.



Answer the following questions: (a) What is the total number of microstates in this system (b) What is the most likely arrangement of the molecules (c) What is the least likely arrangement of the molecules (d) What is the probability of finding the system in the most likely arrangement of the molecules

►Answer: (a) 3 microstates: left population, right population, mixed (b) mixed distribution (c) left or right population (d) $5/7 \times 100$

Equivalence between microscopic and macroscopic entropy We have addressed two different definitions of entropy, a macroscopic definition based



on heat and a microscopic definition based on configurations. Each description is based in a different formula. The macroscopic description of entropy is based on the Clausius' formula whereas the microscopic description is based on Boltzmann's formula. Here we will explain why both descriptions are indeed equivalent. First, both types of entropies are state functions, macroscopic entropy depends on the initial and final temperature, volume or pressure and not the path taken to reach the final state. Similarly, the microscopic entropy depends on the initial and final microstates, not the transition between both states. Macroscopic entropy is extensive and depends on the size of the system, and microscopic entropy is extensive as well as the larger the system the more configurations would be. Finally, when the size of a system increases the energy levels that its particle occupies become more packed and the particles are able to distribute among these states. At low temperatures all particles occupy only the lowest level energy level and hence there is only one configuration or micro state for the system, being its entropy zero.

7.3 Standard molar entropies

Enthalpies are relative properties and when we compute the formation energy of water we need the formation energy of oxygen and oxygen gas. These two values are zero and are assumed the reference. Entropies are absolute values. The term absolute refers to the absolute scale of temperatures where the lowest value is well defined and equal to zero. Similarly, there is the lowest value for entropy two and we will discuss this value when dealing with the third law of thermodynamics.

Standard molar entropies, S° The standard molar entropy of a substance is the absolute entropy of one mole substance at 1 atm. Entropies are absolute properties in contrast to other relative thermodynamic functions like the enthalpy in which a set of molecular states act as a reference. A few standard entropy values are tabulated in Table 7.1 at one bar and 25 °C, the conventional temperature of reporting thermodynamic data. More values are tabulated in Table 7.5, at the end of the chapter. The units of molar entropy are J/molK. Molar entropies tend to be small values—as the unit joule is a small unit of energy. Finally, entropies can be positive or negative values.

Sample Problem 86

Using the thermodynamic tables at the end of the chapter, locate the values of molar entropies for the following molecules: O_{2(g)}, NH_{3(g)}, K_(s), SiBr_{4(l)}.

SOLUTION

The molar entropy of oxygen is 205.0 J/molK, whereas the molar entropy for gas ammonia is 192.3 J/molK. The molar entropy for solid potassium is 64.2 J/molK, whereas the molar entropy for liquid silicon tetrabromide is 277.8 J/molK.

◆ STUDY CHECK

Using the thermodynamic tables at the end of the chapter, locate the values of molar entropies for the following molecules: (a) Ag_(s) (b) SO_{2(g)} (c) Zn_(s) (d) Br_{2(l)}

►Answer: (a) 42.6 J/molK (b) 248.1 J/molK (c) 41.6 J/molK (d) 152.2 J/molK

Factors affecting S We can qualitatively rationalize the trends between the standard molar entropy values for different substances and for different conditions (temperature, volume, pressure) by using some simple rules described below:

¶ **The state of matter:** The standard entropy of gases is larger than the standard entropy of liquids as gases present large degree of freedom (possible configurations) than liquids. The standard entropy of liquids is larger than the standard entropy of solids as liquids present large degree of freedom than solids. The molecules of a liquid molecules can jiggle more in comparison with the molecules of a solid. Overall, we can assume that liquids and solid has almost null entropy whereas gases have very large entropy. For example, the entropies of ice, water and steam are respectively 41, 69.95, and 69.95 J/molK.

¶ **Molar mass:** For monoatomic substances (e.g. Ne, Ar, etc.) the larger the atomic weight the larger entropy. This is because the energy levels of larger molecules are more packed, and hence are easier to access at a given temperature.

¶ **Molecular complexity:** For substances with comparable molar mass (O_3 and F_2), the more complex the molecule the larger entropy, as the number of degrees of freedom are directly correlated with the number of microstates.

¶ **Temperature:** Temperature increases entropy as the system have more accessible microstates. The plot below represents the entropy change with temperature for a substance.

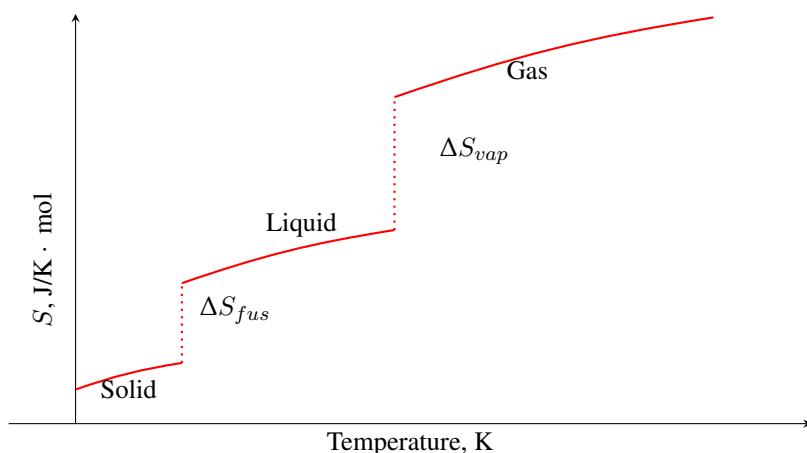


Figure 7.1 Entropy as function of temperature indicating the entropy changes for the fusion and vaporization processes.

¶ **Number of particles:** The larger the number of particles of a system, the larger entropy, as the more particles the more microstates or possible configurations.

¶ **Volume:** The larger the volume of a system, the larger entropy, as the larger volume the more microstates or possible configurations.

Sample Problem 87

Compare entropy for the following systems: (a) Liquid ammonia at 25°C and 1 bar and gas ammonia at 25°C and 1 bar (b) Liquid ammonia at 25°C and 1 bar and liquid ammonia at 45°C and 1 bar (c) 3 moles of an ideal gas and 5 moles of the same gas at fixed temperature and pressure

SOLUTION

Gas ammonia has a larger entropy than liquid ammonia as gases in general tend



to have larger entropy. When dealing with temperature, the higher temperature the higher entropy. Hence liquid ammonia at 45°C and 1 bar will have a larger entropy than liquid ammonia at 25°C and 1 bar. Finally, entropy is an extensive property and 5 moles of a gas will have larger entropy than 3 moles of the same gas.

STUDY CHECK

Compare entropy for the following systems: (a) CO₂ at 25°C and 1 bar and SO₂ at 25°C and 1 bar (b) 3L of a gas at 25°C and 1 bar and 4L of the same gas at 25°C and 1 bar (c) H₂ at 25°C and 1 bar and He at 25°C and 1 bar

►Answer: (a) SO₂ (b) 4L (c) H₂

Table 7.1 Standard entropy S° at 25 °C in J/(mol· K)

Substance	S°	Substance	S°	Substance	S°	Substance	S°
Br _{2(l)}	152	Br _{2(g)}	245	CH ₃ OH _(l)	127	CH ₃ OH _(g)	240
CS _{2(l)}	151	CS _{2(g)}	238	H ₂ O _(l)	70	H ₂ O _(g)	189
H ₂ O _{2(l)}	233	H ₂ O _{2(g)}	189	Rb _(s)	70	Rb _(g)	170
Cs _(s)	83	Cs _(g)	176	He _(g)	126	Ne _(g)	146
Ar _(g)	155	Kr _(g)	164	O _{3(g)}	238	F _{2(g)}	203

7.4 Calculating entropy changes

We have that when a system receives heat its entropy increases. At the same time, when a system receives heat its temperature increases. Therefore, there should be a relation between the temperature increase and the entropy increase. At the same time if we compress or decompress a gas at constant temperature, its entropy also changes based on the change of volume or the change of pressure. In particular, if we apply some mechanical work to a system so its volume decreases its entropy will increase as the system has received work—mechanical energy. Mind the opposite trend here. Similarly, if the pressure of a system increases as a result of applying an external force its entropy will also increase.

Entropy change and temperature The following formula can be used to calculate the entropy change of a system when its temperature increases (or decreases). Temperature changes can be measured at constant volume or constant pressure and as such, the formula will have to be adjusted for these two different conditions.

$$\Delta S = C \ln \left(\frac{T_2}{T_1} \right) \quad (7.4)$$

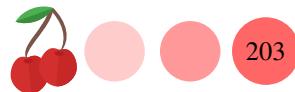
where:

ΔS is the entropy change in J/K

C is heat capacity in J/K

T_1 is the absolute initial temperature (in K)

T_2 is the absolute final temperature (in K)



C represents the heat capacity. Mind molar heat capacity C_m and heat capacity C are related by the number of moles: $C = n \cdot C_m$. If the change in temperature is measured at constant pressure, the molar heat capacity is called constant-pressure molar heat capacity $C_{p,m}$, whereas if the change in temperature is measured at constant volume, the molar heat capacity is called constant-volume molar heat capacity $C_{v,m}$. For ideal gases the $C_{v,m}$ values are (mind R is the constant of the gases 8.314J/molK): $\frac{3}{2}R$ (for atoms), $\frac{5}{2}R$ (for linear molecules), and $\frac{6}{2}R$ (for nonlinear molecules). For ideal gases the $C_{p,m}$ values are: $\frac{5}{2}R$ (for atoms), $\frac{7}{2}R$ (for linear molecules), and $\frac{8}{2}R$ (for nonlinear molecules). $C_{p,m}$ and $C_{v,m}$ are related by $C_{p,m} = C_{v,m} + R$.

Entropy change and volume The following formula can be used to calculate the entropy change of an ideal gas when its volume changes at constant temperature. A volume decrease will cause an entropy decrease:

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) \quad (7.5)$$

where:

ΔS is the entropy change in J/K

n is the number of moles

R is the constant of the gases in energy units (8.314J/molK)

V_1 is the initial volume

V_2 is the final volume

Entropy change and pressure The following formula can be used to calculate the entropy change of an ideal gas when its pressure changes at constant temperature. A pressure decrease will cause an entropy increase:

$$\Delta S = nR \ln \left(\frac{P_1}{P_2} \right) \quad (7.6)$$

where:

ΔS is the entropy change in J/K

n is the number of moles

R is the constant of the gases in energy units (8.314J/molK)

P_1 is the initial pressure

P_2 is the final pressure

Entropy change, pressure and volume The following formula can be used to calculate the entropy change of an ideal gas when its pressure and volume change at constant temperature.

$$\Delta S = nR \ln \left(\frac{P_1}{P_2} \right) + nR \ln \left(\frac{V_2}{V_1} \right) \quad (7.7)$$

where:

ΔS is the entropy change

n is the number of moles

R is the constant of the gases in energy units (8.314J/molK)

P_1 and V_1 is the initial pressure and volume

P_2 and V_2 is the final pressure and volume



Sample Problem 88

A 5L sample of Helium, an ideal gas, at 1atm is heated from 300K to 400K.
 (a) Calculate the entropy change if the gas is heated at constant volume. (b) Calculate the entropy change if the gas is heated at constant pressure.

SOLUTION

We have that the formula that related the entropy change with a temperature change is:

$$\Delta S = C \ln \left(\frac{T_2}{T_1} \right)$$

Still the heat capacity can be computed at constant volume or constant pressure. For an ideal monoatomic gas, the molar heat capacity at constant volume is $\frac{3}{2}R$, whereas the molar heat capacity at constant pressure is $\frac{5}{2}R$. Therefore, as we need heat capacities and not molar heat capacity, we have that the heat capacity at constant volume is $n \cdot \frac{3}{2}R$, whereas the heat capacity at constant pressure is $n \cdot \frac{5}{2}R$, with n being the number of moles. At this point we have that the entropy change at constant volume would be $n \cdot \frac{3}{2}R \ln \left(\frac{T_2}{T_1} \right)$, whereas the entropy change at constant pressure would be $n \cdot \frac{5}{2}R \ln \left(\frac{T_2}{T_1} \right)$. The number of moles of gas is:

$$n = \frac{PV}{RT} = \frac{1 \cdot 5}{0.082 \cdot 300} = 0.20 \text{ moles}$$

the initial temperature is $T_1 = 300\text{K}$ and the final temperature is $T_2 = 400\text{K}$. Therefore the entropy change at constant volume would be:

$$\Delta S_V = 0.20 \cdot \frac{3}{2} \cdot 8.314 \ln \left(\frac{400}{300} \right) = 0.71 \text{ J/K}$$

and the entropy change at constant pressure would be:

$$\Delta S_p = 0.20 \cdot \frac{5}{2} \cdot 8.314 \ln \left(\frac{400}{300} \right) = 1.19 \text{ J/K}$$

We have that for a monoatomic ideal gas, the entropy change at constant pressure is larger than the entropy change at constant volume.

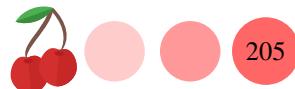
◆ STUDY CHECK

A 4.9×10^{-3} mol sample of methane is heated from 100K to 300K. Assuming ideal gas behavior: (a) Calculate the entropy change if the gas is heated at constant volume. (b) Calculate the entropy change if the gas is heated at constant pressure.

►Answer: (a) 0.13 J/K (b) 0.18 J/K

7.5 Calculating entropy changes in chemical reactions

This section covers the calculation and estimation of the entropy change of a reaction. Entropies as well as enthalpies are tabulated and one can compute the entropy change of a reaction by using the tabulated molar entropies. On the other hand it is very convenient to be able to estimate the just the sign of the entropy change of a reaction. Here we will provide a set of general rules to do this.



Standard entropy of reaction, ΔS_R° We can calculate the standard entropy of a reaction in a similar way as we calculate the standard enthalpy of a reaction:

$$\boxed{\Delta S_R^\circ = \Delta S_{products}^\circ - \Delta S_{reactants}^\circ} \quad \text{Entropy change} \quad (7.8)$$

where:

ΔS_R° is the standard entropy change of the reaction

$\Delta S_{products}^\circ$ is the standard entropy of all products

$\Delta S_{reactants}^\circ$ is the standard entropy of all reactants

It is important to take into account the stoichiometric coefficients. For example, for the reaction:



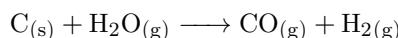
We have the entropy values of: $S^\circ(\text{CH}_3\text{OH}_{(g)})=239.7 \text{ J/K}\cdot\text{mol}$, $S^\circ(\text{O}_{2(g)})=161.1 \text{ J/K}\cdot\text{mol}$, $S^\circ(\text{CO}_{2(g)})=213.79 \text{ J/K}\cdot\text{mol}$, and $S^\circ(\text{H}_2\text{O}_{(l)})=69.95 \text{ J/K}\cdot\text{mol}$. We can calculate ΔS_R° :

$$\begin{aligned} \Delta S_R^\circ &= \Delta S_{products}^\circ - \Delta S_{reactants}^\circ = \\ &\left(2 \cdot S^\circ(\text{CO}_{2(g)}) + 4 \cdot S^\circ(\text{H}_2\text{O}_{(l)})\right) - \left(2 \cdot S^\circ(\text{CH}_3\text{OH}_{(g)}) + 3 \cdot S^\circ(\text{O}_{2(g)})\right) \\ &= \left(2 \cdot 213.79 + 4 \cdot 69.95\right) - \left(2 \cdot 239.7 + 3 \cdot 161.1\right) = -255.32 \text{ J/K} \end{aligned}$$

Interpreting ΔS_R° If the entropy change of a reaction is positive we will say that the reaction produces entropy. Similarly, if the entropy change of a reaction is negative we will say that the reaction consumes entropy. An analog trend can be found for the change of enthalpy—remember the enthalpy of the heat measured at constant pressure conditions—so if the enthalpy change of a reaction is positive we say the reaction is endothermic and consumes heat, whereas a negative enthalpy change for a reaction means the reaction produces heat.

Sample Problem 89

Calculate the entropy change of the following reaction and give an interpretation based on the sign of the change:



Given: $S^\circ(\text{C}_{(s)})=5.69 \text{ J/K}\cdot\text{mol}$, $S^\circ(\text{H}_2\text{O}_{(g)})=188.7 \text{ J/K}\cdot\text{mol}$, $S^\circ(\text{CO}_{(g)})=197.9 \text{ J/K}\cdot\text{mol}$, $S^\circ(\text{H}_{2(g)})=131 \text{ J/K}\cdot\text{mol}$.

SOLUTION

Using the formula for ΔS_R° we have:

$$\begin{aligned} \Delta S_R^\circ &= \Delta S_{products}^\circ - \Delta S_{reactants}^\circ = \\ &\left(S^\circ(\text{CO}_{(g)}) + S^\circ(\text{H}_{2(g)})\right) - \left(S^\circ(\text{C}_{(s)}) + S^\circ(\text{H}_2\text{O}_{(g)})\right) \\ &= \left(197.9 + 131\right) - \left(5.69 + 188.7\right) = 134.51 \text{ J/K} \end{aligned}$$

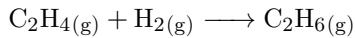
This produces entropy.

◆ STUDY CHECK

Calculate the entropy change of the following reaction and give an interpretation



based on the sign of the change:



Given: $S^\circ(\text{C}_2\text{H}_4(\text{g})) = 219.5 \text{ J/K} \cdot \text{mol}$, $S^\circ(\text{C}_2\text{H}_6(\text{g})) = 229.5 \text{ J/K} \cdot \text{mol}$,
 $S^\circ(\text{H}_2(\text{g})) = 131 \text{ J/K} \cdot \text{mol}$.

►Answer: -121 J/K , consumes entropy

Estimate the sign for ΔS_R° Often times we are more interested in predicting the sign of the entropy change of a reaction than to compute the exact value. This is because the sign can be used in order to estimate whether a reaction proceeds spontaneously. Two basic rules are used in order to estimate the entropy change sign:

¶ **The state of matter:** solids and liquids have very low entropy in comparison to gases. For example, in the case below, we have the production of liquid water from ice produces entropy as liquids have more entropy than solids:



On the other hand, the condensation of water vapor to produce a liquid consumes entropy, as liquids have less entropy than gases:



¶ **The number of molecules:** the larger the number of molecules of gas the larger entropy. For example, in the reaction below we have that we produce three molecules from two molecules. Hence, the entropy increases.



However, this rule only works if we only take into account the number of gas molecules. For example, in the reaction below we produce two gas molecules from three gas molecules and hence we lose entropy:



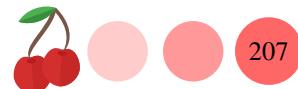
Sample Problem 90

Estimate the sign of the entropy change for the following reactions:

- (a) $2 \text{SO}_{3(\text{g})} \longrightarrow 2 \text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})}$
- (b) $\text{H}_{2(\text{g})} + \frac{1}{2} \text{O}_{2(\text{g})} \longrightarrow \text{H}_2\text{O}_{(\text{l})}$
- (c) $2 \text{CH}_3\text{OH}_{(\text{g})} + 3 \text{O}_{2(\text{g})} \longrightarrow 2 \text{CO}_{2(\text{g})} + 4 \text{H}_2\text{O}_{(\text{g})}$

SOLUTION

We will calculate the change in the number of moles of gases in the reaction Δn in order to estimate the sign of the entropy change. This is just the total number of product molecules with respect to the total number of reactant molecules. We have that Δn for the first reaction is 1 and hence $\Delta S_R^\circ > 0$. For the second reaction we have that Δn is -1.5 and hence $\Delta S_R^\circ < 0$. Remember that liquids and solids are not counted towards Δn as their entropy is very small. Finally for



the last reaction, we have that Δn is 1 and hence $\Delta S_R^\circ > 0$.

STUDY CHECK

Estimate the sign of the entropy change for the following reactions:

- (a) $\text{C}_2\text{H}_{2(g)} + 4 \text{F}_{2(g)} \longrightarrow 2 \text{CF}_{4(g)} + \text{H}_{2(g)}$
- (b) $2 \text{Al}_{(s)} + 3 \text{Br}_{2(l)} \longrightarrow 2 \text{AlBr}_{3(s)}$

►Answer: $\Delta S_R^\circ > 0$, $\Delta S_R^\circ \approx 0$

7.6 The second and third law of thermodynamics

The second law of thermodynamics claims that any spontaneous evolution is accompanied by an increase in entropy. However, the entropy of certain common systems spontaneously decreases. For example, ice freezes below 0°C going from less-ordered liquid water to more-ordered ice. At the same time, cold packs spontaneously get colder going from a high-temperature and entropy state into a low-temperature low-entropy state. In order to understand how some systems decrease their entropy spontaneously, we need to further our analysis of the system taking into account not only the system under study but also its surroundings.

System, its surroundings and the universe Thermodynamics studies systems involving heat transfer such as a hot cup of coffee cooling down in a room or a chemical reaction happening at a beaker on a lab bench. The system just means the problems we are dealing with, for example, the cup of coffee or the beaker. However, every system has its surroundings. For example, the cup of coffee is surrounded by air and the beaker is in contact with the lab bench. The surroundings of a system represent everything else but the system and in general tend to be as important as the system, in particular when understanding the changes of entropy during a spontaneous change. Both the system and its surroundings are called the universe, which is an isolated system. If we study how a system loses heat or a reaction consumes entropy it is convenient to think about where the heat goes or where the entropy lost is coming from.

Calculating $\Delta S_{surr}^{T,P}$ Now, let us focus on the surroundings of the system under study considering only fixed temperature and pressure conditions. If a system loses heat, the heat is received by its surroundings. To calculate the entropy of the surroundings we just need to use the formula working under fixed pressure and temperature conditions (think about a reaction happening on an open beaker in which pressure is always atmospheric and temperature will always be room temperature):

$$\Delta S_{surr}^{T,P} = -\frac{\Delta H}{T} \quad (7.9)$$

where:

$\Delta S_{surr}^{T,P}$ is the entropy change on the surroundings

ΔH is the enthalpy change on the system

T is the absolute temperature

This formula derives from Clausius expression that related the entropy change with heat, given that the surroundings receive or give away the heat exchanged by the



system—hence the negative sign—and under fixed-pressure conditions, heat is equivalent to enthalpy. Moreover, as the surroundings are in general larger than the system its temperature will not change and any heat transfer will be reversible. Also, this expression predicts that the same heat exchanged at higher temperatures is less effective in changing the surroundings' entropy. At the same time, an exothermic process will increase the entropy of the surroundings whereas an endothermic process will decrease the entropy of the surroundings.

Calculating ΔS_{univ} : the second law of thermodynamics Now that we have included the surroundings in our analysis we can combine both the system and its surroundings in order to track the overall change in entropy in the universe:

$$\boxed{\Delta S_{univ} = \Delta S + \Delta S_{surr} = \Delta S - \frac{\Delta H}{T}} \quad (7.10)$$

where:

ΔS_{univ} is the entropy change on the universe

ΔS is the entropy change on the system

ΔH is the enthalpy change on the system

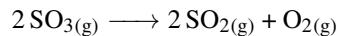
T is the absolute temperature

Overall, the *second law of thermodynamics* states that spontaneous process increase the entropy of the universe. If a reaction is exothermic and heat is being released the entropy of the surroundings increase whereas the entropy of the system can increase or decrease. If this change is negative, it has to be smaller than the entropy increase of the surroundings if the process is spontaneous. If a reaction is endothermic and heat is being absorbed the entropy change of the system has to be positive enough to compensate the decrease of entropy of the surroundings if the process is spontaneous.

- ꝝ $\Delta S_{univ} > 0$: The forward process or reaction is spontaneous
- ꝝ $\Delta S_{univ} = 0$: The process or reaction is in equilibrium
- ꝝ $\Delta S_{univ} < 0$: The forward process or reaction is not spontaneous hence the backwards is spontaneous

Sample Problem 91

For the reaction:



we have that ΔH_R° is -93kJ/mol and ΔS_R° is -199J/mol. Calculate the entropy change on the system, its surroundings and the overall universe at 25 °C.

SOLUTION

We have that the system is just the reaction we observe, hence $\Delta S_{sys}^\circ = -199$ J/mol. The entropy change of the surroundings—the environment where the reaction takes place—is:

$$\Delta S_{surr} = -\frac{\Delta H_{sys}}{T} = -\frac{-93}{298} = 0.312 \text{ kJ/mol} = 312 \text{ J/mol}$$

If we combine both contributions we have that the entropy change of the universe is:

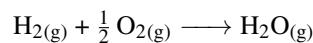
$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = -199 + 312 = 113 \text{ J/mol}$$



As this value is positive, the reaction will happen spontaneously at that temperature.

STUDY CHECK

For the reaction:



we have that ΔH_R° is -250kJ/mol and ΔS_R° is -45J/K· mol. Calculate the entropy change on the system, its surroundings and the overall universe at 298K.

►Answer: $\Delta S_{surr} = 839\text{J/K· mol}$, $\Delta S_{univ} = 884\text{J/K· mol}$

Entropy and equilibrium A system without tendency to change is a system in static equilibrium. A system in dynamic equilibrium has the same tendency to change through forward or backwards evolution. For example, a reaction reaches chemical equilibrium when the mixtures of reactants and products reached a point in which the forward reaction and the backwards reaction have the same speed. A system reaches thermal equilibrium when it releases and gains heat with its surroundings at the same speed. A system reaches mechanical equilibrium—a gas in a piston—when it contracts and expands at the same speed. When an isolated system has reached equilibrium the entropy of the universe does not change:

$$\Delta S_{univ} = 0 \quad (7.11)$$

The third law of thermodynamics Entropy is an absolute—not relative—property. The third law of thermodynamics established the lower possible entropy value that a system can reach under certain conditions. We have that from a microscopic or molecular point of view entropy is associated with the number of molecular configurations, W . For a perfect crystal—a crystalline material without any defects—at the lowest possible temperature, that is the absolute zero in the Kelvin scale, 0K, there is no molecular motion and hence the system would have only one possible configuration ($W=1$) that would lead to a null entropy ($k_B \ln 1$).

$$\Delta S_s(0K) = 0 \quad \text{3rd law of thermodynamics} \quad (7.12)$$

where:

ΔS_s is the entropy of a perfect crystal at 0K

The entropy of a solid depends on the number of molecules and the number of possible configurations of each molecule of the solid. For a solid with for example two molecules and with each molecule having three possible configurations we'll have 2^3 possible microstates and the entropy will be $k_B \ln 2^3$. Given that $\ln a^b = b \ln a$ we have $3 \cdot k_B \ln 2$. The entropy of a solid depends on the number of molecules and the number of possible configurations of each molecule of the solid. For a solid with for example two molecules and with each molecule having three possible configurations we'll have 2^3 possible microstates and the entropy will be $k_B \ln 2^3$. Given that $\ln a^b = b \ln a$ we have $3 \cdot k_B \ln 2$. For a larger sample, containing one mole of atoms, the number of microstates is very larger, in particular $2^{6.02 \times 10^{23}}$. Hence the value of the entropy is $6.02 \times 10^{23} \cdot k_B \ln 2 = 5.75\text{J/K}$. This value is called the residual entropy of a sample, the entropy at 0K that results from positional disorder.



Sample Problem 92

Calculate the residual entropy for one mole of methane CH₄ at 0K.

SOLUTION

Methane has four possible arrangements due to its symmetry as the molecules of methane are tetrahedral. Hence for a mole of molecules we have that the residual entropy would be

$$6.02 \times 10^{23} \cdot k_B \ln 4 = 11.5 J/K$$

given that $k_B = 1.38 \times 10^{-23} J/K$.

◆ STUDY CHECK

Calculate the residual entropy for one mole of water at 0K and compare your value with the experimental result of 3.4J/K. Assume water has two equivalent configurations.

►Answer: 5.76

The laws of thermodynamics: a review There are four laws of thermodynamics. The zeroth law deals with heat transfer and says that two systems in thermal equilibrium are also in thermal equilibrium with a third system equilibrated with one of them. On the other hand, the first law of thermodynamics deals with internal energy, claiming that the internal energy of a system is conserved. The second law deals with entropy claiming that the entropy of the universe can only increase. Finally, the last and third law of thermodynamics deals with the scale of entropies defining the minimum entropy value.

7.7 Gibbs free-energy

We have addressed two thermodynamic functions at this point: enthalpy and entropy. The first is associated with the energy exchange whereas the second is associated with the spreading of energy. At the same time, the second law of thermodynamics helps predicts the spontaneity of a process. Still, this second law is written in terms of two different entities, the system, and its surroundings. If we combine both the entropy and the enthalpy we obtain a new thermodynamic function associated with spontaneity, the Gibbs free-energy.

Definition of Gibbs free-energy The Gibbs free-energy is just a combination of enthalpy and entropy for a given temperature:

$$G = H - T \cdot S \quad (7.13)$$

Working at constant temperature, we can compute the change in Gibbs free energy as:

$$\Delta G^T = \Delta H - T \Delta S \quad \text{Gibbs free-energy} \quad (7.14)$$

where:

ΔG^T is the Gibbs free-energy change at constant temperature

ΔH is the enthalpy change



ΔS is the entropy change

T is the temperature

Gibbs free-energy is a state function that only depends on the final and initial state and not the path followed. At the same time, Gibbs free-energy depends on temperature and pressure—we will discuss more about this at the end of the section. More importantly, the change in Gibbs free-energy is associated with the spontaneity of the process. Gibbs free-energy decreases with temperature and the decrease is sharper for gases in comparison to liquids, and at the same time, the decrease is also sharper for liquids in comparison to solids.

Gibbs free-energy and spontaneity The Gibbs free-energy change of a reaction is associated with the spontaneity of the process or with its state of equilibrium. In particular, reactions that produce Gibbs free-energy are nonspontaneous. Differently, reaction consuming free-energy are indeed spontaneous. Finally, reaction without a change in free-energy are in equilibrium.

- ꝝ $\Delta G < 0$: The reaction is spontaneous
- ꝝ $\Delta G = 0$: The reaction is in equilibrium
- ꝝ $\Delta G > 0$: The reaction is nonspontaneous

This is because the expression of Gibbs free energy is related to the total entropy change of the universe given by the second law of thermodynamics:

$$\Delta G^T = \Delta H - T\Delta S \quad \text{and} \quad T\Delta S_{univ}^{T,P} = -(\Delta H - T\Delta S) \quad (7.15)$$

Hence, we have that

$$\Delta G^T = T\Delta S_{univ}^{T,P} \quad (7.16)$$

This last expression means that an increase in total entropy is accompanied by a decrease in Gibbs free energy at constant pressure and temperature. At the same time the expression indicates that the direction of spontaneous change corresponds to a decrease of Gibbs free energy, at constant temperature and pressure.

Estimating spontaneity based on the sign of H and S As Gibbs free-energy depends on the enthalpy and entropy. We can estimate the sign of ΔG from the signs of ΔH and ΔS . Table 7.2 below show the different sign combinations.

Table 7.2 Sign combination of entropy and enthalpy in connection with G

ΔH Sign	ΔS Sign	ΔG Sign	Spontaneity
–	+	–	Always spontaneous
+	–	+	Always nonspontaneous
–	–	– for $T < T_c$ and + for $T > T_c$	Conditionally Spontaneous: below T_c
+	+	+ for $T < T_c$ and – for $T > T_c$	Conditionally Spontaneous: above T_c

The reasoning behind the different sign combinations is that as Gibbs free-energy is related to minus the entropy, to achieve a final negative value of G we need negative enthalpy and positive entropy that would lead to a spontaneous process that consumes free-energy. In other words, exothermic processes that produce heat and processes that produce entropy are spontaneous. Differently, endothermic processes that consume



heat and processes that consume entropy are nonspontaneous. For entropy and enthalpy changes with the same sign, then the spontaneity will depend on temperature. For example, to carry endothermic processes and processes that produce entropy, we would need high temperatures that help enthalpy. In the case of an exothermic process that consumes entropy, we would need low temperatures that help alleviate the entropy. For both cases, the critical temperature for spontaneity is given by:

$$T_c = \frac{\Delta H}{\Delta S} \quad (7.17)$$

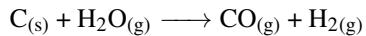
where:

T_c is the critical temperature for spontaneity in Kelvins

Mind that the units of ΔH tend to be kJ/mol, whereas the units of ΔS tend to be J/mol. Therefore, we need to remove the kilo prefix to calculate T_c . For example, to combine an enthalpy value of 100kJ/mol with an entropy value of 5J/mol, we would have to convert the enthalpy value into 100000J/mol.

Sample Problem 93

For the reaction:



we have that ΔH_R° is 113kJ/mol and ΔS_R° is 133J/K· mol. Indicate whether the reaction will proceed spontaneously. Will it proceed at 200K? Will it proceed at 900K?

SOLUTION

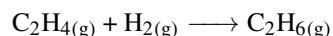
When the entropy change and the enthalpy change have the same sign, the reaction will be conditionally spontaneous. In this case, we would need to overcome the positive enthalpy change and we can do this at very high temperatures. In particular, temperatures higher than a critical value give by:

$$T_c = \frac{\Delta H}{\Delta S} = \frac{113 \times 10^3}{133} = 850K$$

The reaction will not proceed at temperatures below 850K as such it will not proceed at 100, but it will work at 900K.

❖ STUDY CHECK

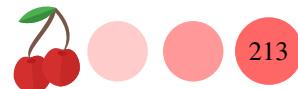
For the reaction:



we have that ΔH_R° is -135kJ/mol and ΔS_R° is -120J/K· mol. Indicate under which temperature conditions will the reaction proceed spontaneously.

►Answer: spontaneous below 1125K

Standard Gibbs free-energy of formation The Gibbs free-energy G of a compound depends on temperature, pressure as well as composition, which means that for every pressure, temperature, and molarity we have a different free-energy value. Similar to the case of enthalpy, a standard state is defined in order to tabulate the free-energy values ΔG° (see Table 7.5). The standard states of an element represent its most stable form at 1atm and 298K. In the case of solutions, the standard state corresponds to



a 1 molar concentration and in the case of gases to a 1 atm pressure. Table 7.3 lists the reference state for a few elements. For example, you can find Bromine as a solid, liquid or gas. However, its natural state is liquid. That is the reason why $\Delta G^\circ(\text{Br}_2\text{(g)}) = 3\text{KJ/mol}$, whereas $\Delta G^\circ(\text{Br}_2\text{(l)}) = 0\text{KJ/mol}$. In general, for metals, its natural state is solid. For non-metallic elements, such as hydrogen, oxygen, nitrogen, fluorine, chlorine, its natural state is in the form of a diatomic gas molecule. For example, $\Delta G^\circ(\text{H}_2\text{(g)}) = 0\text{KJ/mol}$, $\Delta G^\circ(\text{N}_2\text{(g)}) = 0\text{KJ/mol}$ or $\Delta G^\circ(\text{O}_2\text{(g)}) = 0\text{KJ/mol}$. For the case of carbon, its natural state is graphite, $\Delta G^\circ(\text{C}_{\text{graphite(s)}}) = 0\text{KJ/mol}$. Molecules such as H_2O or NO have standard free-energy different than zero. Mind that molecules are made of elements. The establishment of a Gibbs free energy scale based on a set of reference states allows the calculation of standard Gibbs free energies of formation ΔG_f° : the Gibbs free energy of formation per mole of the formation of a compound from its elements on its most stable states. The values for Gibbs free energy of formation ΔG_f° are tabulated at 25°C. These values inform about the stability of the compound with respect to its elements. For example, ΔG_f° for ammonia is -16KJ/mol, which means that ammonia is thermodynamically stable and will not decompose to produce hydrogen and nitrogen spontaneously. Different, ΔG_f° for NO_2 is 51KJ/mol. This positive value indicates that nitrogen dioxide will spontaneously decompose into nitrogen and oxygen. Still, even when the decomposition of a chemical is favored by the laws of thermodynamics, its rate might be slow, and only kinetics can inform about the timing of the decomposition. Chemicals are called labile (nonlabile) when they decompose or react quickly (slowly).

Table 7.3 Standard states for different elements. For all $\Delta G^\circ = 0 \text{ KJ/mol}$

Element	Standard state	Element	Standard state
Hydrogen	$\text{H}_2\text{(g)}$	Oxygen	$\text{O}_2\text{(g)}$
Nitrogen	$\text{N}_2\text{(g)}$	Chlorine	$\text{Cl}_2\text{(g)}$
Iron	$\text{Fe}_{\text{(s)}}$	Aluminium	$\text{Al}_{\text{(s)}}$
Carbon	$\text{C}_{\text{graphite(s)}}$	Phosphorus	$\text{P}_{\text{(s)}}$
Fluorine	$\text{F}_2\text{(g)}$	Bromine	$\text{Br}_{\text{(l)}}$
Mercury	$\text{Hg}_{\text{(l)}}$	Sulfur	$\text{S}_{\text{8(s)}}$
Iodine	$\text{I}_{\text{2(s)}}$	Silicon	$\text{Si}_{\text{(s)}}$

Standard free-energy of a reaction, ΔG_R° We can calculate the standard free-energy of a reaction in a similar way as we calculate the standard enthalpy or entropy of a reaction:

$$\Delta G_R^\circ = \Delta G_{\text{products}}^\circ - \Delta G_{\text{reactants}}^\circ \quad \text{Free-energy change} \quad (7.18)$$

where:

ΔG_R° is the standard Gibbs free-energy change of the reaction

$\Delta G_{\text{products}}^\circ$ is the standard Gibbs free-energy of all products

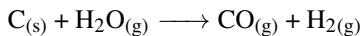
$\Delta G_{\text{reactants}}^\circ$ is the standard Gibbs free-energy of all reactants

There are two possible ways to calculate ΔG_R° . We can compute ΔG_R° from the enthalpy and entropy change at fixed 298K. Remember the standard thermodynamic parameters are computer at this temperature. Or we can compute ΔG_R° from the tabulated G_R° values. The next two examples walk you through these two possible scenarios.



Sample Problem 94

Use the data below to calculate the Gibbs free-energy of the reaction at 298K:



Compound	ΔH_f°	S°
$\text{C}_{(\text{s})}$	0	5.7
$\text{H}_2\text{O}_{(\text{g})}$	-241.8	188.7
$\text{CO}_{(\text{g})}$	-110.5	197.6
$\text{H}_{2(\text{g})}$	0	130.6

SOLUTION

As we have the standard formation enthalpy values and the standard entropy values, we can compute the entropy and enthalpy of reaction. We have that:

$$\begin{aligned}\Delta H_R^\circ &= \Delta H_{\text{products}}^\circ - \Delta H_{\text{reactants}}^\circ = \\ (\Delta H_f^\circ(\text{CO}_{(\text{g})}) + \Delta H_f^\circ(\text{H}_{2(\text{g})})) &- (\Delta H_f^\circ(\text{C}_{(\text{s})}) + \Delta H_f^\circ(\text{H}_2\text{O}_{(\text{g})})) \\ &= (-110.5 + 0) - (0 + -241.8) = 131.3 \text{ kJ}\end{aligned}$$

We also have:

$$\begin{aligned}\Delta S_R^\circ &= \Delta S_{\text{products}}^\circ - \Delta S_{\text{reactants}}^\circ = \\ (\Delta S^\circ(\text{CO}_{(\text{g})}) + \Delta S^\circ(\text{H}_{2(\text{g})})) &- (\Delta S^\circ(\text{C}_{(\text{s})}) + \Delta S^\circ(\text{H}_2\text{O}_{(\text{g})})) \\ &= (197.6 + 130.6) - (5.7 + 188.7) = 133.8 \text{ J/K}\end{aligned}$$

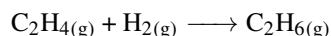
We have that the Gibbs free-energy will be:

$$\Delta G = \Delta H - T\Delta S = 131.3 \times 10^3 - 298 \cdot 133.8 = 91427.6 \text{ J} = 91.4 \text{ kJ}$$

As the free-energy is positive the reaction is not spontaneous. The reason for this non-spontaneity is the endothermicity. As such working at high temperatures we can overcome the enthalpy, in particular working at temperatures higher than 981K.

◆ STUDY CHECK

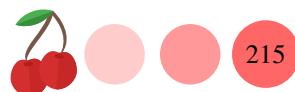
Use the data below to calculate the Gibbs free-energy of the reaction at 298K:



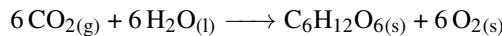
Compound	ΔH_f°	S°
$\text{C}_2\text{H}_4_{(\text{g})}$	-52.5	219.5
$\text{H}_{2(\text{g})}$	0	130.6
$\text{C}_2\text{H}_6_{(\text{g})}$	-84.7	229.5

$$\blacktriangleright \Delta H_R^\circ = -32 \text{ kJ}; \Delta S_R^\circ = -120.6 \text{ J/K}; \Delta G_R^\circ = 4 \text{ kJ}; \text{spontaneous for } T < 265 \text{ K}$$

In the following example we will show how to compute Gibbs free-energy of a reaction by means of standard Gibbs free-energies of the molecules involved in the reaction.

**Sample Problem 95**

Use the data below to calculate the Gibbs free-energy of the reaction at 298K:



Compound	ΔG_f°
$\text{CO}_{2(\text{g})}$	-394.4
$\text{H}_2\text{O}_{(\text{l})}$	-237.2
$\text{C}_6\text{H}_{12}\text{O}_{6(\text{s})}$	-910.56

SOLUTION

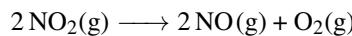
We can compute the Gibbs free-energy of a reaction by means of the free-energies of the molecules involved in the reaction:

$$\begin{aligned}\Delta G_R^\circ &= \Delta G_{products}^\circ - \Delta G_{reactants}^\circ = \left[\Delta G_f^\circ(\text{C}_6\text{H}_{12}\text{O}_{6(\text{s})}) + \right. \\ &\quad \left. 6 \Delta G_f^\circ(\text{O}_{2(\text{g})}) \right] - \left[6 \cdot \Delta G_f^\circ(\text{CO}_{2(\text{g})}) + 6 \cdot \Delta G_f^\circ(\text{H}_2\text{O}_{(\text{l})}) \right] \\ &= \left[-910.56 - 6 \cdot 0 \right] - \left[6 \cdot -394.4 + 6 \cdot -237.2 \right] = 2879 \text{ KJ}\end{aligned}$$

As the free-energy is positive the reaction is not spontaneous.

◆ STUDY CHECK

Use the data below to calculate the Gibbs free-energy of the reaction at 298K:



Compound	ΔG_f°
$\text{NO}_{2(\text{g})}$	51.3
$\text{NO}_{(\text{g})}$	86.6

$$\blacktriangleright \Delta G_R^\circ = 71 \text{ kJ; nonspontaneous}$$

7.8 Gibbs free-energy and equilibrium

We can use the principles of thermodynamics to study different phase transitions such as the transition between solid and liquid (melting or fusion) or liquid and gas (vaporization or boiling). These phase transitions are examples of equilibrium. During these transitions the temperature remains constant and all energy supplied is used to convert molecules between the two equilibrated phases and not to warm up the system. For example, the boiling point of water at 1 atm is 100°C and during boiling—also called vaporization—even when we continue the heating the temperature of water remains constant at 100°C until all water molecules become vapor. At the same time during a phase transition the Gibbs free energy of the two phase in equilibrium are the same.

Gibbs free-energy in equilibrium In equilibrium a system does not evolve in any direction, or it evolved back and forth in the same direction. For example in equilibrium a reaction proceed forward and backwards at the same pace. In these



conditions, the total entropy of the system and universe do not change ($\Delta S_{univ}^{T,P} = 0$). In these conditions the Gibbs free energy do not change either. Overall we have:

$$\Delta G^{T,P} = 0 \quad (7.19)$$

Gibbs free-energy and phase transitions Gibbs free energy are useful to calculate phase transition temperatures, that is the temperature to melt a solid or vaporize a liquid. As a phase transition is an equilibrium process and as in equilibrium we have that $\Delta G_{T,P}^{\circ} = 0$ we can estimate the fusion and vaporization temperatures using the formulas below involving the entropy and enthalpy values for a phase transition (see Table 7.4 for those values):

$$T_{fus} = \frac{\Delta H_{fus}^{\circ}}{\Delta S_{fus}^{\circ}} \quad \text{and} \quad T_{vap} = \frac{\Delta H_{vap}^{\circ}}{\Delta S_{vap}^{\circ}} \quad (7.20)$$

where:

T_{melt} and T_{vap} are the fusion and vaporization temperature in Kelvins
 ΔH_{fus}° and ΔS_{fus}° is the enthalpy and entropy of fusion
 ΔH_{vap}° and ΔS_{vap}° is the enthalpy and entropy of vaporization

The following example describes how to compute phase transition temperatures using thermodynamic data.

Sample Problem 96

Calculate the fusion and vaporization temperatures of benzene given that $\Delta H_{fus}^{\circ} = 10.9\text{ kJ/mol}$, $\Delta H_{vap}^{\circ} = 33.9\text{ kJ/mol}$, $\Delta S_{fus}^{\circ} = 38.0\text{ J/mol}\cdot\text{K}$ and $\Delta S_{vap}^{\circ} = 87.19\text{ J/mol}\cdot\text{K}$.

SOLUTION

In order to calculate the temperature of fusion for benzene we just need to divide the enthalpy and entropy of fusion making sure the units are consistent (converting enthalpy into J/mol)

$$T_{fus} = \frac{\Delta H_{fus}^{\circ}}{\Delta S_{fus}^{\circ}} = \frac{10.9 \times 10^3}{38.0} = 287\text{ K}$$

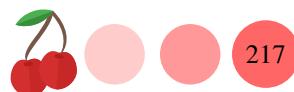
Similarly, in order to calculate the temperature of vaporization for benzene we just need to divide the enthalpy and entropy of vaporization making sure the units are consistent (converting enthalpy into J/mol)

$$T_{vap} = \frac{\Delta H_{vap}^{\circ}}{\Delta S_{vap}^{\circ}} = \frac{33.9 \times 10^3}{87.19} = 389\text{ K}$$

❖ STUDY CHECK

Estimate the fusion and vaporization temperatures in celcius of water given that $\Delta H_{fus}^{\circ} = 6.007\text{ kJ/mol}$, $\Delta H_{vap}^{\circ} = 40.66\text{ kJ/mol}$, $\Delta S_{fus}^{\circ} = 22.00\text{ J/mol}\cdot\text{K}$ and $\Delta S_{vap}^{\circ} = 109.00\text{ J/mol}\cdot\text{K}$.

►-0.3°C and 100°C

**Table 7.4 Standard entropies and enthalpies of phase transition at 1atm**

Compound	ΔH_{fus}° (kJ/mol)	ΔH_{vap}° (kJ/mol)	Compound	ΔS_{fus}° (J/mol·K)	ΔS_{vap}° (J/mol·K)
Ar(g)	1.188	6.447	Ar(g)	14.17	74.53
Br ₂ (g)	–	29.8	Br ₂ (g)	39.76	88.61
C ₆ H ₆ (g)	10.9	33.9	C ₆ H ₆ (g)	38.00	87.19
CH ₃ COOH _(g)	23.7	11.72	CH ₃ COOH _(g)	40.40	61.90
H ₂ O _(g)	6.01	40.66	H ₂ O _(g)	22.00	109.00
NH ₃ (g)	5.65	23.35	NH ₃ (g)	28.93	97.41

Gibbs free-energy and work The Gibbs free-energy of a reaction gives an estimate of the thermodynamic feasibility of a reaction. In other words, if Gibbs free-energy predicts that a reaction will not likely happen there is no need to invest time in energy trying to make a reaction work. The change in Gibbs free-energy, as its name indicates, also gives insight into the maximum amount of work—in particular nonexpansive work—that can be extracted from a system (chemical reaction, an engine, etc). More precisely, ΔG represents the maximum amount of work that can be extracted from a system at fixed pressure and temperature conditions. It represents the amount of useful energy to do work that a system has. When this value is positive, it represents the amount of work that needs to be put into the system in order to make the process work:

$$w \leq \Delta G_R \quad (7.21)$$

Gibbs free energy also tells about how efficient the energy conversion is. Let us analyze the energy contained in the battery of a cell phone. We could use this energy to produce work and power the cell phone. However, every electricity flow implies a loss of heat due to friction, and hence all energy contained in the battery could only be used if the electricity flow is very very small and under these conditions, the battery will not be able to do real work. Hence, energy can only fully used to do work in a hypothetical scenario in which the process works reversibly. However, all real processes are irreversibly and energy will always be lost. For such reason, it will take more energy to charge a battery than the energy given by the battery, as an irreversible electric flow implies energy loss. In other words, energy irreversibly used degrades on its use.

7.9 Gibbs free-energy and pressure conditions

Thermodynamics studies states of equilibrium, whereas chemical kinetics studies the rate at which chemical reactions reach equilibrium. Gibbs free energy ΔG is a thermodynamic function used to describe how a system spontaneously approaches equilibrium. During a spontaneous chemical reaction, ΔG decreases until reaching a minimum value when the reaction reaches equilibrium. Differently, ΔG° —defined in standard pressure conditions—has a fixed value that does not change during a reaction. Still, this function depends on temperature and pressure and until now we did not address how the pressure conditions affect the equilibrium.

Impact of pressure on Gibbs free-energy The standard Gibbs free-energy of reaction is calculated at standard pressure conditions (1 atm) and tabulated at 298K. What if we are not in standard conditions? When a reaction involving gas-phase reactants advances towards equilibrium forming products, the pressure in the container



increases. As gas molecules are being produced the pressure will depart from 1 atm. We can use the following expression to include the effect of pressure on ΔG_R° :

$$\Delta G_R = \Delta G_R^\circ + RT \ln Q_p \quad (7.22)$$

where:

ΔG_R is the Gibbs free-energy of a reaction not at standard conditions

ΔG_R° is the Gibbs free-energy of a reaction at standard conditions (1 atm and 298 K)

Q_p is the reaction ratio in terms of pressure

R is the constant of the gases in energy units (8.314 J/mol · K)

T is the absolute temperature

Pressure is another variable—similar to temperature—that can be used to favor chemical reactions. For example, the reaction between hydrogen and iodine exhibits a positive standard Gibbs free-energy ($\Delta H_R^\circ = +53\text{ kJ}$; $\Delta S_R^\circ = +166.3\text{ J/K}$). Under standard conditions, at 1 atm and 298 K, the reaction will not likely happen



Including the effects of pressure on the calculation of Gibbs free energy we have that at very low products pressures and relatively large reactant pressures ($P_{\text{HI}} = 1 \times 10^{-5}$ atm and $P_{\text{H}_2} = 1 \times 10^5$ atm) Gibbs free energy is negative:

$$\begin{aligned} \Delta G_R &= \Delta G_R^\circ + RT \ln Q_p = \Delta G_R^\circ + RT \ln \left[\frac{P_{\text{HI}}^2}{P_{\text{H}_2}} \right] \\ &= 3.44 \times 10^3 + 8.314 \cdot 298 \ln \left[\frac{(1 \times 10^{-5})^2}{1 \times 10^5} \right] = -8.2 \times 10^4 \text{ J/mol} \end{aligned}$$

These calculations demonstrate that one can tune the pressure conditions to favor a reaction. In general large reactant pressures and low products pressures can alleviate positive Gibbs free-energy values.

Sample Problem 97

Predict whether the reaction will proceed spontaneously at 298 K under the following pressure conditions: $P_{\text{NO}_2} = 1 \times 10^5$ atm and $P_{\text{N}_2\text{O}_4} = 1 \times 10^{-5}$ atm

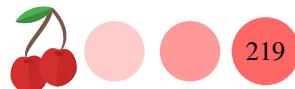


SOLUTION

The working pressure-conditions consist of large product pressures and small reactant pressures, and these conditions do not tend to favor spontaneity. Before proving this, we need to remember to remove the kilo prefix in the standard Gibbs free energy value, as R is expressed in J:

$$\begin{aligned} \Delta G_R &= \Delta G_R^\circ + RT \ln Q_p = \Delta G_R^\circ + RT \ln \left[\frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} \right] \\ &= 5.4 \times 10^3 + 8.314 \cdot 298 \ln \left[\frac{(1 \times 10^5)^2}{1 \times 10^{-5}} \right] = 9 \times 10^4 \text{ J/mol} \end{aligned}$$

As Gibbs free-energy is a positive number, the reaction will not proceed spontaneously.



◆ STUDY CHECK

Predict whether the reaction will proceed spontaneously at 298K under the following pressure conditions: $P_{\text{NO}_2} = 1 \times 10^{-5}$ atm and $P_{\text{N}_2\text{O}_4} = 1 \times 10^5$ atm



$$\blacktriangleright \Delta G_R = -8 \times 10^4 \text{ J/mol spontaneous}$$

Relationship between ΔG_R° and K_p On one hand, at fixed pressure and temperature, the Gibbs free-energy does not change: $\Delta G_R = 0$. On the other hand, at fixed pressure and temperature, the entropy of the universe does not change: $\Delta S_{univ} = 0$.

At the same time, in equilibrium conditions, the value of the equilibrium constant is the same as the value of the reaction ration: $Q_p = K_p$. Hence, we can relate the equilibrium constant and the standard Gibbs free-energy:

$$\boxed{\Delta G_R^\circ = -RT \ln K_p} \quad (7.23)$$

where:

K_p the equilibrium constant in terms of pressure

ΔG_R° is the Gibbs free-energy of a reaction at standard conditions (1atm and 298K)

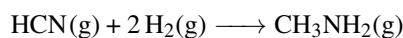
R is the constant of the gases in energy units (8.314J/mol· K)

T is the absolute temperature

In other words, the value of the equilibrium constant and the standard Gibbs free-energy convey the same information. On one hand, when $\Delta G_R^\circ < 0$ we have that $K_p > 1$ and in the reactive mixture we will have more products than reactants: the reaction will happen spontaneously. On the other hand, when $\Delta G_R^\circ > 0$ we have that $K_p < 1$ and in the reactive mixture will have more reactants than products: the reaction will not happen spontaneously.

Sample Problem 98

Use the data below to calculate the equilibrium constant of the reaction at 400K:



Compound	G_f° (kJ/mol)
$\text{CH}_3\text{NH}_{2(\text{g})}$	23.99
$\text{HCN}_{(\text{s})}$	124.7

SOLUTION

We can compute the Gibbs free-energy of a reaction by means of the free-energies of the molecules involved in the reaction:

$$\begin{aligned} \Delta G_R^\circ &= \Delta G_{products}^\circ - \Delta G_{reactants}^\circ = \\ &\left[\Delta G_f^\circ(\text{CH}_3\text{NH}_{2(\text{g})}) \right] - \left[1 \cdot \Delta G_f^\circ(\text{HCN}_{(\text{g})}) + 2 \cdot \Delta G_f^\circ(\text{H}_{2(\text{g})}) \right] \\ &= [23.99] - [1 \cdot 124.7 + 2 \cdot 0] = -100.71 \text{ KJ} \end{aligned}$$



Now we can convert the Gibbs free-energy of the reaction into K_c . Mind that we need to remove the Kilo prefix in the Gibbs free energy:

$$-100.71 \times 10^3 = -RT \ln K_p = -8.314 \cdot 400 \ln K_p$$

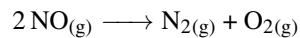
Solving for K_p we have that:

$$K_p = e^{\frac{100.71 \times 10^3}{8.314 \cdot 400}} = 1.4 \times 10^{13}$$

We have that, as the Gibbs free-energy of reaction is negative, the value of the equilibrium constant is larger than 1. This means that the reaction will proceed spontaneously and that there will have more products than reactants in the reaction mixture.

❖ **STUDY CHECK**

Use the data below to calculate the equilibrium constant of the reaction at 400K given that $G_f^\circ(\text{NO}_{(\text{g})})=87.60\text{KJ/mol}$:



$$\blacktriangleright K_p = 7.6 \times 10^{22}$$

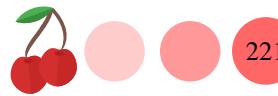


Table 7.5 Standard thermodynamic functions at 1 atm and 298 K.*

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	ΔS° (J/mol · K)	Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	ΔS° (J/mol · K)	Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	ΔS° (J/mol · K)	
Al	0	0	28.3	Ba(BrO ₃) _{2(s)}	-752.7	-577.4	243.0	BN _(s)	-254.4	-228.4	14.8	CaCl ₂ · 6H ₂ O _(s)
Al _(s)	5483.9	NA [†]	149.9	Ba(BrO ₃) ₂ · H ₂ O _(s)	-1054.8	-824.6	292.5	B ₂ S _{3(s)}	-240.6	-229.0	57.4	Ca(ClO ₄) _{2(s)}
Al ²⁺ _(g)	-524.7	-481.2	—	BaL _(s)	-602.1	-609.0	167.0	Br	0	0	152.2	CaBr _{2(s)}
Al ^{3+(aq)}	-1504.1	-1425.1	66.4	BaL · 2H ₂ O _(s)	-1216.7	NA [†]	0.63	Br ₍₂₀₎	30.9	3.1	245.4	CaBr ₂ · 6H ₂ O _(s)
AlF _{3(s)}	-704.2	-628.9	110.7	Ba(IIO ₃) _{2(s)}	-1027.2	-864.8	249.0	Br _(g)	-233.9	-238.7	163.4	Ca(BrO ₃) _{2(s)}
AlCl _{3(s)}	-2691.6	NA [†]	NA [†]	Ba(IIo ₃) ₂ · H ₂ O _(s)	-1322.1	-1104.2	297.0	Cd	Cal ₍₂₎	—	—	Na [†]
AlCl ₃ · 6H ₂ O _(s)	-572.2	-488.4	163.2	BaO _(s)	-553.5	-525.1	70.4	Cd _(s)	0	0	51.8	Ca ₂ H ₂ O _(s)
AlB _{3(s)}	-313.8	-300.8	159.0	BaO _{2(s)}	-634.3	-572.0	65.7	Cd ₂₊	0	0	51.8	Ca ₂ H ₂ O _(s)
Al ₍₃₎	-1675.7	-1582.4	50.9	Ba(OH) _{2(s)}	-944.7	-855.2	99.7	Cd _(g)	262.5	NA [†]	167.7	Ca(IIO ₃) _{2(s)}
Al ₂ O _{3(s)}	-1287.4	-1149.8	85.4	BaCO _{3(s)}	-1216.3	-1137.6	112.1	CdF _{2(s)}	70.04	-647.7	77.4	Ca(IIO ₃) ₂ · H ₂ O _(s)
Al(OH) _{3(s)}	-2850.5	-2203.9	467.8	Ba(HCO ₃) _{2(s)}	-1921.6	-1734.3	192.0	CdCl _{2(s)}	-391.5	-344.0	115.3	Ca(IIO ₃) ₂ · 6H ₂ O _(s)
Al(NO ₃) ₃ · 6H ₂ O _(s)	-723.8	NA [†]	decomp.	Ba(S _s)	-992.1	-796.7	213.8	CdCl ₂ · H ₂ O _(s)	-68.4	-587.1	167.8	CaO _(s)
Al ₂ S _{3(s)}	-3440.0	-3100.1	239.3	Ba(S ₄) _{2(s)}	-460.0	-456.0	78.2	Cd(ClO ₄) _{2(aq)}	-334.6	-94.8	290.8	Ca(OH) _{2(s)}
Al ₂ (SO ₄) _{3(s)}	-5311.7	-4622.6	469.0	BaCrO _{4(s)}	-1428.0	-1362.3	151.9	Cd(ClO ₄) ₂ · 6H ₂ O _(s)	-305.7	NA [†]	—	Na [†]
Al ₂ (SO ₄) ₃ · 6H ₂ O _(s)	-8878.9	-7437.5	—	BaC ₂ O _{4(s)}	-1368.6	NA [†]	5.2 × 10 ⁻⁵	Cd ₂ _(s)	-303.3	-201.4	161.1	CaCO _{3(s)} , calcite
Sb ³⁺	2703.3	NA [†]	168.7	Be	—	—	5.20 × 10 ⁻⁵	Cd(IIO ₃) _{2(s)}	NA [†]	377.1	NA [†]	Ca(NO ₃) _{2(s)}
SbH _{3(g)}	145.1	147.7	232.7	Be _(s)	0	0	9.5	Cd(OH) _{2(s)}	-258.2	-228.4	54.8	Ca(NO ₃) ₂ · 2H ₂ O _(s)
SbF _{3(s)}	-915.2	-807.0	105.4	Be ₂₊	299.3	NA [†]	136.2	Cd(CN) _{2(s)}	-560.7	-473.6	96.0	Ca(NO ₃) ₂ · 3H ₂ O _(s)
SbCl _{3(s)}	-382.7	-323.7	184.0	Be ₂ _(s)	-1026.8	-979.5	53.2	Cd(NO ₃) ₂ · 2H ₂ O _(s)	-162.2	-207.9	104.2	Ca ₂ N ₂ _(g)
SbCl _{5(l)}	-440.2	-350.2	301.0	BeCl _{2(s)}	-490.4	-445.6	82.7	Cd(NO ₃) ₂ · 4H ₂ O _(s)	-1055.6	-748.9	NA [†]	Na [†]
Sb ₄ O _{6(g)}	-1440.6	-1268.2	220.9	BeCl ₂ · 4H ₂ O _(s)	-1808.3	-1563.0	243.1	Cd(NO ₃) ₂ · 4H ₂ O _(s)	-1649.0	-1217.1	NA [†]	CaSO _{4(s)}
Sb ₂ S ₃ (black) _(s)	-174.9	-173.6	182.0	BeBr _{2(s)}	-353.5	-354.0	112.1	CdS _(s)	-161.9	-156.5	64.8	CaSO ₄ · 0.5H ₂ O _(s)
Sb ₂ (SO ₄) _{3(s)}	-2402.5	NA [†]	—	BeO _(s)	-609.6	-580.3	14.1	CdSO _{4(s)}	-93.3	-822.8	123.0	Ca ₃ (PO ₄) _{2(s)}
As	0	0	35.1	Be(OH) _{2(s)}	-902.4	-815.0	51.9	CdSO ₄ · 2.67H ₂ O _(s)	-1729.4	-1465.3	229.6	Ca ₃ CrO ₄ · 2H ₂ O
As _(s)	5950.2	NA [†]	162.3	Be(S ₂) ₃ · 3H ₂ O _(s)	-787.8	NA [†]	0.804	Cs	0	0	0	Na [†]
AsBr _{3(s)}	66.4	68.9	222.7	BeS _(4s)	-234.3	-232.0	35.0	Cs _(s)	0	0	0	Ca ₂ O _{4(s)}
AsH _{3(g)}	-956.3	-909.1	181.2	BeSO ₄ · 4H ₂ O _(s)	-1205.2	-1093.9	77.9	Cs ₁₊	458.0	NA [†]	169.7	Ca ₂ O ₄ · H ₂ O _(s)
AsF _{3(l)}	-920.6	-905.7	289.0	Bi	-2423.7	-2080.7	234.0	CsF _(s)	-533.5	-525.5	92.8	CaS _{2(s)}
AsF _{3(g)}	-305.0	-259.4	216.3	Bi _(s)	0	0	56.9	Cs ₂ Cl _{3(s)}	-443.0	-414.5	101.2	CaSiO _{3(s)}
As ₃ C _{3(l)}	-197.5	-169.0	161.1	Bi ₂₊	500.57	NA [†]	56.9	Cs ₂ ClO _{3(s)}	-411.7	-307.9	156.1	Ca ₂ SiO _{5(s)}
AsBr _{3(s)}	-65.3	-57.0	117.0	Bi _{3(s)}	-379.1	-315.1	177.0	Cs ₂ Br _(s)	-405.8	-391.4	175.1	C _(s) , graphite
As ₂ O _{5(s)}	-924.9	-782.4	105.4	Bi(CIO ₃) _{3(s)}	-366.9	-322.2	120.5	Cs ₂ I _(s)	-346.0	-340.6	123.1	C _(g) , diamond
As ₂ O _{3(s)}	-169.0	-168.6	163.6	Bi ₃ _(s)	-105.3	-175.3	233.9	Cs ₂ O _{4(s)}	-343.0	-380.7	184.0	Ca ₂ Ge
As ₄ O _{6(s)}	-1314.0	-1153.0	223.0	Bi ₃ O _{3(s)}	-57.9	-493.7	151.5	C ₃ O _{5(s)}	-345.8	-308.2	146.9	C ₃ G
Ba	0	0	66.9	Bi ₂ S _{3(s)}	-143.1	-140.6	200.46	Cs ₂ OH _(s)	-417.2	-359.0	86.0	CCl _{4(l)}
Ba _(s)	1660.5	NA [†]	170.2	Bi ₂ (SO ₄) _{3(s)}	-2544.3	-2583.6	NA [†]	CsHCO _{3(s)}	-96.1	-831.8	130.0	CO _{2(g)}
Ba ²⁺	-53.0	-56.0	9.6	B _(s)	0	0	5.9	CsNO _{3(s)}	-506.0	-406.6	155.2	CO _{2(g)}
Ba ^{2+(aq)}	-178.7	-132.2	NA [†]	B	7468.0	NA [†]	138.5	Cs ₂ SO _{4(s)}	-1443.0	-1323.7	211.9	CO _{2(aq)}
BaH _{2(s)}	-1207.1	-1156.9	96.4	B ₂ H _{6(g)}	35.6	86.6	232.0	Ca	0	0	0	Na [†]
BaCl _{2(s)}	-85.6	-81.0	123.7	B ₂ F _{6(g)}	-137.0	-1120.3	254.0	Ca ₂₊	1925.0	NA [†]	154.8	C ₂ N _{2(g)}
BaCl ₂ · 2H ₂ O _(s)	-1406.1	-1296.5	202.9	B ₂ C _{3(l)}	-427.2	-387.4	206.3	CaH _{2(s)}	-186.2	-147.3	42.0	C ₂ S _(g)
Ba(ClO ₃) _{2(s)}	-762.7	-556.9	231.0	B ₂ Cl _{3(g)}	-403.7	-388.7	290.0	CaF _{2(s)}	-1219.6	-1167.3	68.9	T _{73.1}
Ba(ClO ₄) ₂ · H ₂ O _(s)	-1069.0	-NA [†]	0.125	B ₃ (g)	71.1	20.8	349.1	CaCl _{2(s)}	-79.5	-748.1	104.6	Cl _{2(g)}
Ba(ClO ₄) _{2(s)}	-80.0	-535.1	249.0	B ₂ O _{3(s)}	-1272.8	-1193.7	54.0	CaCl ₂ · H ₂ O _(s)	-1109.2	-1010.9	NA [†]	Cl _{1(g)}
BaBr _{2(s)}	-757.3	-736.8	146.0	B ₂ O _{3(l)}	-1254.5	-1182.4	77.8	CaCl ₂ · 2H ₂ O _(s)	-1042.9	NA [†]	0.665	Cl ₂ O _(g)
BaBr ₂ · 2H ₂ O _(s)	-1366.1	-1230.5	226.0	B(OH) _{3(s)}	-1094.0	-969.0	88.8	CaCl ₂ · 4H ₂ O _(s)	-2009.6	-1724.0	212.6	ClO _{2(g)}

* Adapted from: https://issr.edu.kh/science/Reference_Tables_and_Values/20Science%20Book%20Data%20Field%20Advances%20Science%20Tables_and_Values/10545-Nuffield%20Field%20Data.pdf



Table 7.5 (continued) Standard thermodynamic functions at 1 atm and 298K.

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	ΔS° (J/mol·K)	Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	ΔS° (J/mol·K)	Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	ΔS° (J/mol·K)	
Cr	0	23.8	Cu(I) O_3) ₂ ·H ₂ O(s)	-377.8	-190.4	137.2	HBr(g)	-364	-53.4	198.6	FeBr ₂ (s)	
Cr ³⁺ (aq)	-232.0	-NA [†]	Cu ₂ O(s)	-692.0	-468.6	247.2	H(g)	26.5	1.7	206.5	FeI ₂ (s)	
CrF ₃ (s)	-1159.0	-1088.0	93.9	CuO ₂ (s)	-168.6	-146.0	93.1	HIO ₃ (s)	-230.1	-144.3	118.0	FeI ₃ (g)
CrCl ₂ (s)	-326.0	-282.0	115.0	Cu(OH) ₂ (s)	-157.3	-129.7	42.6	H ₂ O(l)	-285.8	-237.2	69.9	FeO ₃ (s)
CrCl ₃ (s)	-556.5	-486.2	115.3	Cu(NO ₃) ₂ (s)	-449.8	-359.4	75.0	H ₂ O(g)	-241.8	-228.6	188.7	Fe ₂ O ₃ (s)
CrO ₂ ·L ₂ (l)	-579.5	-510.9	221.8	Cu(NO ₃) ₂ ·3H ₂ O(s)	-1217.1	-NA [†]	0.570	H ₂ O ₂ (l)	-187.8	-120.4	109.6	Fe ₃ O ₄ (s)
Cr ₂ O ₃ (s)	-205.0	-202.5	NA [†]	Cu(NO ₃) ₂ ·6H ₂ O(s)	-2110.8	NA [†]	0.824	H ₂ AsO ₃ (aq)	-902.5	NA [†]	-113.0	-128.4
CrO ₃ (s)	-1139.7	-1058.1	81.2	CuS(s)	-79.0	-86.2	120.9	HCN(l)	108.9	124.9	112.8	Fe(OH) ₃ (s)
Cr ₂ (SO ₄) ₃ (s)	-598.5	-501.0	NA [†]	CuS ₂ (s)	-53.1	-53.6	66.5	HCN(g)	135.1	124.7	201.7	Fe(CO) ₅ (l)
Cr ₂ (SO ₄) ₃ ·18H ₂ O(s)	-3025.0	NA [†]	0.163	CuSO ₄ (s)	-771.4	-661.9	109.0	H ₂ CO ₃ (aq)	-699.6	-623.3	187.4	FeS ₂ (s)
Cr(CO) ₆ (s)	-1076.9	-975.0	NA [†]	CuSO ₄ ·5H ₂ O(s)	-2279.6	-1880.1	300.4	HCO ₃ ⁻ (aq)	-692.0	-586.8	91.2	FeS ₂ (s)
Co	0	0	30.0	F ₂ (g)	0	0	202.7	H ₂ S _(g)	-174.1	-80.8	266.3	FeSO ₄ (s)
Co ²⁺ (g)	2841.6	NA [†]	178.8	F ₂ O _(g)	-21.7	-4.7	247.3	H ₂ S _(aq)	-20.6	-33.6	205.7	FeSO ₄ ·7H ₂ O(s)
Co ₃ (g)	-810.9	-707.0	94.6	Ga ³⁺	5816.0	NA [†]	161.6	H ₂ SO ₄ (l)	-39.7	-27.9	121.3	Fe ₂ (s) ₄ 3(s)
CoCl ₂ (s)	-312.5	-269.9	109.2	Ga ³⁺	-1163.0	-1085.3	84.0	H ₂ SO ₄ (aq)	-909.3	-744.5	20.1	decomp.
CoCl ₂ ·2H ₂ O(s)	-923.0	-764.8	188.0	GaF ₃ (s)	-524.7	-454.8	142.0	H ₂ Te(g)	154.0	138.0	234.0	PbF ₆ (s)
CoCl ₂ ·6H ₂ O(s)	-2115.4	-1725.5	343.0	GaCl ₃ (s)	-386.6	-359.8	180.0	H ₃ PO ₄ (s)	-1279.0	-1192.2	110.5	PbCl ₂ (s)
Co(ClO ₄) ₂ (aq)	-316.7	-71.5	251.0	GaBr ₃ (s)	-238.9	-217.6	49.0	H ₃ BO ₃ (s)	-1094.3	-969.0	88.8	PbCl ₄ (l)
Co(ClO ₄) ₂ ·6H ₂ O(s)	-2038.4	NA [†]	0.707	Ga ₃ (s)	-1089.1	-998.3	85.0	H ₃ O ₁₊ ^(g)	979.9	NA [†]	NA [†]	PbBr ₂ (s)
CoBr ₂ (s)	-220.0	-210.0	135.6	Ga ₂ O ₃ (s)	Ge	OH _(g)	1328.4	NA [†]	NA [†]	NA [†]	-134.0	Pb(BrO ₃) ₂ (s)
CoBr ₂ ·6H ₂ O(s)	-2020.0	NA [†]	-101.3	158.2	Ge ⁴⁺	10412.3	NA [†]	OH _(g)	-140.9	NA [†]	-175.5	PbI ₂ (s)
CoI ₂ (s)	-88.7	-NA [†]	125.5	GeF ₄ (g)	-NA [†]	302.8	decomp.	H ₂ S _(aq)	995.0	NA [†]	-217.3	PbO(s)
Co(II) O_3) ₂ (aq)	-500.8	-310.4	267.8	GeCl ₂ (s)	-NA [†]	NA [†]	I	I	0	0	64.8	Na [†]
Co(II) O_3) ₂ ·2H ₂ O(s)	-1081.9	-795.8	53.0	GeCl ₄ (l)	-531.8	-462.8	245.6	I _(g)	-814.0	-690.1	916.8	Na [†]
Co ₃ O ₄ (s)	-237.9	-214.2	102.5	GeBr ₄ (l)	-347.7	-331.4	12(s)	I _(g)	-909.3	-744.5	-1.7	-24.4
Co(OH) ₂ (s)	-539.7	-454.4	79.0	GeBr ₄ (g)	-300.0	-318.0	280.7	I _(g)	-95.6	-118.5	-644.0	-617.1
Co(II) O_3) ₂ (s)	-420.5	-237.0	192.0	GeO(s)	-212.1	-237.2	50.0	I _(g)	967.5	NA [†]	-594.4	-314.1
Co(II) O_3) ₂ ·2H ₂ O(s)	-1021.7	NA [†]	GeO ₂ (s)	-551.0	-497.1	55.3	ICl _(s)	-35.1	NA [†]	-100.4	-240.9	
Co(II) O_3) ₂ ·3H ₂ O(s)	-1325.9	NA [†]	GeS _(s)	-69.0	-71.5	71.0	ICl ₃ (s)	-89.5	-22.3	167.4	PbSO ₄ (s)	
Co(II) O_3) ₂ ·4H ₂ O(s)	-1630.5	NA [†]	GeS ₂ (s)	-189.5	-NA [†]	0.00329	IBr(s)	-10.5	-NA [†]	138.1	PbCl ₄ O _(s)	
Co(II) O_3) ₂ ·6H ₂ O(s)	-2211.2	-1655.6	NA [†]	Au(s)	0	0	I ₂ O ₅ (s)	-158.1	-38.0	NA [†]	-899.6	
CoS _(s)	-80.8	-82.8	67.4	Au ₂ O ₃ (s)	-363.0	-297.5	211.0	NA [†] -	-196.6	-221.9	169.1	-1851.0
CoSO ₄ (s)	-888.3	-782.4	118.0	AuF ₃ (s)	294.9	265.7	174.7	Fe	0	0	52.7	NA [†]
CoSO ₄ (s)	-2979.9	-2473.8	406.1	AuH _(g)	-NA [†]	0	47.7	I _(g)	27.0	Li _(s)	336.4	472.5
Cu	0	0	33.2	AuCl ₃ (s)	-117.6	-55.2	210.9	Fe ₂ ⁺	2752.2	NA [†]	679.6	28.4
Cu ²⁺ (g)	3054.0	NA [†]	179.0	AuCl ₃ ·2H ₂ O(s)	-715.0	-519.0	147.3	Fe ₂ ⁺	-89.1	-78.9	137.7	Li _(aq) ⁺
CuF ₂ (s)	-542.7	-481.0	88.0	AuBr ₃ (s)	-53.3	-31.0	226.0	Fe ₃ ⁺	-48.5	-4.7	315.9	LiH _(s)
CuF ₂ ·2H ₂ O(s)	-981.6	NA [†]	AuI(s)	0.0	-0.2	119.2	FeF ₂ (s)	-686.0	-644.0	87.0	Li ₃ H _(s)	
CuCl _(s)	-137.2	-119.9	86.2	Au ₂ O ₃ (s)	-3.3	76.2	NA [†] -	FeF ₃ (aq)	-1046.4	-841.0	357.0	LiF _(s)
CuCl ₂ (s)	-220.1	-175.7	108.1	H ₂ (g)	H	H	FeCl ₂ (s)	-341.8	-302.3	117.9	LiCl(s)	
Cu(ClO ₄) ₂ (aq)	-193.1	48.3	264.4	very	Fe ₃ ⁺	Fe ₂ ⁺	FeCl ₂ ·2H ₂ O(s)	-953.1	-797.5	NA [†]	LiClO ₃ (s)	
Cu(ClO ₄) ₂ ·6H ₂ O(s)	-1928.4	NA [†]	118.0	HCl _(g)	-27.1	-273.2	173.7	FeCl ₃ (s)	-1549.3	-1275.7	NA [†]	LiClO ₄ (s)
CuBr ₂ (s)	-141.8	-108.7	293.7	HCl _(aq)	-92.3	-95.2	186.8	FeCl ₃ ·6H ₂ O(s)	-399.5	-334.1	142.3	LiClO ₄ ·3H ₂ O(s)
CuBr ₂ ·4H ₂ O(s)	-1326.3	-1081.1	-131.3	HCl _(aq)	-167.2	-131.2	56.5	Fe(ClO ₄) ₂ (aq)	-347.7	-96.1	226.4	LiBr _(s)
Cu ¹⁺ (s)	-67.7	-69.5	96.7	HClO _(aq)	-131.3	-80.2	106.8	Fe(ClO ₄) ₂ ·6H ₂ O(s)	-2086.6	NA [†]	0.270	LiBr _(s)



Table 7.5 (continued) Standard thermodynamic functions at 1 atm and 298K.

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	ΔS° (J/mol · K)	Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	ΔS° (J/mol · K)	Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	ΔS° (J/mol · K)
$\text{LiBr} \cdot 2\text{H}_2\text{O}_{(s)}$	-962.7	-840.6	162.3	$\text{MgSiO}_3^{(s)}$	-1549.0	-11462.1	67.7	$\text{NH}_4\text{OH}_{(l)}$	-361.2	-254.1	165.6
$\text{LiBrO}_3^{(s)}$	-347.0	NA [†]	86.8	$\text{MgSiO}_4^{(s)}$	-2174.0	-2055.2	95.1	$\text{NH}_4\text{NO}_3^{(s)}$	-365.6	-184.0	151.1
$\text{Li}_2^{(s)}$	-270.4	-270.3	123.0	$\text{Mn}_{(s)}$	0	0	32.0	$(\text{NH}_4)_2\text{SO}_4^{(s)}$	-1180.9	-901.9	220.1
$\text{Li}_1\text{H}_2\text{O}_{(s)}$	-590.3	-531.4	184.0	$\text{Mn}_{2+}^{(s)}$	2519.0	NA [†]	173.6	$\text{NH}_3^{(g)}$	46.1	-16.5	192.3
$\text{Li}_1\text{H}_2\text{O}_{(s)}$	-890.4	-780.3	233.0	$\text{Mn}_{(\text{aq})}^{(s)}$	-233.0	-228.0	-74.6	$\text{O}_{2(g)}$	0	0	205
$\text{Li}_1\text{H}_2\text{O}_{(s)}$	-1192.1	NA [†]	0.804	$\text{Mn}_{2+}^{(s)}$	-481.3	-440.5	118.2	$\text{O}_{3(g)}(\text{ozone})$	142.7	163.2	238.8
$\text{Li}_1\text{O}_3^{(s)}$	-503.4	NA [†]	0.442	$\text{MnCl}_{2(s)}$	-789.9	-696.2	174.1	$\text{OH}_{(\text{aq})}^{-1}$	-230.0	-157.2	-10.8
$\text{Li}_1\text{O}_2^{(s)}$	-597.9	-561.2	37.6	$\text{MnCl}_2 \cdot \text{H}_2\text{O}_{(s)}$	-1042.2	-942.2	182.8	$\text{P}_{(\text{s}),\text{white}}$	303.3	0	41.1
$\text{Li}_1\text{OH}_{(s)}$	-484.4	-439.0	42.8	$\text{MnCl}_2 \cdot 2\text{H}_2\text{O}_{(s)}$	-1687.4	-1423.8	303.3	$\text{P}_{4(g)}$	314.5	278.3	163.2
$\text{Li}_1\text{OH}_{(s)}$	-788.0	-681.0	71.2	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}_{(s)}$	-384.9	-365.7	138.0	$\text{PH}_{3(g)}$	5.4	13.4	210.1
$\text{Li}_2\text{CO}_3^{(s)}$	-1215.9	-1132.1	90.4	$\text{MnBr}_{2(s)}$	-705.0	NA [†]	-150.3	$\text{PH}_{4(g)}$	-69.9	0.8	123.0
$\text{Li}_1\text{CO}_3^{(s)}$	-969.6	-880.9	123.4	$\text{MnBr}_2 \cdot \text{H}_2\text{O}_{(s)}$	-155.4	-1292.4	291.6	Rb^{+}	490.1	NA [†]	164.2
$\text{Li}_3\text{N}_{(s)}$	-199.0	-155.4	37.7	$\text{MnBr}_2 \cdot 4\text{H}_2\text{O}_{(s)}$	-150.3	-152.7	152.7	$\text{RbH}_{(s)}$	-52.1	-32.2	NA [†]
$\text{Li}_1\text{NO}_3^{(s)}$	-483.1	-381.2	90.0	$\text{MnI}_{2(\text{aq})}^{(s)}$	-331.0	-250.6	NA [†]	$\text{PF}_{3(g)}$	-1595.8	NA [†]	82.1
$\text{Li}_1\text{NO}_3 \cdot 3\text{H}_2\text{O}_{(s)}$	-1374.4	-1103.7	223.4	$\text{MnI}_2 \cdot 2\text{H}_2\text{O}_{(s)}$	-842.7	-842.7	NA [†]	$\text{PF}_{5(g)}$	-319.7	-272.4	425.3
$\text{Li}_1\text{SO}_4^{(s)}$	-1436.5	-1321.8	115.1	$\text{MnI}_2 \cdot 4\text{H}_2\text{O}_{(s)}$	-1438.9	NA [†]	NA [†]	$\text{PCl}_{3(l)}$	-443.5	NA [†]	402.9
$\text{Li}_1\text{S}_2\text{O}_4^{(s)} \cdot \text{H}_2\text{O}_{(s)}$	-1735.5	-1565.7	163.6	$\text{MnO}_{(\text{s})}^{-1}$	-385.2	-362.9	59.7	$\text{POCl}_{3(l)}$	-597.1	222.5	427.2
$\text{Li}_1\text{PO}_4^{(s)}$	-2095.8	NA [†]	0.000257	$\text{MnO}_{4(\text{aq})}^{-1}$	-542.7	-449.4	191.0	$\text{PB}_{3(l)}$	-184.5	-175.7	240.2
$\text{LiAlH}_4^{(s)}$	-116.3	-44.8	78.7	$\text{Mn}_3\text{O}_4^{(s)}$	-1387.8	-1283.2	155.6	$\text{PB}_{5(l)}$	-269.9	NA [†]	300.4
$\text{Mg}_{(s)}$	0	0	32.5	$\text{MnO}_{2(\text{s}),\text{pyrolusite}}$	-959.0	-881.2	110.5	$\text{POB}_{3(s)}$	-458.6	NA [†]	151.9
$\text{Mg}_{2+}^{(s)}$	-466.9	-454.8	-138.1	$\text{Mn(OH)}_{2(s)}$	-520.0	-465.2	53.1	$\text{P}_{\text{OB}_{3(s)}}$	-164.0	NA [†]	30.5
$\text{MgF}_2^{(\text{s})}$	-1123.4	-1070.3	57.2	$\text{MnCO}_{3(s)}$	-695.4	-615.0	99.2	$\text{P}_4\text{O}_{6(s)}$	-1640.1	decomp.	NA [†]
$\text{MgCl}_{2(s)}$	-641.3	-591.8	89.6	$\text{Mn}(\text{NO}_3)_{2(s)}$	-894.1	-816.7	85.8	$\text{P}_4\text{O}_{10(s)}$	-2984.0	-2697.8	228.9
$\text{MgCl}_2 \cdot \text{H}_2\text{O}_{(s)}$	-966.6	-861.8	137.7	$\text{Mn}(\text{NO}_3)_{2 \cdot 6}\text{H}_2\text{O}_{(s)}$	-576.3	-503.3	168.6	$\text{P}_2\text{S}_{5(s)}$	251.0	NA [†]	84.1
$\text{MgCl}_2 \cdot 2\text{H}_2\text{O}_{(s)}$	-1279.7	-1118.1	179.9	$\text{MnS}_{(\text{s})}^{(s)}$	-2371.9	-1809.6	78.2	$\text{K}_+(\text{g})$	0	0	NA [†]
$\text{MgCl}_2 \cdot 4\text{H}_2\text{O}_{(s)}$	-1898.9	-1623.5	264.0	$\text{MnSO}_{4(\text{s})}$	-1065.2	-957.4	112.1	$\text{KF}_{(\text{g})}$	-567.3	-537.8	748.9
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}_{(s)}$	-2499.0	-2115.0	366.1	$\text{MnSO}_4 \cdot \text{H}_2\text{O}_{(s)}$	-1376.5	-1214.6	NA [†]	$\text{K}_-(\text{g})$	-1163.6	-1021.6	1051.0
$\text{Mg}(\text{ClO}_4)_{2(s)}$	-568.9	-432.2	213.0	$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}_{(s)}$	-2258.1	-1908.3	NA [†]	$\text{KCl}_{(\text{s})}$	-436.7	-409.2	82.6
$\text{Mg}(\text{ClO}_4)_{2 \cdot 2\text{H}_2\text{O}_{(s)}}$	-1218.7	NA [†]	NA [†]	$\text{MnSO}_4 \cdot 5\text{H}_2\text{O}_{(s)}$	-253.1	-2140.0	NA [†]	$\text{KClO}_{3(\text{s})}$	-397.7	-296.3	143.1
$\text{Mg}(\text{ClO}_4)_{2 \cdot 4\text{H}_2\text{O}_{(s)}}$	-1837.2	NA [†]	NA [†]	$\text{Hg}_{(s)}$	0	0	76.1	$\text{KClO}_{4(\text{s})}$	-432.8	-303.2	151.0
$\text{Mg}(\text{ClO}_4)_{2 \cdot 6\text{H}_2\text{O}_{(s)}}$	-2445.5	-1863.1	520.9	$\text{Hg}_{(\text{g})}$	0	0	16.0	$\text{KBr}_{(\text{s})}$	-393.8	-380.7	93.6
$\text{MgBr}_{2(s)}$	-524.3	-503.8	117.2	$\text{Hg}_{(\text{g})}$	61.32	-178.6	146.0	$\text{KBrO}_{3(\text{s})}$	-567.3	-535.8	181.4
$\text{MgBr}_2 \cdot 6\text{H}_2\text{O}_{(s)}$	-2410.0	-2056.0	397.0	$\text{Hg}_{2+}^{(s)}$	2890.4	NA [†]	174.9	$\text{KBrO}_{3(s)}$	-1163.6	-1021.6	147.3
$\text{MgI}_{2(s)}$	-364.0	-358.2	129.7	$\text{Hg}_{2+}^{2+}^{(s)}$	172.3	153.6	84.5	$\text{KBrO}_{4(\text{s})}$	-1630.7	-155.2	339.0
$\text{MgO}_{(\text{s})}$	-601.7	-569.4	26.9	$\text{Hg}_{2+}^{2+}^{(\text{aq})}$	-485.0	-455.6	160.7	$\text{KClO}_{3(s)}$	-1435.6	-1317.0	197.4
$\text{Mg}(\text{OH})_{2(s)}$	-924.5	-833.6	63.2	$\text{Hg}_{2+}^{2+}^{(\text{s}),\text{calomel}}$	-265.2	-210.8	192.5	$\text{KIO}_{3(s)}$	-432.8	-303.2	89.6
$\text{MgCO}_{3(s)}$	-1095.8	-1012.1	65.7	$\text{Hg}_{2+}^{2+}^{(\text{s})}$	-224.3	-178.7	146.0	$\text{KIO}_4(\text{s})$	-467.2	-361.4	4627.0
$\text{Mg}_2\text{N}_{2(s)}$	-460.7	-406.0	90.0	$\text{Hg}_{2+}^{2+}^{(\text{aq})}$	-160.9	-181.1	218.0	$\text{KIO}_4(\text{s})$	-360.2	-271.2	NA [†]
$\text{Mg}(\text{NO}_3)_{2(s)}$	-790.7	-589.5	164.0	$\text{Hg}_{2+}^{2+}^{(\text{aq})}$	-170.7	-153.1	172.0	$\text{KIO}_4(\text{s})$	-287.9	-174.5	149.2
$\text{Mg}(\text{ClO}_4)_{2 \cdot 2\text{H}_2\text{O}_{(s)}}$	-1409.2	NA [†]	soluble	$\text{Hg}_{2+}^{2+}^{(\text{s})}$	-121.3	-111.0	233.5	$\text{KIO}_4(\text{s})$	-327.9	-324.9	116.7
$\text{Mg}(\text{NO}_3)_{2 \cdot 6\text{H}_2\text{O}_{(s)}}$	-2613.3	-2080.7	452.0	$\text{Hg}_{2+}^{2+}^{(\text{s})}$	red	-105.4	-101.7	$\text{KOH} \cdot 2\text{H}_2\text{O}_{(s)}$	-501.4	-418.4	164.9
$\text{MgS}_{(\text{s})}$	-346.0	-341.8	50.3	$\text{Hg}_{2+}^{2+}^{(\text{s}),\text{red}}$	-90.8	-58.6	174.0	$\text{KOH}_{(\text{s})}$	-467.2	-361.4	1629.2
$\text{MgSO}_4^{(s)}$	-1284.9	-1170.7	91.6	$\text{Hg}(\text{OH})_{2(aq)}$	-355.2	-274.9	142.3	$\text{KCO}_3^{(s)}$	-361.4	-271.2	NA [†]
$\text{MgSO}_4 \cdot 2\text{H}_2\text{O}_{(s)}$	-1896.2	-1376.5	NA [†]	$\text{Hg}(\text{NO}_3)_{2 \cdot 2\text{H}_2\text{O}_{(s)}}$	-868.2	-563.2	NA [†]	$\text{KHO}_{3(s)}$	-369.8	-306.6	116.7
$\text{MgSO}_4 \cdot 4\text{H}_2\text{O}_{(s)}$	-2496.6	-2138.9	NA [†]	$\text{Hg}(\text{S})_{(\text{s}),\text{black}}$	-53.6	-47.7	88.3	$\text{KNO}_{3(s)}$	-494.6	-349.9	133.1
$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}_{(s)}$	-3086.9	-2632.2	348.1	$\text{Hg}(\text{S})_{(\text{s}),\text{red}}$	-58.6	-50.6	82.4	$\text{KCN}_{(\text{s})}$	-113.0	-101.9	134.3
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}_{(s)}$	-3388.7	-2871.9	372.0	$\text{Hg}_{2+}^{2+} \text{SO}_4^{(s)}$	-743.1	-625.9	200.7	$\text{KSCN}_{(\text{s})}$	-200.2	-178.3	124.3
$\text{Mg}(\text{PO}_4)_{2 \cdot 2\text{H}_2\text{O}_{(s)}}$	-4022.9	NA [†]	7.61×10^{-5}	$\text{Hg}_{2+}^{2+} \text{O}_{4(s)}$	-707.5	-590.0	145.0	$\text{K}_2\text{S}_{2(s)}$	-380.7	-364.0	104.6
$\text{Mg}_2\text{Si}_{2(s)}$	-75.0	-75.0	75.0	$\text{Hg}_{2+}^{2+} \text{O}_{4(s)}$	-1437.8	-1321.4	NA [†]	$\text{K}_2\text{SO}_{4(s)}$	-1437.8	-1321.4	175.6



Table 7.5 (continued) Standard thermodynamic functions at 1 atm and 298K.

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	ΔS° (J/mol · K)	Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	ΔS° (J/mol · K)	Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	ΔS° (J/mol · K)
$\text{Sn}^{4+}_{(\text{g})}$	10428.5	NA^\dagger	229.8	$\text{Na}_2\text{S}_2\text{O}_3(\text{s})$	-1123.0	-1028.0	155.0	$\text{Sn}^{4+}_{(\text{g})}$	9323.2	NA^\dagger	9943.3
$\text{Ag}_{(\text{g})}$	0	0	42.6	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}(\text{s})$	-2607.9	-2230.1	372.4	$\text{SnH}_4(\text{g})$	162.8	227.6	$\text{V}_{(\text{g})}^{4+}$
$\text{Ag}^+_{(\text{g})}$	1019.2	NA^\dagger	167.2	$\text{Na}_3\text{PO}_4(\text{s})$	-1917.4	-1788.9	173.8	$\text{SnCl}_{2(\text{s})}$	-325.1	NA^\dagger	-1403.3
$\text{Ag}^+_{(\text{aq})}$	105.2	77.1	72.7	$\text{Na}_2\text{SiO}_3(\text{s})$	-1554.9	-1461.0	113.8	$\text{SnCl}_{2(\text{s})} \cdot 2\text{H}_2\text{O}(\text{s})$	-921.3	-787.8	VF_{50}
$\text{AgF}^{(\text{s})}$	-204.6	-186.6	80.1	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}(\text{s})$	-3096.2	-291.1	189.2	$\text{SnCl}_{4(\text{l})}$	-511.3	-440.2	$\text{VF}_{5(\text{g})}$
$\text{AgF} \cdot 2\text{H}_2\text{O}(\text{s})$	-800.8	-671.1	174.9	$\text{NaNH}_2(\text{s})$	-123.8	-64.0	76.9	$\text{SnBr}_{2(\text{s})}$	-243.5	-205.6	$\text{VCl}_{2(\text{s})}$
$\text{AgF} \cdot 4\text{H}_2\text{O}(\text{s})$	-1388.3	-1147.3	268.0	$\text{Sr}^{2+}_{(\text{g})}$	268.0	Sr	1790.6	Na^\dagger	-243.5	-205.6	$\text{VC}_{3(\text{s})}$
$\text{AgCl}(\text{s})$	-127.1	-109.8	96.2	$\text{Sr}_{2(\text{s})}$	149.4	$\text{Sr}_{2(\text{s})}$	-1216.3	-1164.8	82.1	$\text{SnI}_{2(\text{s})}$	-285.8
$\text{AgClO}_3(\text{s})$	-25.5	61.7	80.1	$\text{SrCl}_{2(\text{s})}$	-828.9	-781.2	114.9	$\text{SnO}_{2(\text{s})}$	-580.7	-519.7	$\text{VBr}_{4(\text{g})}$
$\text{AgClO}_4(\text{s})$	-31.1	77.0	NA †	Na^\dagger	-96.9	107.1	-1136.8	-1036.4	172.0	$\text{V}_{12(\text{s})}$	-100.0
$\text{AgBr}(\text{s})$	-100.4	-96.9	152.7	$\text{SrCl}_{2(\text{s})} \cdot \text{H}_2\text{O}(\text{s})$	-1438.0	-1282.0	218.0	$\text{SnS}_{(\text{s})}$	-1629.2	-1443.0	$\text{VO}_{(\text{s})}$
$\text{AgBrO}_3(\text{s})$	-27.2	54.4	115.5	$\text{SrCl}_{2(\text{s})} \cdot 6\text{H}_2\text{O}(\text{s})$	-2623.8	-2241.2	390.8	$\text{Sn}(\text{SO}_4)_{2(\text{s})}$	155.2	155.2	$\text{V}_2\text{O}_3(\text{s})$
$\text{AgI}(\text{s})$	-61.8	-66.2	121.3	$\text{SrCl}(\text{O}_4)_{2(\text{s})}$	-762.8	Na^\dagger	247.1	$\text{Ti}^{2+}_{(\text{g})}$	2450.6	NA^\dagger	-155.0
$\text{Ag}_2\text{O}(\text{s})$	-31.0	-11.2	167.4	$\text{SrBr}_{2(\text{s})}$	-717.6	-697.1	135.1	$\text{Ti}^{3+}_{(\text{g})}$	9290.2	NA^\dagger	-149.6
$\text{Ag}_2\text{CO}_3(\text{s})$	-505.8	-436.8	140.9	$\text{SrI}_{2(\text{s})}$	-558.1	-562.3	159.0	$\text{TiH}_{2(\text{s})}$	-119.7	-80.3	$\text{XeF}_{2(\text{s})}$
$\text{Ag}_2\text{NO}_3(\text{s})$	-124.4	-33.5	107.2	$\text{SrI}_2 \cdot \text{H}_2\text{O}(\text{s})$	-886.0	Na^\dagger	-1182.4	$\text{TiCl}_{2(\text{s})}$	-513.8	-464.4	$\text{XeF}_{4(\text{s})}$
$\text{AgCN}(\text{s})$	146.0	156.9	-29.4	150.6	$\text{SrI}_2 \cdot 2\text{H}_2\text{O}(\text{s})$	-2388.6	Na^\dagger	$\text{TiCl}_{3(\text{s})}$	-720.9	-653.5	$\text{XeF}_{6(\text{s})}$
$\text{Ag}_2\text{S}(\text{s})$	-715.9	-618.5	206.4	$\text{SrI}_2 \cdot 6\text{H}_2\text{O}(\text{s})$	-1019.2	-855.2	234.0	$\text{TiCl}_{4(\text{s})}$	-804.2	-737.2	$\text{XeO}_{3(\text{s})}$
$\text{Ag}_2\text{SO}_4(\text{s})$	-712.1	-621.7	216.7	$\text{SrI}(\text{O}_3)_{2(\text{s})}$	-592.0	-561.9	54.4	$\text{TiBr}_{2(\text{s})}$	-402.0	-375.0	$\text{Zn}(\text{S})$
Na^\dagger	0	0	51.0	$\text{Sr}(\text{OH})_{2(\text{s})}$	-959.0	-869.4	88.0	$\text{TiBr}_{3(\text{s})}$	-548.5	-523.8	$\text{Zn}^{2+}_{(\text{g})}$
$\text{Na}^{+}_{(\text{g})}$	609.0	NA^\dagger	147.9	$\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}(\text{s})$	-3352.2	Na^\dagger	0.00655	$\text{TiBr}_{4(\text{s})}$	-616.7	-589.5	$\text{Zn}^{2+}_{(\text{aq})}$
$\text{Na}^{+}_{(\text{aq})}$	-240.1	-261.9	59.0	$\text{SrCO}_{3(\text{s})}$	-1220.1	-1104.4	97.1	$\text{TH}_{(\text{s})}$	-375.7	-371.5	$\text{ZnCl}_{2(\text{s})}$
$\text{NaH}(\text{s})$	-56.1	-33.5	40.0	$\text{Sr}(\text{HCO}_3)_{2(\text{aq})}$	-1927.9	-1731.3	150.6	$\text{TiO}_{2(\text{s})}$	-939.7	-884.5	$\text{ZnBr}_{2(\text{s})}$
$\text{NaF}(\text{s})$	-573.6	-543.5	51.5	$\text{Sr}(\text{NO}_3)_{2(\text{s})} \cdot 4\text{H}_2\text{O}(\text{s})$	-978.2	-780.1	194.6	$\text{Ti}_2\text{O}_{3(\text{s})}$	-1520.9	-1434.3	$\text{ZnL}_{2(\text{s})}$
$\text{NaCl}(\text{s})$	-411.2	-384.2	72.1	$\text{Sr}(\text{NO}_3)_{2(\text{s})} \cdot 4\text{H}_2\text{O}(\text{s})$	-215.48	-1730.7	369.0	W^\ddagger	1625.9	NA^\dagger	$\text{ZnO}(\text{s})$
$\text{NaClO}_3(\text{s})$	-365.8	-262.2	123.4	$\text{SrS}_{(\text{s})}$	-453.1	-448.5	68.2	$\text{W}^\ddagger_{(\text{g})}$	-1747.7	-1631.4	$\text{ZnCO}_{3(\text{s})}$
$\text{NaClO}_4(\text{s})$	-383.3	-254.9	142.3	$\text{SrSO}_{4(\text{s})}$	-1453.1	-1341.0	117.0	WF_{60}	-255.0	-213.6	$\text{Zn}(\text{NO}_3)_{2(\text{s})}$
$\text{NaBr}(\text{s})$	-361.1	-349.0	86.8	$\text{S}_{(\text{s}),\text{thrombic}}$	0	0	31.8	$\text{WCl}_{2(\text{s})}$	-467.0	-303.1	$\text{Zn}(\text{NO}_3)_{2(\text{s})} \cdot 6\text{H}_2\text{O}(\text{s})$
$\text{NaBrO}_3(\text{s})$	-951.9	-828.4	179.1	$\text{S}_{(\text{s}),\text{trombic}}$	33.1	85.8	-14.6	$\text{WCl}_{4(\text{s})}$	-682.5	-548.9	$\text{ZnS}_{(\text{s}),\text{wurtzite}}$
$\text{NaI}(\text{s})$	-344.1	-242.8	128.9	$\text{S}_{(\text{s}),\text{trombic}}$	-74.5	-731.4	291.9	$\text{WBr}_{6(\text{s})}$	-348.5	-328.0	$\text{ZnS}_{(\text{s}),\text{blende}}$
$\text{NaIO}_3(\text{s})$	-287.8	-286.1	98.5	$\text{S}_{4(\text{g})}$	-1209.0	-1105.4	291.7	$\text{WO}_{3(\text{s}),\text{wulfite}}$	-842.9	-764.1	$\text{ZnSO}_4^{(4)}(\text{s})$
$\text{NaIO}_3 \cdot \text{H}_2\text{O}(\text{s})$	-481.8	NA^\dagger	135.1	$\text{S}_{6(\text{g})}$	-77.5	-19.7	NA^\dagger	$\text{WS}_{2(\text{s})}$	-209.0	NA^\dagger	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$
$\text{NaIO}_3 \cdot 5\text{H}_2\text{O}(\text{s})$	-779.5	-634.1	162.3	$\text{SCl}_{4(\text{l})}$	-56.1	NA^\dagger	decomp.	$\text{WC}_{(\text{s})}$	-40.5	-40.2	35.6
$\text{Na}_2\text{O}(\text{s})$	-414.5	-375.5	75.1	$\text{S}_2\text{Cl}_{2(\text{s})}$	-59.4	4.2	NA^\dagger	U^\ddagger	-2112.9	-2029.3	379.7
$\text{Na}_2\text{O}_2(\text{s})$	-510.9	-447.7	95.0	$\text{SOCl}_{2(20)}$	-245.6	-197.9	307.9	$\text{UF}_{6(\text{g})}$	-1433.8	-1373.2	456.9
$\text{NaOH}_{(\text{s})}$	-425.6	-379.5	64.5	$\text{SO}_2\text{Cl}_{2(\text{l})}$	-394.1	-305.0	216.7	$\text{UCl}_{2(\text{s})}$	-1263.1	-1159.0	57.7
$\text{NaOH} \cdot \text{H}_2\text{O}(\text{s})$	-734.5	-629.4	99.5	$\text{SO}_2(\text{g})$	-29.8	-300.2	248.1	$\text{UCl}_{2(\text{O}_2(\text{s}))}$	-1129.7	-1075.3	150.5
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}(\text{s})$	-1130.7	-1044.5	135.0	$\text{SO}_3(\text{l})$	-441.0	-368.4	95.6	$\text{UO}_{2(\text{s})}$	-1263.6	-1184.1	77.8
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}(\text{s})$	-4081.3	-3428.2	564.0	$\text{SO}_3(\text{g})$	-396.0	-370.0	256.0	$\text{UO}_{3(\text{s})}$	-105.0	-101.0	98.6
$\text{NaHCO}_3(\text{s})$	-950.8	-851.0	101.7	$\text{S}_{(\text{g})}$	-278.8	238.3	167.8	$\text{U}_2\text{C}_{3(\text{s})}$	-1377.4	-1142.7	105.6
$\text{NaNO}_2(\text{s})$	-358.7	-284.6	103.8	$\text{S}_{2(\text{g})}$	128.4	79.3	228.1	$\text{UO}_2(\text{NO}_3)_{2(\text{s})}$	-1263.6	-1184.1	276.1
$\text{NaCN}(\text{s})$	-87.5	-76.4	115.6	$\text{S}_{6(\text{g})}$	102.3	49.7	430.9	$\text{UO}_2(\text{NO}_3) \cdot 6\text{H}_2\text{O}(\text{s})$	-3197.8	-2615.0	505.6
$\text{Na}_2\text{S}(\text{s})$	-364.8	-349.8	83.7	$\text{Sn}_{(\text{s},\text{white})}$	0	0	51.6	$\text{US}_{2(\text{s})}$	-502.0	-531.7	110.5
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(\text{s})$	-1387.1	-1270.2	149.6	$\text{Sn}_{(\text{s},\text{white})}^{+}$	2434.9	NA^\dagger	168.4	$\text{V}_{2(\text{g})}^{2+}$	-2590.5	NA^\dagger	169.4
$\text{NaHSO}_4(\text{s})$	-4327.3	-3647.4	592.0	$\text{Sn}_{(\text{s})}^{2+}$	-8.8	-27.2	-17.0	$\text{V}_{2(\text{g})}^{2+}$	5430.5	NA^\dagger	171.5
NaHSO_4	-1125.5	-992.9	113.0	$\text{Sn}_{(\text{aq})}^{2+}$							



CHAPTER 7

SPONTANEITY

7.1 Which of the following processes are spontaneous:

- (a) An apple falls down a tree
- (b) Water flowing down a river
- (c) Water flowing up a river
- (d) A ball rolling downhill

7.2 Which of the following processes are spontaneous:

- (a) A ball rolling uphill
- (b) Sugar dissolving in coffee
- (c) Cacao powder dissolving in cold water
- (d) An iron pipe rusting

7.3 Which of the following processes are spontaneous:

- (a) Boiling of water at 100°C and 1atm
- (b) Boiling of water at 50°C and 1atm
- (c) Boiling of water at 100°C and 2atm

7.4 Which of the following processes are spontaneous:

- (a) Melting of ice at 0°C
- (b) Melting of ice at 10°C
- (c) A diamond becoming graphite

ENTROPY

7.5 A hot container submerged in water releases 100J of energy at 298K. Calculate the entropy change of the hot container.

7.6 A cup of milk cools down in a refrigerator at 15°C, releasing 20J. Calculate the change in entropy in the milk.

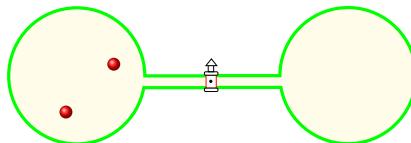
7.7 Calculate the entropy change in a gold nugget when it receives 50KJ at 100°C.

7.8 Calculate the entropy change in a gold nugget when it receives 50KJ at 50°C.

7.9 Calculate the entropy change when 200KJ of heat are being reversibly transferred from a hot reservoir at 300K into a cold reservoir at 200K.

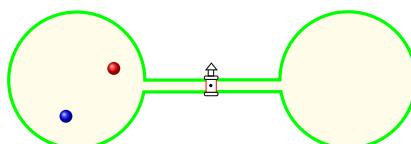
7.10 Calculate the entropy change when 40KJ of heat are being reversibly transferred from a cold reservoir at 100K into a cold reservoir at 400K.

7.11 Think about the possible arrangements of two identical molecules in a two-bulbed flask:



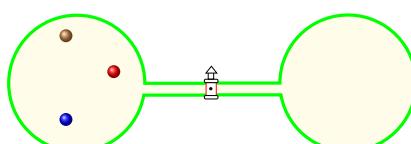
- (a) How many arrangements are possible?
- (b) Which is the most likely arrangement?
- (c) Which is the probability of the most likely arrangement?

7.12 Think about the possible arrangements of two different molecules in a two-bulbed flask:



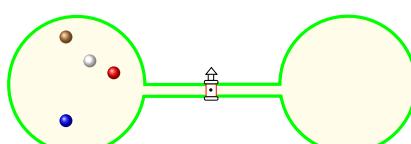
- (a) How many arrangements are possible?
- (b) Which is the most likely arrangement?
- (c) Which is the probability of the most likely arrangement?

7.13 Think about the possible arrangements of three different molecules in a two-bulbed flask:

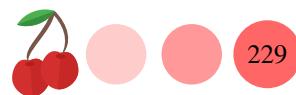


- (a) How many arrangements are possible?
- (b) Which is the most likely arrangement?
- (c) Which is the probability of the most likely arrangement?

7.14 Think about the possible arrangements of four different molecules in a two-bulbed flask:



- (a) How many arrangements are possible?
- (b) Which is the most likely arrangement?
- (c) Which is the probability of the most likely arrangement?

**STANDARD MOLAR ENTRPIES**

7.15 Indicate which substance in the pair will have a larger molar entropy at the same conditions: (a) NO or CO (b) H₂O or D₂O (ps: D is a heavy isotope of hydrogen) (c) NaCl(s) or NaCl(aq)

7.16 Indicate which substance in the pair will have a larger molar entropy at the same conditions: (a) I₂(s) or I₂(g) (b) CH₄(g) or CH₃Cl(g) (c) H₂(g) at 1atm or H₂(g) at 2atm

7.17 Indicate which substance in the pair will have a larger molar entropy at the same conditions: (a) H₂(g) at 298K or H₂(g) at 400K (b) C(graphite) or C(diamond) (c) He(g) or Ar(g)

7.18 Indicate which substance in the pair will have a larger molar entropy at the same conditions: (a) 2 moles H₂O(g) or 5 moles H₂O(g) (b) 5L H₂O(g) or 3L H₂O(g) (c) KCl(l) or KCl(aq)

CALCULATING ENTROPY CHANGES

7.19 A piece of metal with a heat capacity of 3 J/K is warmed up from 100°C to 300°C. Calculate the entropy change of the metal.

7.20 A piece of metal with a heat capacity of 5 J/K is cooled from 100°C to 50°C. Calculate the entropy change of the metal.

7.21 A 50-g piece of metal with a specific heat capacity of 0.5 J/g· K is warmed up from 300K to 400K. Calculate the entropy change of the metal.

7.22 A 4-g piece of metal with a specific heat capacity of 0.1 J/g· K is cooled from 300K to 200K. Calculate the entropy change of the metal.

7.23 Calculate the heat capacity of 3 moles of an ideal monoatomic gas measured at constant volume.

7.24 Calculate the heat capacity of 3 moles of an ideal monoatomic gas measured at constant pressure.

7.25 Calculate the heat capacity of 6 moles of an ideal diatomic gas measured at constant pressure.

7.26 Calculate the heat capacity of 9 moles of an ideal polyatomic gas measured at constant pressure.

7.27 Answer the following questions: (a) Calculate the entropy change of 3 moles of an ideal gas which volume increases two times at constant temperature. (b) Calculate the entropy change of 3 moles of an ideal gas which volume decreases two times at constant temperature.

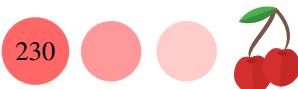
7.28 Answer the following questions: (a) Calculate the entropy change of 10 moles of an ideal gas which volume changes from 2L to 3L at constant temperature. (b) Calculate the entropy change of 1 moles of an ideal gas which volume changes from 2L to 3L at constant temperature.

7.29 Answer the following questions: (a) Calculate the entropy change of 2 moles of an ideal gas which pressure increases four times at constant temperature. (b) Calculate the entropy change of 2 moles of an ideal gas which pressure decreases four times at constant temperature.

7.30 Answer the following questions: (a) Calculate the entropy change of 10 grams of Helium (MW=2g/mol), an ideal gas, which pressure changes from 1 atm to 10 atm at constant temperature. (b) Calculate the entropy change of 10 grams of Helium (MW=2g/mol), an ideal gas, which pressure changes from 1 atm to 0.5 atm at constant temperature.

7.31 Answer the following questions: (a) We expand 10 moles of an ideal gas from 1L to 2L isothermally, and after that we increase its pressure from 1 atm to 5 atm. Calculate the entropy change of the gas. (b) We compress 10 moles of an ideal gas from 1 atm to 5 atm isothermally and after we expand the gas from 1L to 2L isothermally. Calculate the entropy change of the gas. (c) Compare the answers of the previous questions and justify its difference.

7.32 Answer the following questions: (a) A 10 moles sample of a monoatomic ideal gas ($C_v = \frac{3}{2}R$ and $C_p = \frac{5}{2}R$) is compressed from 10L to 1L and during the process its temperature increases from 200K to 300K. Calculate the entropy change of the gas. (b) A 10 moles sam-



ple of a monoatomic ideal gas ($C_v = \frac{3}{2}R$ and $C_p = \frac{5}{2}R$) is compressed from 1 atm to 5 atm and during the process its temperature increases from 100 K to 200 K. Calculate the entropy change of the gas.

STANDARD ENTROPY OF REACTION

7.33 Predict the sign (> 0 , < 0 or $\simeq 0$) of the standard entropy change for the following reactions:

- sublimation of a solid
- liquefaction of a gas
- melting of a solid

7.34 Predict the sign (> 0 , < 0 or $\simeq 0$) of the standard entropy change for the following reactions:

- vaporization of a liquid
- boiling of a liquid
- condensation of a liquid
- freezing of a liquid

7.35 Predict the sign (> 0 , < 0 or $\simeq 0$) of the standard entropy change for the following reactions:

- $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \longrightarrow \text{NH}_4\text{Cl}(\text{g})$
- $\text{C}_3\text{H}_8(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 3 \text{CO}(\text{g}) + 4 \text{H}_2(\text{g})$
- $\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$

7.36 Predict the sign (> 0 , < 0 or $\simeq 0$) of the standard entropy change for the following reactions:

- $\text{C}_{(s)} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$
- $\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \longrightarrow 2 \text{NH}_3(\text{g})$

7.37 Predict the sign (> 0 , < 0 or $\simeq 0$) of the standard entropy change for the following reactions:

- $\text{NH}_4\text{HS}_{(\text{g})} \longrightarrow \text{NH}_3(\text{g}) + \text{H}_2\text{S}_{(\text{g})}$
- $\text{PCl}_5(\text{g}) \longrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
- $\text{O}_2(\text{g}) + \text{O}_{(\text{g})} \longrightarrow \text{O}_3(\text{g})$

7.38 Predict the sign (> 0 , < 0 or $\simeq 0$) of the standard entropy change for the following reactions:

- $2 \text{NaCl}_{(\text{s})} + \text{F}_2(\text{g}) \longrightarrow 2 \text{NaF}_{(\text{s})} + \text{Cl}_2(\text{g})$
- $\text{CaCO}_{3(\text{s})} \longrightarrow \text{CaO}_{(\text{s})} + \text{CO}_2(\text{g})$
- $2 \text{Mg}_{(\text{s})} + \text{O}_2(\text{g}) \longrightarrow 2 \text{MgO}_{(\text{s})}$

7.39 Compute the standard entropy change for the following reaction filling the table below:

$\text{CH}_{4(\text{g})}$	+	$2 \text{O}_{2(\text{g})}$	\longrightarrow	$\text{CO}_{2(\text{g})}$	+	$2 \text{H}_2\text{O}_{(\text{g})}$
$S^\circ(\text{J/molK})$	186.3	205		213		188.7
n						
$S^\circ \cdot n$						
$\Delta S^\circ(\text{J/molK})$						

7.40 Compute the standard entropy change for the following reaction:

$6 \text{CO}_{2(\text{g})}$	+	$6 \text{H}_2\text{O}_{(\text{l})}$	\longrightarrow	$\text{C}_6\text{H}_{12}\text{O}_6_{(\text{s})}$	+	$6 \text{O}_{2(\text{g})}$
$S^\circ(\text{J/molK})$	213.7	69.95		209.2		205.1
n						
$S^\circ \cdot n$						
$\Delta S^\circ(\text{J/molK})$						

7.41 Compute the standard entropy change for the following reaction:

$2 \text{H}_2\text{O}_{(\text{l})}$	\longrightarrow	$2 \text{H}_{(\text{g})}$	+	$\text{O}_{2(\text{g})}$
$S^\circ(\text{J/molK})$	69.9		131.0	205.1
n				
$S^\circ \cdot n$				
$\Delta S^\circ(\text{J/molK})$				

7.42 Compute the standard entropy change for the following reaction:

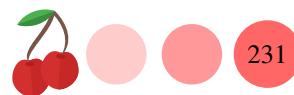
$\text{Fe}_2\text{O}_3_{(\text{s})}$	+	$3 \text{CO}_{(\text{g})}$	\longrightarrow	$2 \text{Fe}_{(\text{s})}$	+	$3 \text{CO}_2_{(\text{g})}$
$S^\circ(\text{J/molK})$	87.28	197.7		27.78		213.74
n						
$S^\circ \cdot n$						
$\Delta S^\circ(\text{J/molK})$						

7.43 Compute the standard entropy of the missing molecule given the entropy change for the following reaction:

$2 \text{H}_{2(\text{g})}$	+	$2 \text{NO}_{(\text{g})}$	\longrightarrow	$2 \text{H}_2\text{O}_{(\text{l})}$	+	$\text{N}_{2(\text{g})}$
$S^\circ(\text{J/molK})$	X	210.76		69.91		191.61
n						
$S^\circ \cdot n$						
$\Delta S^\circ(\text{J/molK})$				-315.29		

7.44 Compute the standard entropy of the missing molecule given the entropy change for the following reaction:

$\text{SO}_{(\text{g})}$	+	$\text{O}_{3(\text{g})}$	\longrightarrow	$\text{SO}_2_{(\text{g})}$	+	$\text{O}_{2(\text{g})}$
$S^\circ(\text{J/molK})$	221.94	X		248.22		205.15
n						
$S^\circ \cdot n$						
$\Delta S^\circ(\text{J/molK})$				-7.5		



THE SECOND AND THIRD LAW OF THERMODYNAMICS

7.45 For the following examples, identify the system, its surroundings and the universe: (a) A hot cup of coffee cooling on your desk (b) An air balloon in the atmosphere

7.46 For the following examples, identify the system, its surroundings and the universe: (a) An hot pot of soup in the refrigerator(b) Ice melting in a closed cup of water

7.47 Predict the spontaneity of the following processes selecting whether the forward process is spontaneous, the backwards process is spontaneous or both the forward and backwards are spontaneous:

Process	ΔS	ΔS_{surr}	ΔS_{univ}	Spontaneous \leftarrow	Spontaneous \rightarrow
A	100	100	200		
B	-100	100	0		
C	50	-100	-50		

7.48 Predict the spontaneity of the following processes selecting whether the forward process is spontaneous, the backwards process is spontaneous or both the forward and backwards are spontaneous:

Process	ΔS	ΔS_{surr}	ΔS_{univ}	Spontaneous \leftarrow	Spontaneous \rightarrow
D	-50	-50	-100		
E	100	-50	50		
F	20	10			

7.49 The standard entropy of vaporization of a chemical is 80J/K at its boiling point of 300K being the standard enthalpy of vaporization 20KJ. Answer the following questions: (a) Indicate the standard entropy of vaporization at its boiling point (b) Calculate the standard entropy of the surroundings during the vaporization (c) Calculate the total standard entropy during the vaporization (d) Is the process spontaneous?

7.50 For a certain process, the standard entropy is 30J/K at 300K whereas the standard enthalpy is -100KJ. Answer the following questions: (a) Calculate the standard entropy of the surroundings (b) Calculate the total standard entropy (c) Is the process spontaneous?

GIBBS FREE-ENERGY

7.51 Indicate if the following compounds are stable with respect to its corresponding elements at standard conditions: (a) SbH₃(g) (b) AlF₃(s) (c) B₂H₆(g)

7.52 Indicate if the following compounds are stable with respect to its corresponding elements at standard conditions: (a) As₂O₅(s) (b) AsH₃(g) (c) BaCl₂(s)

7.53 Compute the standard Gibbs free energy for the following reaction:

4 NH _{3(g)}	+	5 O _{2(g)}	→	4 NO _(g)	+	6 H ₂ O _(g)
$G_f^\circ(KJ/mol)$	-16.45	0		86.55		-228.57
n						
$G_f^\circ \cdot n(KJ)$						
$\Delta G_f^\circ(KJ)$						

7.54 Compute the standard Gibbs free energy for the following reaction:

Fe ₂ O _{3(s)}	+	3 CO _(g)	→	2 Fe _(s)	+	3 CO _{2(g)}
$G_f^\circ(KJ/mol)$	-742.2	-137.168		0		-394.359
n						
$G_f^\circ \cdot n(KJ)$						
$\Delta G_f^\circ(KJ)$						

7.55 Compute the standard Gibbs free energy for the following reaction at 298K:

CO _(g)	+	H ₂ O _(g)	→	CO _{2(g)}	+	H _{2(g)}
$H_f^\circ(KJ/mol)$	-110.525	-241.818		-393.509		0
$S^\circ(J/molK)$	197.674	188.825		213.74		130.684
$G_f^\circ \cdot n(KJ)$						
$\Delta G_f^\circ(KJ)$						

7.56 Compute the standard Gibbs free energy for the following reaction at 298K:

2 Fe ₂ O _{3(s)}	+	C _(s)	→	Fe _(s)	+	3 CO _{2(g)}
$H_f^\circ(KJ/mol)$	-824.2	0		0		-393.509
$S^\circ(J/molK)$	87.4	5.74		27.78		213.74
$G_f^\circ \cdot n(KJ)$						
$\Delta G_f^\circ(KJ)$						

7.57 Use the following thermodynamic data to predict if the following reactions are spontaneous, non spontaneous or conditionally spontaneous at 298K and 1atm: (a) Reaction 1: $\Delta H^\circ(KJ/mol)=100KJ$ and $\Delta S^\circ(J/K)=50J/K$ (b) Reaction 2: $\Delta H^\circ(KJ/mol)=10KJ$ and $\Delta S^\circ(J/K)=-50J/K$ (c) Reaction 3: $\Delta H^\circ(KJ/mol)=-100KJ$ and $\Delta S^\circ(J/K)=50J/K$ (d) Reaction 4: $\Delta H^\circ(KJ/mol)=-100KJ$ and $\Delta S^\circ(J/K)=-50J/K$

7.58 Use the following thermodynamic data to predict if the following reactions are spontaneous, non spontaneous or conditionally spontaneous at 298K and 1atm: (a) Re-

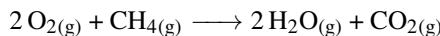


action 1: $\Delta H^\circ(KJ/mol) = -20KJ$ and $\Delta S^\circ(J/K) = -10J/K$ (b) Reaction 2: $\Delta H^\circ(KJ/mol) = 20KJ$ and $\Delta S^\circ(J/K) = 10J/K$ (c) Reaction 3: $\Delta H^\circ(KJ/mol) = -20KJ$ and $\Delta S^\circ(J/K) = 10J/K$ (d) Reaction 4: $\Delta H^\circ(KJ/mol) = 20KJ$ and $\Delta S^\circ(J/K) = -10J/K$

7.59 Use the following thermodynamic data to predict the temperature range over which the reaction will proceed spontaneously. Assume that $\Delta H^\circ(KJ/mol)$ and $\Delta S^\circ(J/K)$ do not significantly change with temperature: (a) Reaction 1: $\Delta H^\circ(KJ/mol) = 200KJ$ and $\Delta S^\circ(J/K) = 30J/K$ (b) Reaction 2: $\Delta H^\circ(KJ/mol) = 300KJ$ and $\Delta S^\circ(J/K) = -400J/K$

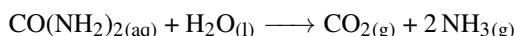
7.60 Use the following thermodynamic data to predict the temperature range over which the reaction will proceed spontaneously. Assume that $\Delta H^\circ(KJ/mol)$ and $\Delta S^\circ(J/K)$ do not significantly change with temperature: (a) Reaction 3: $\Delta H^\circ(KJ/mol) = 500KJ$ and $\Delta S^\circ(J/K) = 300J/K$ (b) Reaction 4: $\Delta H^\circ(KJ/mol) = -100KJ$ and $\Delta S^\circ(J/K) = -300J/K$

7.61 For the following reaction, the $\Delta H^\circ(KJ/mol)$ is $-800KJ$ whereas $\Delta S^\circ(J/K)$ is $-5J/K$:



- (a) Calculate ΔG° at 298K (b) Calculate ΔG° at 1000K
 (c) In which temperature range will the reaction proceed spontaneously

7.62 For the following reaction, the $\Delta H^\circ(KJ/mol)$ is $119KJ$ whereas $\Delta S^\circ(J/K)$ is $354J/K$:



- (a) Calculate ΔG° at 298K (b) Calculate ΔG° at 100K
 (c) Calculate ΔG° at 400K (d) In which temperature range will the reaction proceed spontaneously

GIBBS FREE-ENERGY AND EQUILIBRIUM

7.63 The standard enthalpy of fusion of methanol is $35.3KJ/mol$ and the standard entropy of fusion is $105J/molK$. Calculate the normal melting point of methanol.

7.64 The standard enthalpy of fusion of acetone is $29.1KJ/mol$ and the standard entropy of fusion is $88.3J/molK$. Calculate the normal melting point of acetone.

GIBBS FREE-ENERGY AND PRESSURE

CONDITIONS

7.65 Using the thermodynamic data presented below, calculate: (a) The Gibbs free energy at 298K and standard pressure conditions (b) The Gibbs free energy at 298K and the pressure conditions A (c) The Gibbs free energy at 298K and the pressure conditions B

$\text{CO}_{2(\text{g})}$	+	$3 \text{H}_{2(\text{g})}$	\longrightarrow	$\text{CH}_3\text{OH}_{(\text{g})}$	+	$\text{H}_2\text{O}_{(\text{g})}$
$G^\circ(KJ/mol)$	-394.359	0		-161.96		-228.572
$P_i(\text{atm})(\text{Conditions A})$	3	3		1		1
$P_i(\text{atm})(\text{Conditions B})$	1	1		2		2

7.66 Using the thermodynamic data presented below for the synthesis of dichloromethane, calculate: (a) The Gibbs free energy at 298K and standard pressure conditions (b) The Gibbs free energy at 298K and the pressure conditions A (c) The Gibbs free energy at 298K and the pressure conditions B

$\text{CH}_{4(\text{g})}$	+	$\text{Cl}_{2(\text{g})}$	\longrightarrow	$\text{CH}_2\text{Cl}_{2(\text{g})}$	+	$\text{HCl}_{(\text{g})}$
$G^\circ(KJ/mol)$	-50.72	0		-66.32		-95.299
$P_i(\text{atm})(\text{Conditions A})$	1×10^{-5}	1×10^{-5}		1×10^5		1×10^5
$P_i(\text{atm})(\text{Conditions B})$	1×10^2	1×10^2		1×10^{-4}		1×10^{-4}

7.67 Using the thermodynamic data presented below for the synthesis of methylamine, calculate: (a) The Gibbs free energy at 298K and standard pressure conditions (b) The equilibrium constant for the reaction at 298K (c) The equilibrium constant for the reaction at 500K

$\text{HCN}_{(\text{g})}$	+	$2 \text{H}_{2(\text{g})}$	\longrightarrow	$\text{CH}_3\text{NH}_{2(\text{g})}$
$G^\circ(KJ/mol)$	124.7	0		23.99

7.68 Using the thermodynamic data presented below for the synthesis of hydrofluoric acid, calculate: (a) The Gibbs free energy at 298K and standard pressure conditions (b) The equilibrium constant for the reaction at 298K (c) The equilibrium constant for the reaction at 500K

$2 \text{H}_2\text{O}_{(\text{g})}$	+	$2 \text{F}_{2(\text{g})}$	\longrightarrow	$4 \text{HF}_{(\text{g})}$	+	$\text{O}_{2(\text{g})}$
$G^\circ(KJ/mol)$	-228.572	0		-273.2		0

Ch. 8. Electrochemistry

BATTERIES are portable power devices, essential in our every day life. They power cellphones and even cars. Batteries use the principles of chemistry to produce electricity. Galvanic cells are textbook batteries, not intended to generate electricity as they function reversibly and in equilibrium. In the eighteenth century, Luigi Galvani discovered that animals' muscles—in particular dead frogs—could be artificially moved by touching the muscles with rods of different metals. The generated electricity at first was believed to come from the muscles. However, Alessandro Volta proved that the source of electricity in muscle movement was indeed the metals. Volta created the first Voltaic pile by stacking metallic silver and zinc disks separated by paper soaked in saltwater. This early discovery jumpstarted electrochemistry, a new field of chemistry. Indeed, chemical reactions can produce electricity, and electricity can drive chemical reactions.

8.1 Introduction to galvanic cells

Galvanic cells—also known as voltaic cells or piles—are electrochemical cells that generate electricity from spontaneous redox reactions. They contain two different metals immersed in electrolyte solutions. Each half-cell contains a metal in contact with a liquid solution of the same metal in ionic form. Both half-cells are either connected by a salt bridge or separated by a porous membrane. Galvanic cells differ from batteries. Batteries are composed of multiple single cells working out of equilibrium while producing electricity. Galvanic cells are textbook batteries. They are reversible devices unable to produce electricity.

Components of a galvanic cell Galvanic cells are composed of two different electrodes, an anode, and a cathode, connected by means of a salt bridge or a membrane. The role of the salt bridge or membrane is to complete the electrical circuit. Anodes are sources of electrons, whereas cathodes are electron sinks. At the same time, anodes generate positive cations, whereas cathodes generate negative anions. The role of the salt bridge or membrane is also to allow the charges generated in the cathode to be compensated by the charges generated in the anode. Electrodes contain two different redox states of the same element in contact with each other. An example of an electrode would be a piece of metallic copper Cu in contact with a solution of $\text{Cu}_{(\text{aq})}^{2+}$ ions. However, electrodes are not always made of metals. For example, electrodes can contain gas in contact (e.g. $\text{H}_{2(\text{g})}$) with an electrolyte solution (e.g. $\text{H}_{(\text{aq})}^+$). Electrodes without a metall being directly involved in the redox reaction need to include an external metall to support the charge transfer. Metals such as Pt are normally used for this



purpose.

The electrodes: anode and cathode Every galvanic cell is composed of two electrodes: an anode and a cathode. Electrodes produce ionic and electronic charges. The oxidation occurs on the anode which is indicated with a negative (–) sign. Electrons are being produced in the anode resulting from an oxidation reaction. The reduction occurs on the cathode, indicated with a positive (+) sign. Electrons are being consumed in the cathode resulting from a reduction reaction. These electrodes also produce ions, in particular cations and anions which have a tendency to migrate inside the cell. Anodes generate cations (and consume anions, depending on the chemical reaction involved), whereas cathodes generate anions (and consume cations, again, depending on the chemical reaction involved). As such, anions have a tendency to migrate to the anode, as their concentration is lower there, whereas cations have a tendency to migrate to the cathode. The excess ionic charge is compensated in the interface between the electrode and the salt bridge or the membrane. Mind that in a galvanic cell only electrons flow through the circuit, by means of the wire connecting both electrodes. The ions involved have a tendency to migrate inside each of the electrodes but do not leave the electrode. The name of the electrodes—anode and cathode—results from the ionic flow involved in the galvanic cell: anions have a tendency to migrate towards the anode and cations to the cathode.

Cell potential Water flows down a waterfall due to the difference of potential energy between the high and low parts of the waterfall. Similarly, heat flows between a hot and a cold reservoir due to the difference in temperature between both locations. The force that drives the flow is heat is temperature. Electricity flows through a galvanic cell resulting from the difference of cell potential ΔE between both electrodes, the anode, and the cathode. The cell potential—also referred to as cell voltage, cell electromotive force, or cell *emf*—is the force that drives the flow of electrons. Anodes and cathodes have a characteristic cell potential associated with the electrochemical half-reaction happening in the electrode. The voltage of the anode (E_{anode}) is always lower than the one from the cathode ($E_{cathode}$). The combination of the anodic and cathodic voltage gives the overall cell potential measured in a galvanic cell. In particular, the overall voltage results from the voltage of the cathode with respect to the anode, so that the overall voltage of a galvanic cell is always positive.

Role of the salt bridge or the membrane The role of the salt bridge or the porous membrane is to compensate for the excess of ions generated in each electrode hence closing the electric circuit. Salt bridges contain saturated solutions of electrolytes containing ions with similar ionic mobility (KCl or NH₄NO₃). These electrolytes are also non-reactive with the chemicals involved in the galvanic cell. Each side of the salt bridge or membrane becomes charged due to ionic accumulation, with negative ions accumulating near the cathode and positive charges near the anode. Porous membranes impact the galvanic cell potential with an extra contribution called the liquid junction voltage. This voltage is due to the ion accumulation on both sides of the membrane. When using a salt bridge, the liquid junction voltage on the left side of the bridge compensates the salt bridge on the right side of the bridge so that overall the galvanic cell potential remains unaffected by the bridge.

A galvanic cell example Below we display a representation of the Daniell cell, a classical galvanic cell in which copper is oxidized by zinc. The name of the cell is in honor of John Daniell, a British chemist from the nineteenth century who was trying to develop an electric power supply to sustain telegraphy. He connected with a metallic

wire a zinc electrode in contact with a zinc sulfate solution to a copper electrode in contact with a copper (II) sulfate solution. In this cell, Copper(II) ions are converted into metallic copper in the cathode by means of the reaction $\text{Cu}_{(\text{aq})}^{2+} + 2 \text{e}^- \longrightarrow \text{Cu}_{(\text{s})}$, whereas metallic zinc is converted into zinc ions in the anode following the reaction $\text{Zn}_{(\text{s})} \longrightarrow \text{Zn}_{(\text{aq})}^{2+} + 2 \text{e}^-$. Copper(II) ions are being reduced whereas zinc is being oxidized. The cathode solution becomes negatively charged whereas the anode solution becomes positively charged. A porous membrane permeable to ions was used to avoid the charge buildup.

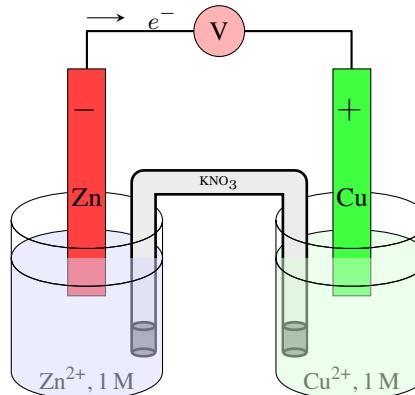
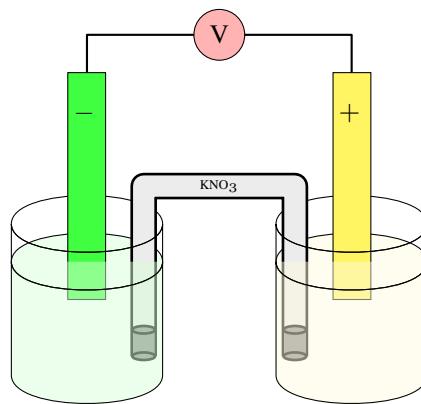


Figure 8.2 The Daniell galvanic cell

The potentiometer Voltmeters are devices used to measure cell potential, the number of Volts, in electric circuits. These devices work by drawing current through a known resistance. Voltmeter can not be used to precisely measure the voltage of a galvanic cell. As electricity flows into the voltmeter, frictional heating will occur and energy will be wasted. Hence the voltage measured would be lower than the real voltage. In order to avoid this problem in a lab setting, we normally use potentiometers to measure galvanic cells. Potentiometers apply a counter-voltage to compensate the cell voltage without drawing any significant current. Due to their high internal resistivity, there is no electricity flow in a voltaic cell connected to a voltmeter. The cell remains in equilibrium, and the electrodes are not consumed. Still, an ammeter could be used to measure the tendency of the cell to generate a measurable intensity flow, the number of Amperes.

Sample Problem 99

For the galvanic cell below, indicate: (a) label the electrode as anode and cathode (b) identify the flow of electrons (c) identify the flow of cations and anions (d) identify the oxidation and reduction





SOLUTION

(a) The electrode labeled with the – sign located on the left is the anode, where the oxidation takes place. Electrons are being produced in the anode and cations are also being generated in the anode (or perhaps anions are being consumed, it depends on the redox reaction happening). The electrode labeled with the + sign located on the right is the cathode, where the reduction takes place. Electrons are consumed in the cathode and anions are also being generated in the cathode.

(b) The flow of electrons goes from the anode on the left to the cathode on the right

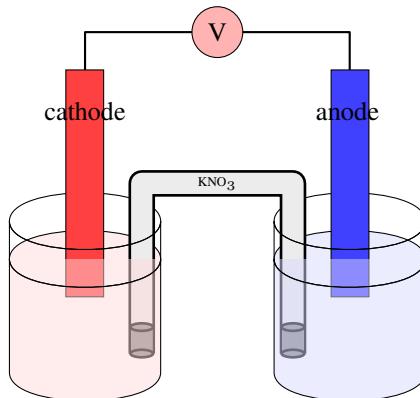
(c) Cations are being produced in the anode and they have a tendency to migrate towards the cathode. Anions are being produced in the cathode and they have a tendency to migrate towards the anode.

(d) The oxidation takes place on the anode on the left, whereas the reduction takes place on the cathode on the left.

◆ STUDY CHECK

For the galvanic cell below, indicate:

- label the signs of the electrodes
- identify the flow of electrons
- identify the flow of cations and anions
- identify the oxidation and reduction

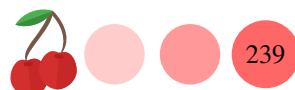


►Answer: (a) Anode, right, –; Cathode, left, + (b) from right to left (c) anions from left to right; cations from right to left (d) Oxidation on the right; reduction on the left

8.2 Standard reduction potentials

In a galvanic cell, each electrode—also called half-cell—has a given potential. When combining two electrodes, we obtain the measurable cell potential. This magnitude represents the force that pushed electrons from the anode to the cathode producing a measurable current. This section covers electrode potentials. We will define the concept of electrode potential, and we will identify the anode and cathode when two electrodes are in contact based on the electrode potentials.

Electrode potentials A galvanic cell consists of two electrodes, an anode, and a cathode. Each electrode contains two chemical species with different redox numbers in contact through an interface. For example, we can build up an electrode by soaking a piece of metallic copper on a solution of copper(II) sulfate. The interface consist of the liquid phase containing $\text{Cu}_{(\text{aq})}^{2+}$ in contact with the metal phase made of $\text{Cu}_{(\text{s})}$. Each electrode has a reduction potential— E , expressed in volts (V)—that informs about



the drive of the redox process in the electrode. The larger this value the stronger the tendency of the redox process to occur.

Standard conditions for reduction potentials The potential of a single electrode cannot be accurately measured as electrodes only exist in the context of a two-electrode galvanic cell. Single electrode potentials are defined in a galvanic cell made of the electrode and a reference electrode with null potential under certain conditions. The standard hydrogen electrode (SHE) is universally accepted as the reference electrode in electrochemistry, hence having null potential. The hydrogen electrode contains gas hydrogen in contact with an acidic 1M HCl solution at 25°C with a wire made of platinum—an inert metal—that mediates the electron transfer. Below you can find the reaction involved in the hydrogen electrode:



The voltage of a galvanic cell made of an electrode combined with the reference hydrogen electrode will directly measure the electrode potential. Still, electrode potentials depend on concentration (or pressure for gases) and temperature conditions. The standard conditions for electrode potentials are a molar concentration of 1M for all electrolytes and pressure of 1atm. The electrode potential measured at these conditions is called standard potential E° , where the symbol $^\circ$ represents standard state. At the same time, every redox reaction can be written as a reduction-consuming electrons—or an oxidation reaction-producing electrons. As we tabulate standard electrode potentials, all reactions will be written as reduction reactions and the standard potentials are called standard reduction potential E° .

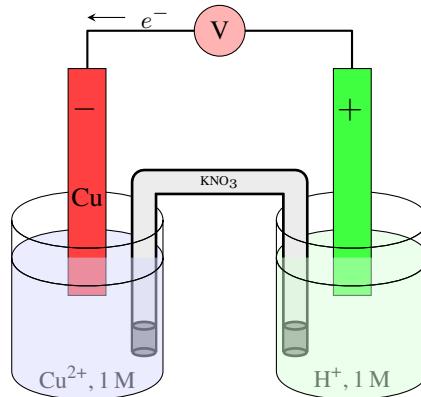
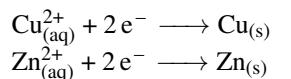


Figure 8.2 A galvanic cell with a hydrogen anode and a copper cathode. The hydrogen electrode is the reference electrode with null electrode voltage. Hence the voltage of this cell will directly give the copper electrode voltage.

Anodes and cathodes The standard reduction potential of an electrode predicts the tendency of an electrode to act as an anode or cathode. Imagine we have two different electrodes involving the following reaction with the standard potentials indicated on the side, and we need to set up a galvanic cell:



$$\begin{aligned} E^\circ &= +0.34 \text{ V} \\ E^\circ &= -0.76 \text{ V} \end{aligned}$$



How to determine which electrode will act as anode and which will act as cathode? The rule is the smaller the electrode potential the more tendency of the electrode to act as an anode. If we compare the copper and zinc electrodes, as the electrode potential of zinc is smaller—more negative—than the electrode potential of copper. Therefore, zinc will act as an anode and copper will act as a cathode. The standard reduction potential is not affected by the stoichiometry of the reaction. For example, the standard reduction potential of cesium is -3.03V :



At the same time, the standard reduction potential of two moles of cesium is still -3.03V .



Differently, inverting the reduction reaction switches the sign of the reduction potential. For example, the standard reduction potential of Titanium(II) is -1.63V

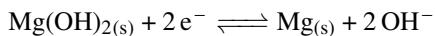


while the standard potential of oxidation of Titanium into Titanium(II) is $+1.63\text{V}$



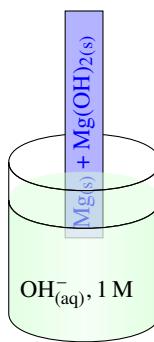
Sample Problem 100

Sketch a semi-cell for the semi reaction below, indicate if the electrode is a solid-liquid electrode or gas-liquid electrode. Assume standard conditions:



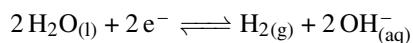
SOLUTION

This is a solid-liquid electrode. The solid piece would be made of Magnesium covered with magnesium hydroxide. The liquid phase would contain a base (OH^-). At standard conditions all molarities would be 1M.

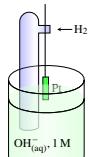


◆ STUDY CHECK

Sketch a semi-cell for the semi reaction below, indicate if the electrode is a solid-liquid electrode or gas-liquid electrode. Assume standard conditions:



► Answer:



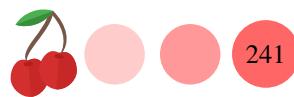


Table 8.1 Standard reduction potentials at 298K

Element	Reaction	E° (V)	Element	Reaction	E° (V)
Sr	$\text{Sr}^+ + \text{e}^- \rightleftharpoons \text{Sr}_{(s)}$	-4.10	H	$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(g)$	0.00
Ca	$\text{Ca}^+ + \text{e}^- \rightleftharpoons \text{Ca}_{(s)}$	-3.80	Ag	$\text{AgBr}_{(s)} + \text{e}^- \rightleftharpoons \text{Ag}_{(s)} + \text{Br}^-$	+0.07
Li	$\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li}_{(s)}$	-3.04	S	$\text{S}_4\text{O}_6^{2-} + 2\text{e}^- \rightleftharpoons 2\text{S}_2\text{O}_3^{-2}$	+0.08
Cs	$\text{Cs}^+ + \text{e}^- \rightleftharpoons \text{Cs}_{(s)}$	-3.03	N	$\text{N}_2(g) + 2\text{H}_2\text{O} + 6\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{NH}_4\text{OH}_{(aq)}$	+0.09
Ca	$\text{Ca}(\text{OH})_2 + 2\text{e}^- \rightleftharpoons \text{Ca}_{(s)} + 2\text{OH}^-$	-3.02	Hg	$\text{HgO}_{(s)} + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Hg}(l) + 2\text{OH}^-$	+0.10
Ba	$\text{Ba}(\text{OH})_2 + 2\text{e}^- \rightleftharpoons \text{Ba}_{(s)} + 2\text{OH}^-$	-2.99	C	$\text{C}_{(s)} + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{CH}_4(g)$	+0.13
Rb	$\text{Rb}^+ + \text{e}^- \rightleftharpoons \text{Rb}_{(s)}$	-2.98	Sn	$\text{Sn}^{4+} + 2\text{e}^- \rightleftharpoons \text{Sn}_2^{+}$	+0.15
K	$\text{K}^+ + \text{e}^- \rightleftharpoons \text{K}_{(s)}$	-2.93	Cu	$\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+$	+0.159
Ba	$\text{Ba}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ba}_{(s)}$	-2.91	Fe	$3\text{Fe}_2\text{O}_3_{(s)} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{Fe}_3\text{O}_4_{(s)} + \text{H}_2\text{O}$	+0.22
Sr	$\text{Sr}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sr}_{(s)}$	-2.90	Ag	$\text{AgCl}_{(s)} + \text{e}^- \rightleftharpoons \text{Ag}_{(s)} + \text{Cl}^-$	+0.22
Sr	$\text{Sr}(\text{OH})_2 + 2\text{e}^- \rightleftharpoons \text{Sr}_{(s)} + 2\text{OH}^-$	-2.88	Cu	$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}_{(s)}$	+0.34
Ca	$\text{Ca}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ca}_{(s)}$	-2.87	Fe	$\text{Fe}^+ + \text{e}^- \rightleftharpoons \text{Fe}_{(s)}$	+0.40
Li	$\text{Li}^+ + \text{C}_6\text{s}_{(s)} + \text{e}^- \rightleftharpoons \text{LiC}_6\text{s}_{(s)}$	-2.84	O	$\text{O}_2(g) + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^{-}_{(aq)}$	+0.40
Na	$\text{Na}^+ + \text{e}^- \rightleftharpoons \text{Na}_{(s)}$	-2.71	Cu	$\text{Cu}^+ + \text{e}^- \rightleftharpoons \text{Cu}_{(s)}$	+0.520
Mg	$\text{Mg}(\text{OH})_2 + 2\text{e}^- \rightleftharpoons \text{Mg}_{(s)} + 2\text{OH}^-$	-2.69	C	$\text{CO}_{(g)} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{C}_{(s)} + \text{H}_2\text{O}$	+0.52
Mg	$\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg}_{(s)}$	-2.37	I	$\text{I}_2(l) + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	+0.54
H	$\text{H}_2(g) + 2\text{e}^- \rightleftharpoons 2\text{H}^-$	-2.23	Mn	$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightleftharpoons \text{MnO}_2_{(s)} + 4\text{OH}^-$	+0.595
Sr	$\text{Sr}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sr}(\text{Hg})$	-1.79	O	$\text{O}_2(g) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_{(aq)}$	+0.70
Al	$\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al}_{(s)}$	-1.66	Fe	$\text{Fe}_2\text{O}_3_{(s)} + 6\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{Fe}^{2+} + 3\text{H}_2\text{O}$	+0.728
Ti	$\text{Ti}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ti}_{(s)}$	-1.63	Fe	$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
Ti	$\text{Ti}^{3+} + 3\text{e}^- \rightleftharpoons \text{Ti}_{(s)}$	-1.37	Ag	$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}_{(s)}$	+0.80
Ti	$\text{TiO}_{(s)} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Ti}_{(s)} + \text{H}_2\text{O}$	-1.31	Hg	$\text{Hg}_2^{2+} + 2\text{e}^- \rightleftharpoons 2\text{Hg}(l)$	+0.80
Mn	$\text{Mn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mn}_{(s)}$	-1.18	N	$\text{NO}_3^-_{(aq)} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{NO}_2(g) + \text{H}_2\text{O}$	+0.80
V	$\text{V}^{2+} + 2\text{e}^- \rightleftharpoons \text{V}_{(s)}$	-1.13	Fe	$2\text{FeO}_2^{2-} + 5\text{H}_2\text{O} + 6\text{e}^- \rightleftharpoons \text{Fe}_2\text{O}_3_{(s)} + 10\text{OH}^-$	+0.81
Ti	$\text{TiO}^{2+} + 2\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Ti}_{(s)} + \text{H}_2\text{O}$	-0.93	Hg	$\text{Hg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Hg}(l)$	+0.85
Si	$\text{SiO}_2(s) + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Si}_{(s)} + 2\text{H}_2\text{O}$	-0.91	Mn	$\text{MnO}_4^- + \text{H}^+ + \text{e}^- \rightleftharpoons \text{HMnO}_4^-$	+0.90
Fe	$\text{Fe}_2\text{O}_3_{(s)} + 3\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{Fe}(\text{OH})_2_{(s)} + 2\text{OH}^-$	-0.86	Hg	$2\text{Hg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Hg}_2^{2+}$	+0.91
H	$2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^-$	-0.828	Pd	$\text{Pd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pd}_{(s)}$	+0.915
Zn	$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}_{(s)}$	-0.762	N	$\text{NO}_3^-_{(aq)} + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{NO}_{(g)} + 2\text{H}_2\text{O}(l)$	+0.96
Cr	$\text{Cr}^{3+} + 3\text{e}^- \rightleftharpoons \text{Cr}_{(s)}$	-0.74	Fe	$\text{Fe}_3\text{O}_4_{(s)} + 8\text{H}^+ + 2\text{e}^- \rightleftharpoons 3\text{Fe}^{2+} + 4\text{H}_2\text{O}$	+0.98
Ni	$\text{Ni}(\text{OH})_{2(s)} + 2\text{e}^- \rightleftharpoons \text{Ni}_{(s)} + 2\text{OH}^-$	-0.72	Br	$\text{Br}_2(aq) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	+1.09
Ag	$\text{Ag}_2\text{S}_{(s)} + 2\text{e}^- \rightleftharpoons 2\text{Ag}_{(s)} + \text{S}_2^-_{(aq)}$	-0.69	Ag	$\text{Ag}_2\text{O}_{(s)} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{Ag}_{(s)} + \text{H}_2\text{O}$	+1.17
Pb	$\text{PbO}_{(s)} + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Pb}_{(s)} + 2\text{OH}^-$	-0.58	Pt	$\text{Pt}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pt}_{(s)}$	+1.188
Fe	$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}_{(s)}$	-0.44	Cl	$\text{ClO}^{-4} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{ClO}_3^- + \text{H}_2\text{O}$	+1.20
Cr	$\text{Cr}^{3+} + \text{e}^- \rightleftharpoons \text{Cr}_2^{+}$	-0.42	O	$\text{O}_2(g) + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.229
Cd	$\text{Cd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cd}_{(s)}$	-0.40	Cl	$\text{Cl}_2(g) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.36
Cu	$\text{Cu}_2\text{O}_{(s)} + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{Cu}_{(s)} + 2\text{OH}^-$	-0.36	Br	$\text{BrO}_3^- + 5\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{HBrO}_{(aq)} + 2\text{H}_2\text{O}$	+1.45
Pb	$\text{PbSO}_4_{(s)} + 2\text{e}^- \rightleftharpoons \text{Pb}_{(s)} + \text{SO}_4^{2-}$	-0.36	Br	$2\text{BrO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightleftharpoons \text{Br}_2(l) + 6\text{H}_2\text{O}$	+1.48
Pb	$\text{PbSO}_4_{(s)} + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{Hg}) + \text{SO}_4^{2-}$	-0.35	Cl	$2\text{ClO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightleftharpoons \text{Cl}_2(g) + 6\text{H}_2\text{O}$	+1.49
Co	$\text{Co}^{2+} + 2\text{e}^- \rightleftharpoons \text{Co}_{(s)}$	-0.28	Mn	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}_2^{+} + 4\text{H}_2\text{O}$	+1.51
Ni	$\text{Ni}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ni}_{(s)}$	-0.25	Au	$\text{Au}^{3+} + 3\text{e}^- \rightleftharpoons \text{Au}_{(s)}$	+1.52
As	$\text{As}_{(s)} + 3\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{AsH}_3(g)$	-0.23	Pb	$\text{Pb}^{4+} + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+}$	+1.69
Ag	$\text{AgI}_{(s)} + \text{e}^- \rightleftharpoons \text{Ag}_{(s)} + \text{I}^-$	-0.15	Mn	$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{MnO}_2_{(s)} + 2\text{H}_2\text{O}$	+1.70
Sn	$\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn}_{(s)}$	-0.13	Ag	$\text{AgO}_{(s)} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{Ag}^+ + \text{H}_2\text{O}$	+1.77
Pb	$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}_{(s)}$	-0.126	O	$\text{H}_2\text{O}_2(aq) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.78
C	$\text{CO}_2(g) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HCOOH}_{(aq)}$	-0.11	Au	$\text{Au}^+ + \text{e}^- \rightleftharpoons \text{Au}_{(s)}$	+1.83
C	$\text{CO}_2(g) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CO}_{(g)} + \text{H}_2\text{O}$	-0.11	Ag	$\text{Ag}^{2+} + \text{e}^- \rightleftharpoons \text{Ag}^+$	+1.98
Fe	$\text{Fe}_3\text{O}_4_{(s)} + 8\text{H}^+ + 8\text{e}^- \rightleftharpoons 3\text{Fe}_{(s)} + 4\text{H}_2\text{O}$	-0.08	Mn	$\text{HMnO}_4^- + 3\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{MnO}_2_{(s)} + 2\text{H}_2\text{O}$	+2.09
Fe	$\text{Fe}^{3+} + 3\text{e}^- \rightleftharpoons \text{Fe}_{(s)}$	-0.04	Fe	$\text{FeO}_4^{2-} + 8\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{Fe}_3^{+} + 4\text{H}_2\text{O}$	+2.20
H	$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(g)$	0.00	F	$\text{F}_2(g) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{HF}_{(aq)}$	+3.05

8.3 Redox reactions in galvanic cells

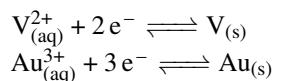
Increasing oxidizing strength (decreasing reducing strength)

Increasing oxidizing strength (decreasing reducing strength)



of charge.

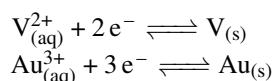
Identifying the anodic and cathodic reaction Let us assume we need to build up a galvanic cell based on the following reactions:



$$\mathcal{E}^\circ = -1.13\text{V}$$

$$\mathcal{E}^\circ = +1.52\text{V}$$

We want to identify the anodic and the cathodic reaction. To do this we should compare the magnitude of the standard reduction potentials for both reactions, the larger this value the larger the tendency of the reaction to proceed as a reduction, and hence the larger the tendency of the electrode based on that reaction to act as a cathode. We have that the reduction of vanadium has a standard reduction potential of -1.13V , whereas the standard reduction potential for the reduction of gold is $+1.52\text{V}$. An electrode made of a piece of vanadium in contact with a solution of vanadium(II) would be the anode and an electrode made of a piece of gold in contact with a solution of gold(III) would be the cathode. Now we can label the reactions as anode and cathode:



$$\mathcal{E}^\circ_{\text{anode}} = -1.13\text{V}$$

$$\mathcal{E}^\circ_{\text{cathode}} = +1.52\text{V}$$

Below is a representation of the gold-vanadium galvanic cell. The anode made of vanadium contains metallic vanadium in contact with a solution of vanadium(II), whereas the cathode made of gold contains metallic gold in contact with a solution of gold(III).

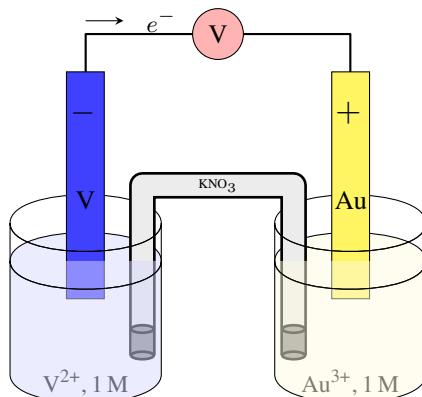
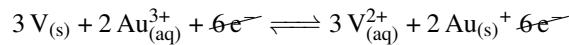
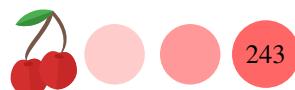


Figure 8.3 A Au-V galvanic cell

Cell potential from electrodic voltages The cell voltage is a combination of the anodic voltage and the cathodic voltage. In particular, the cathodic voltage with respect to the anodic voltage. In the example below we have: $3 \text{V}_{(\text{s})} + 2 \text{Au}_{(\text{aq})}^{3+} + 6 \text{e}^- \rightleftharpoons 3 \text{V}_{(\text{aq})}^{2+} + 2 \text{Au}_{(\text{s})} + 6 \text{e}^-$ $\mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}} = 1.13 + 1.52 = 2.65\text{V}$ The following equation is used to calculate the cell voltage from the separate electronic potentials:

$$\mathcal{E}^\circ_{\text{cell}} = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}} \quad (8.1)$$

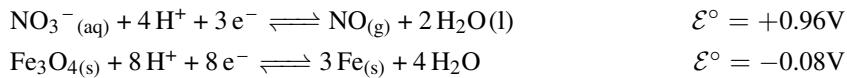
Electrons flowing The number of electrons flowing in a galvanic cell—specifically the moles of electrons flowing—depends on the electrons produced in the anode and consumed in the cathode. Given that the overall charge of the cell needs to be conserved:



In the example above, for the gold-vanadium galvanic cell, we have that gold consumes three moles of electrons and vanadium produces two moles of electrons, overall six moles of electrons flow through the cell.

Sample Problem 101

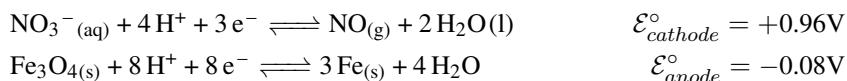
We want to build up a galvanic cell based on the reactions below.



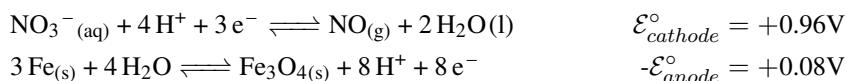
Indicate: (a) the anodic and cathodic reactions (b) the balanced overall redox (c) the number of electrons flowing (d) the overall voltage of the cell (e) draw a diagram of the cell

SOLUTION

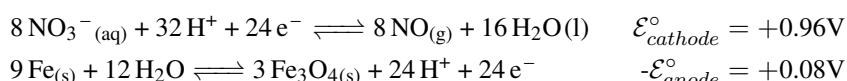
We have two electronic reactions. The first one results from the reduction of nitrate into nitrogen monoxide, with a standard reduction voltage of 0.96V. The second one results from the reduction of iron(III) oxide into metallic iron, with a standard reduction voltage of -0.08V. The reduction of nitrate would act as cathode—with higher voltage—whereas the oxidation of nitrogen monoxide would act as anode, with lower voltage.



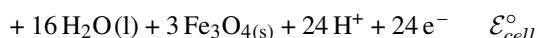
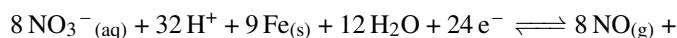
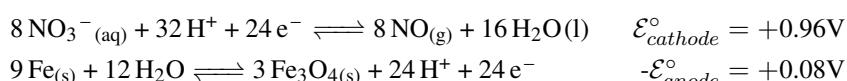
To balance the overall redox reaction we need to first invert the anodic reaction,



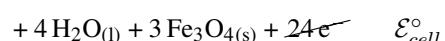
then to multiply the first reaction by eight and the second reaction by three without altering the electronic voltages:



Now we can add both reaction:



We would have to remove water molecules as they appear in both sides and protons as well: $8 \text{NO}_3^-_{(\text{aq})} + 8 \text{H}_{(\text{aq})}^+ + 9 \text{Fe}_{(\text{s})} + 24 \text{e}^- \rightleftharpoons 8 \text{NO}_{(\text{g})} +$

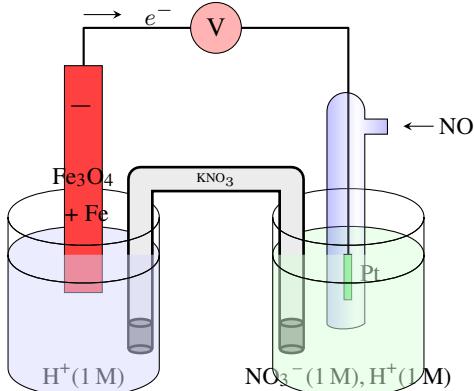


Overall there is 24 moles of electrons going through the cell. The overall voltage would be:

$$\mathcal{E}^\circ_{\text{cell}} = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}} = (0.96) - (-0.08) = 1.04\text{V}$$



The diagram of the cell is presented below:



◆ STUDY CHECK

We want to build up a galvanic cell based on the reactions below.

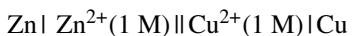


Indicate: (a) the anodic and cathodic reactions (b) the balanced overall redox
(c) the number of electrons flowing (d) the overall voltage of the cell

► Answer: (a) anode $\text{Cr}^{3+} + \text{e}^- \rightleftharpoons \text{Cr}^{2+}$; cathode $\text{Cu}^+ + \text{e}^- \rightleftharpoons \text{Cu}_{(\text{s})}$ (b) $\text{Cr}^{2+} + \text{Cu}^+ + \text{e}^- \rightleftharpoons \text{Cu}_{(\text{s})} + \text{Cr}^{3+} + \text{e}^-$ (c) 1 (d) 0.94V

8.4 Line notation for galvanic cells

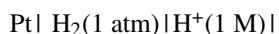
There is a quick and easy way to represent a galvanic cell without having to draw the whole cell diagram. This is called the line notation and galvanic cells are represented in a single line, starting from left to right. The anode is presented in the left, starting from the metallic part and followed by the electrolyte. A single line represents the liquid-solid contact. A double line represents the salt bridge and the cathode is represented in the right, starting for the electrolyte and finishing by the metal. As you can see, the line notation respect all interphase present in the cells: from left to right we have solid, liquid in contact with the salt bridge which is in contact with the liquid part of the cathode and finally we have the solid part of the cathode. For example, the line notation of Daniell cell is:



In case there are several electrolytes in any of the electrodes, as all species are in liquid phase we separate them with just a comma. For example, in the galvanic cell below the cathode contains two different states of iron and uses Pt for the charge transfer:

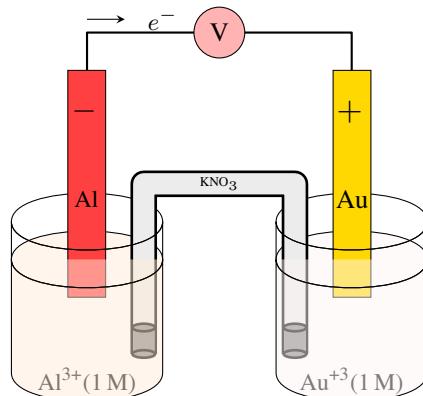


Gases should also be included in the notation with their corresponding pressure. For example, the hydrogen electrode would be written as:



Sample Problem 102

Give the line notation for the galvanic cell below:

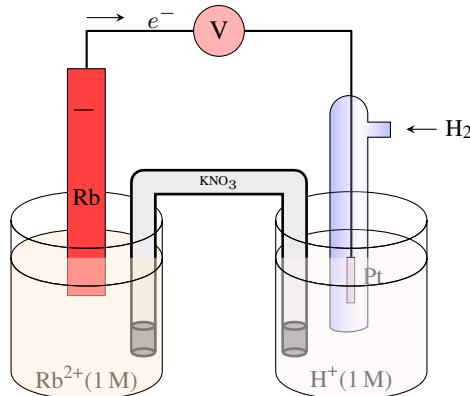
**SOLUTION**

We have that the anode is based on aluminum whereas the cathode is based on gold.

We have two metallic electrodes. The line notations of the galvanic cell will be:

**◆ STUDY CHECK**

Give the line notation for the galvanic cell below:



►Answer: $\text{Rb} \parallel \text{Rb}^{2+}(1\text{ M}) \parallel \text{H}^+(1\text{ M}) \mid \text{H}_2(1\text{ atm}) \mid \text{Cu}$

8.5 Cell potential, Gibbs free energy, and equilibrium constant

Cell potentials are electrochemistry functions that inform about the voltage generated by a galvanic cell. Gibbs free energies are thermodynamic functions that inform about the maximum work—in particular non-expansion- work—that one can extract from a system, under constant pressure and temperature. Both properties are related. At the same time, the equilibrium constant of a system is related to the Gibbs free energy change. Hence, these three properties are indeed related: the cell potential, the Gibbs free energy, and the equilibrium constant.

Maximum work given by a galvanic cell Galvanic cells produce electric-



ity and hence they generate work. The maximum work produced by a galvanic cell is given by:

$$w_{max} = -n_e \cdot F \cdot \mathcal{E}_{cell} \quad (8.2)$$

where:

n_e is the number of moles of electrons flowing through the cell

F is Faraday's constant (96485C/mol), a constant used to convert from moles of electrons to coulombs (a charge unit)

w_{max} is the maximum work produced by the cell (in J)

\mathcal{E}_{cell} is the cell voltage (in V)

For example, a galvanic cell that produced 3V with a flow of 4 electrons can generate less than

$$w_{max} = -n_e \cdot F \cdot \mathcal{E}_{cell} = -4 \cdot 9.6485 \times 10^4 \cdot 3 = -1157820\text{J} = -116\text{KJ}$$

The negative sign on the formula indicates that work is being produced (and not consumed).

Reduction potentials and Gibbs free energy The cell potential of a galvanic cell represents the voltage experienced by the electrons flowing through the cell. The voltage or potential difference—volts are the SI units—is a force that drives the electric flow. In other words, the potential difference generated by a galvanic cell tells about the work needed to carry an electric charge in the cell. A Volt is defined as one joule (J) per coulomb (C) of charge. The maximum amount of work that an electron can do in a galvanic cell is given by the potential difference of the cell times the charge. At the same time, in chemistry, the maximum—nonexpansive—work that a system can do, in reversible conditions, is given by the Gibbs free energy. As both the cell voltage and Gibbs free energy are related to the work generated in the cell, it is simple to see how both thermodynamic functions are related:

$$\Delta G^\circ = -n_e \cdot F \cdot \mathcal{E}_{cell}^\circ \quad (8.3)$$

where:

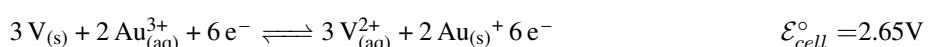
n_e is the number of moles of electrons flowing through the cell

F is Faraday's constant ($9.6485 \times 10^4\text{C/mol}$), a constant used to convert from moles of electrons to coulombs (a charge unit)

ΔG° is the standard Gibbs free energy change (in J)

\mathcal{E}_{cell}° is the standard cell voltage (in V)

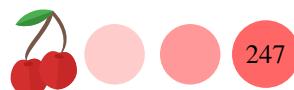
For example, for the redox reaction happening in a galvanic cell:



we have that the cell voltage is 2.65V. As there are six moles of electron flowing through the cell, we have that the change in Gibbs free energy in this reaction would be:

$$\Delta G^\circ = -n_e \cdot F \cdot \mathcal{E}_{cell}^\circ = -6 \cdot 9.6485 \times 10^4 \cdot 2.65 = -1534111.5\text{J} = -1534\text{KJ}$$

The negative sign in the Formula 8.3 is critical. As cell voltages can only be positive numbers, Gibbs free energy changes for working—spontaneously—galvanic cells will



always be negative. At the same time, Formula 8.3 gives the maximum work produced by a galvanic cell working at reversible conditions. In other words, real working cells that produce electricity will always produce voltage lower than the one given by Formula 8.3, as these do not function reversibly. Finally, there exist an equivalent formula to Formula 8.3 without the standard sign for conditions different than the standard ones.

Sample Problem 103

Calculate the standard Gibbs free energy change ΔG° for the following redox reaction:



SOLUTION

We have that in the reaction there is a flow of two moles of electrons. As we know the standard cell potential, we can easily calculate the value of ΔG° :

$$-n_e \cdot F \cdot \mathcal{E}_{cell}^\circ = 2 \cdot 9.6485 \times 10^4 \cdot 2.08 = -401377 \text{J} = -401.4 \text{KJ}$$

As the cell voltage is a positive property, ΔG° should be negative. This means that the cell will produce electricity spontaneously.

◆ STUDY CHECK

Calculate the standard Gibbs free energy change ΔG° for the following redox reaction:



►Answer: -1173KJ

Reduction potentials and equilibrium constant One of the uses of standard reduction potentials (\mathcal{E}°) is to compute standard Gibbs free energy changes from galvanic cell potentials. Another use is to calculate the equilibrium constant (K) from electrochemical data. As standard reduction potentials are related to standard Gibbs free energies and ΔG° is related to the equilibrium constant, we can conclude that \mathcal{E}° is related to K . We use the following equation to compute equilibrium constants from electrochemical data:

$$\ln K = \frac{n_e \cdot F \cdot \mathcal{E}_{cell}^\circ}{RT} \quad (8.4)$$

where:

K is the equilibrium constant

n_e is the number of electrons (a pure number) flowing through the cell

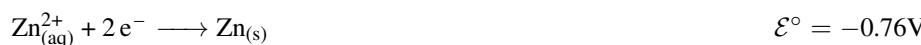
F is Faraday's constant (96485C/mol)

\mathcal{E}_{cell}° is the standard cell voltage (in V)

R is the constant of the gases in energy units (8.314J/molK)

T is the absolute temperature (kelvins)

For example, the reduction of zinc(II) to give metallic zinc is given by:





We can obtain the standard equilibrium constant at 298K by doing:

$$\ln K = \frac{n_e \cdot F \cdot \mathcal{E}_{cell}^\circ}{RT} = \frac{2 \cdot 96485 \cdot (-0.76)}{8.314 \cdot 298} = -59.19$$

Hence the value of the equilibrium constant at 298K would be 1.96×10^{26} . As K is smaller than one, this means that at 298K ionic zinc will not undergo the reduction process spontaneously, and there are more reactants than products in equilibrium.

8.6 Electrochemical series: dissolving metals in acid

Metals dissolve forming ions. The dissolution of a metal involves a redox reaction in which a metallic element transforms into its ionic state. During this process, on one hand, the metal loses electrons producing cations and hence the metal is being oxidized. On the other hand, the solvent reduces. Acids contain protons that can reduce to hydrogen. Indeed, one can use acids to dissolve metals like using water to dissolve table salt. However, not all acids will dissolve a given metal. The electrochemical series is a list of redox pairs going from low standard reduction potential to high standard reduction potential. Using this series, we can find out whether a metal will be dissolved by an acid.

Reducing character We can use the standard reduction potentials table to compare the reducing character of two redox pairs. For example, if we compare the pairs Fe/Fe²⁺ and Zn/Zn²⁺. We have that the reduction potentials are:



We have that the smaller \mathcal{E}° the stronger the reducing character. Hence, the pair Zn/Zn²⁺ is more reducing than Fe/Fe²⁺. We can also compare the oxidizing character of two redox pairs. For example, if we compare the pairs O₂/H₂O and Ag⁺/Ag. We have that the reduction potentials are:



We have that the larger \mathcal{E}° the stronger the oxidizing character. Hence, the pair O₂/H₂O is more oxidizing than Ag⁺/Ag.

Sample Problem 104

Compare the reducing power of the following species:

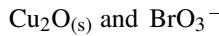


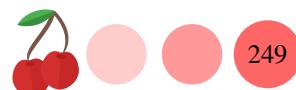
SOLUTION

The larger the standard reduction potential the stronger the reducing power of a redox pair. For Iron(II) we have that the standard reduction potential for the Fe²⁺/Fe_(s) pair is -0.44V . For the PbSO_{4(s)}/Pb_(s) pair is -0.35V . The PbSO_{4(s)}/Pb_(s) pair is more reducing.

◆ STUDY CHECK

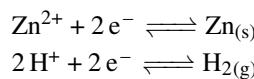
Compare the oxidizing power of the following species:





►Answer: Cu₂O_(s) is more oxidizing

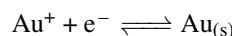
Can an acid dissolve a metal? Let us compare the standard redox potential for two different redox pairs: the reduction of ionic zinc into metallic zinc and the reduction of a proton (found in any acid) into hydrogen



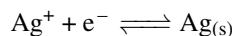
$$\mathcal{E}_1^\circ = -0.762\text{V}$$

$$\mathcal{E}_2^\circ = +0.00\text{V}$$

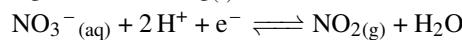
The redox potential of zinc is smaller than the potential of protons. In other words, hydrogen has a stronger oxidizing character than zinc, and zinc has a stronger reducing character than hydrogen. This means that hydrogen would oxidize zinc producing Zn²⁺ and reduce itself producing H_{2(g)}, and hence when pairing both elements, zinc will likely dissolve in a solution containing an acid, at standard conditions. By comparing a redox pair with the origin of the reduction scale, we can find out whether a metal will dissolve in simple acids (nonoxidizing acids e.g. HCl). If the redox potential of the metal is lower than zero then the metal will dissolve in acid. For example, aluminum, lead, or iron will dissolve in HCl. Differently, gold or silver will not. HCl is a nonoxidizing acid. Other acids such as HNO₃ are called oxidizing acids as they have a stronger oxidizing character than hydrochloric acid—a larger redox potential (0.80V). This is because its reduction potential is higher than zero, and as such, they have a stronger capacity to oxidize metals than hydrochloric acid. For example, we can find out whether gold or silver will be dissolved in nitric acid by comparing both redox pairs:



$$\mathcal{E}_1^\circ = +1.83\text{V}$$



$$\mathcal{E}_2^\circ = +0.80\text{V}$$



$$\mathcal{E}_3^\circ = +0.80\text{V}$$

We have that nitric acid will dissolve silver ($\mathcal{E}_2^\circ \simeq \mathcal{E}_3^\circ$) but not gold ($\mathcal{E}_1^\circ > \mathcal{E}_3^\circ$).

8.7 Nernst equation

A galvanic cell connected to a potentiometer works at equilibrium. That means that neither reactants are being consumed nor products are being formed. In working conditions, as a real battery produces electricity reactants are consumed and products are formed. As the galvanic cell works, the concentration of the species inside the cell change and cell potential is certainly affected by that. Standard conditions do not hold anymore as molarities are different than 1M. The Nernst equation—the name honors Walther Nernst, a German electrochemist—gives the dependence of the cell potential with the molarity of the species involved in the redox reaction happening at the cell.

The Nernst equation applied to an electrode The Nernst equation gives the dependence of the cell voltage with the concentration of the ions involved in the redox reaction behind the cell, and with temperature. As such, it is used to compute cell voltage outside the standard conditions. The Nernst equation is given by:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{R \cdot T}{n_e \cdot F} \ln Q \quad (8.5)$$

where:



\mathcal{E} is the cell voltage (in V)

\mathcal{E}° is the standard cell voltage (in V)

R is the constant of the gases in energy units (8.314J/molK)

T is the absolute temperature (kelvins)

F is Faraday's constant (96485C/mol)

n_e is the number of electrons in the redox reaction

$Q = \frac{\text{Products}}{\text{Reactants}}$ is the reaction quotient

$\frac{R \cdot T}{F}$ is 0.025693V at 298.15K

For example, for the electrodic reaction representing the oxygen reduction, the standard voltage at standard conditions ($[H^+] = 1M$ and $p_{O_2} = 1\text{atm}$, mind these are very acidic conditions) is given by:



However, at $[H^+] = 10^{-7}M$ (neutral PH) the electrodic voltage is lower

$$\mathcal{E} = \mathcal{E}^\circ - \frac{R \cdot T}{n_e \cdot F} \ln Q = 1.23 - \frac{8.314 \cdot 298.15}{4 \cdot 96485} \ln \frac{1}{(10^{-7})^4} = 0.81V$$

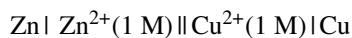
Hence, it is easier to reduce oxygen at neutral PH than it is at very acidic PH.



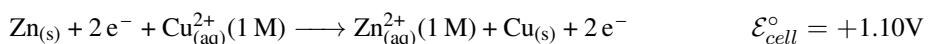
In general, for electrodic reactions involving a single cation, the molarity of this ion will be placed on the bottom of Q . For electrodict reactions involving a single anion, the molarity of this ion will be placed on the top of Q . Finally, Nerns equation can also be expressed in terms if base 10 logarithms at 298K:

$$\boxed{\mathcal{E} = \mathcal{E}^\circ - \frac{0.059}{n_e} \log Q} \quad (8.6)$$

The Nernst equation applied to a galvanic cell We can also apply the Nernst's equation to a galvanic cell, for example the Daniell cell:



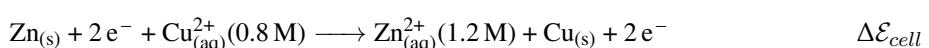
The redox reaction behind this cell oxidizes zinc and reduces copper, with a redox standard potential of 1.10V, with all concentrations fixed at 1M:

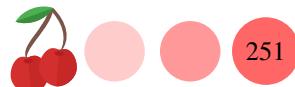


For nonstandard conditions we have that as Zinc is being oxidized, its ionic concentration will increase, whereas as Copper is being reduced its concentration will decrease. One can envision the following galvanic cell,



in which the following redox reaction occurs





Applying Nernst's equation at 298.15K we have:

$$\Delta\mathcal{E}_{cell} = \Delta\mathcal{E}_{cell}^\circ - \frac{R \cdot T}{n_e \cdot F} \ln Q$$

$$\Delta\mathcal{E}_{cell} = 1.10 - \frac{8.314 \cdot 298.15}{2 \cdot 96485} \ln \frac{1.2}{0.8} = 1.09V$$

We have that as the galvanic cell is being consumed, the overall cell potential has decreased. For overall redox reactions behind galvanic cells involving a single ionic species in the anode and cathode, the anode molarity will be on the top side of Q whereas the cathode molarity will be on the bottom:

$$Q = \frac{\text{anode}}{\text{cathode}}$$

Sample Problem 105

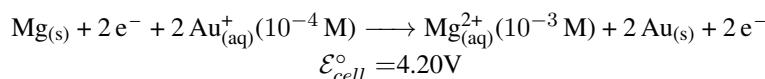
For the galvanic cell below:



- (a) Calculate the standard voltage of the cell, given $\mathcal{E}^\circ(\text{Au}^+/\text{Au})=1.83\text{V}$ and $\mathcal{E}^\circ(\text{Mg}^{2+}/\text{Mg})=-2.37\text{V}$ (b) calculate the cell potential at 298.15K

SOLUTION

The redox reaction being this galvanic cell is indicated below with the standard cell voltage obtained by doing $\mathcal{E}^\circ_{cathode} - \mathcal{E}^\circ_{anode}$:



We have that two electrons flow though the cell. To calculate the cell potential at 298.15K we apply Nernst equation. While calculating Q we have to place the anodic concentration on top and the cathodic on the bottom:

$$\Delta\mathcal{E}_{cell} = \Delta\mathcal{E}_{cell}^\circ - \frac{R \cdot T}{n_e \cdot F} \ln Q = 4.20 - \frac{8.314 \cdot 298.15}{2 \cdot 96485} \ln \frac{10^{-4}}{(10^{-3})^2} = 4.14\text{V}$$

◆ STUDY CHECK

For the galvanic cell below:



- (a) Calculate the standard voltage of the cell, given $\mathcal{E}^\circ(\text{Pb}^{2+}/\text{Pb})=-0.13\text{V}$ and $\mathcal{E}^\circ(\text{Ce}^{4+}/\text{Ce}^{2+})=1.61\text{V}$ (b) Calculate the cell potential at 298.15K

►Answer: (a) 1.74V (b) 1.71V

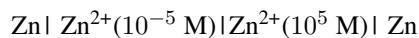
The Nernst equation and a drained galvanic cell A drained galvanic cell loses its capacity to produce voltage. At the same time, when a galvanic cell is drained all ionic concentrations have changed from the initial molarities used to build up the cell. Overall, we have that

$$\boxed{\Delta\mathcal{E} = 0} \quad \text{drained cell} \quad (8.7)$$

Concentration cells What caused a voltage difference in a galvanic cell is the differences in reduction potentials of the anode and cathode. By selecting cathodes



with larger positive \mathcal{E}° and anodes with large negative \mathcal{E}° we can achieve large cell potentials. At the same time, the Nernst equations tell us that \mathcal{E} depends on molarity, hence we could potentially select the same anode and cathode and use the molarity terms in the Nernt equation to drive the potential difference. This is the principle behind concentration cells. These types of galvanic cells contain the same material in the anode and cathode but with different concentrations. The anode is the less concentrated electrode, whereas the cathode is the most concentrated electrode. The concentration difference is what drives the cell potential. Concentration cells in general produce very low voltages, even with very high concentration differences. For example, for the cell:



we have that $\mathcal{E}^\circ = +0.29\text{V}$. At the same time, good concentration cells have very low anodic concentrations and very large cathodic concentrations. For concentration cells we have that as both electrodes are made of the same material $\Delta\mathcal{E}^\circ=0$. Hence, Nernst equation for a concentration cell is simplified to:

$$\Delta\mathcal{E}_{cell} = -\frac{R \cdot T}{n_e \cdot F} \ln Q \quad \text{where } Q = \frac{[\text{anode}]}{[\text{cathode}]}$$

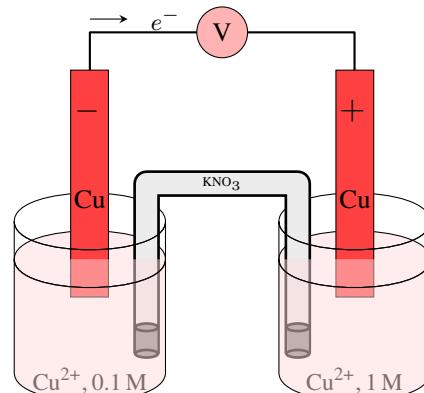


Figure 8.4 A concentration cell

Sample Problem 106

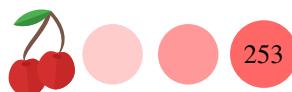
For the concentration cell below:



- (a) Identify the anode and the cathode (b) calculate the cell potential at 298.15K
SOLUTION

The electrode potential depends on concentration. The smaller the concentration the lower the cell potential. On the other hand, we have that electrodes with lower cell potential have a stronger tendency to act as anodes, wheres electrodes with higher cell potential have a stronger tendency to act as cathodes. The less concentrated electrode on the left is the anode, whereas the more concentrated electrode on the right is the cathode. To calculate the cell voltage we use Nernst equation at 298.15K and given that two electrons flow though the cell:

$$\Delta\mathcal{E}_{cell} = -\frac{R \cdot T}{n_e \cdot F} \ln Q = -\frac{8.314 \cdot 298.15}{2 \cdot 96485} \ln \frac{10^{-8}}{10^8} = 0.47\text{V}$$



◆ STUDY CHECK

For the concentration cell below:



- (a) Identify the anode and the cathode (b) calculate the cell potential at 298.15K

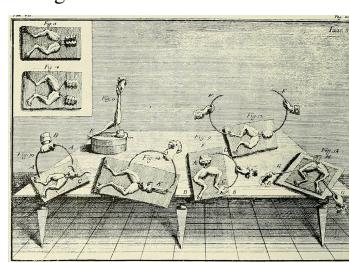
►Answer: (a) left(cathode);right(anode) (b) 0.06V

▼Ph meters function with an electrode



© www.wallpaperflare.com

▼Frog batteries are historic devices



© www.wallpaperflare.com

▼Rust results from electrochemistry



© www.wallpaperflare.com

▼Electrochemistry is central to green transitions



© wikipedia

▼Electrocatalysis uses materials to speed up electrochemistry



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▼Solar technologies convert sunlight into electricity



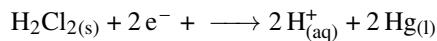
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Figure 8.5 A series of applications of electrochemistry

Ion-selective electrodes Ion-selective electrodes are electrochemical electrodes sensitive to a given ion. One example is the hydrogen electrode, which electrode voltage varies depending on the PH of the solution in the cell. This principle is used in PH meters, chemical instruments employed to measure the PH of aqueous solutions. A PH meter contains an electrochemical cell—a glass electrode—in which one of the electrodes is sensitive to protons and the other electrode is kept as a reference inside a glass bulb that can be dipped onto solutions. One can use several electrodes as a reference, with fixed molarities. The reference electrode makes contact with the external solution by means of a miniature salt bridge. A common one is the calomel electrode:



The redox reaction behind this electrode is:



Another common reference electrode is the Ag/AgCl electrode:



PH meters need to be calibrated with buffer solutions of a known PH, and their potential varies linearly with PH. There are other ion-sensitive electrodes that can be used to detect a variety of ions such as ammonium, calcium or sodium.

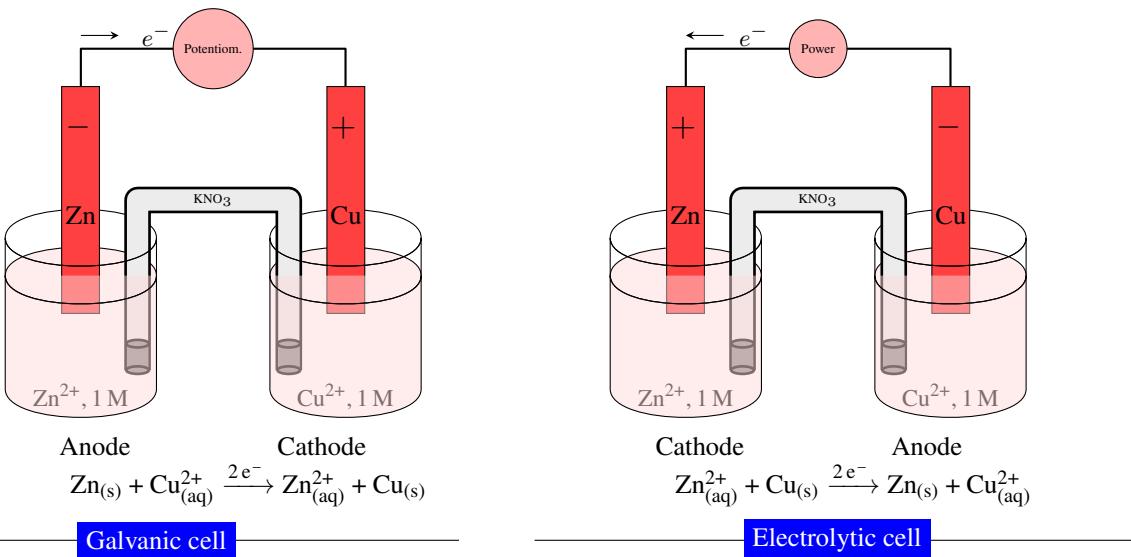


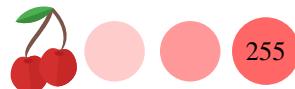
Figure 8.6 A galvanic cell produces voltage from a redox reaction, whereas an electrolytic cell uses voltage to produce a redox reaction. Anodes and cathodes have the opposite sign notation, electrons flow from anode to cathode, whereas ions move towards the electrode of same name (e.g. anions migrate towards the anode). However, galvanic anodes are electrolytic cathodes and viceversa.

8.8 Electrolysis

Electrolysis is a process in which an electric current is forced through a chemical system to induce a chemical reaction that otherwise would not happen spontaneously. Galvanic cells and electrolytic cells follow an opposite sign notation, with anodes being labeled with a positive sign and cathodes with a negative sign in electrolytic cells. Furthermore, the galvanic anode becomes the electrolytic cathode, whereas the galvanic cathode becomes the electrolytic anode.

Galvanic cell vs. electrolytic cell A galvanic cell generates voltage through a spontaneous redox reaction. The electrons are produced in the anode and consumed in the cathode. Anions migrate towards the anode and cations towards the cathode. A voltmeter is used to measure the cell voltage. An electrolytic cell uses an externally applied voltage to force a non-spontaneous redox reaction with a negative voltage. Electrolysis has many applications in science, such as battery charging, metal extraction, production of non-metals, or metal refining. In an electrolytic cell, electrons still flow from the anode to the cathode, and anions also migrate towards the anode, whereas cathodes migrate towards the anode. However, the anode in an electrolytic cell becomes the cathode in the equivalent galvanic cell, whereas the electrolytic cathode becomes the galvanic anode. This is because the externally applied voltage reverts the nature of the electrodes.

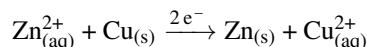
Intensity, charge and time The intensity circulating through an electric circuit refers to the charge circulated per unit of time, to the coulombs per second. Remember that the unit of intensity is the Ampere (A) that equals to coulombs per second (C/s). At the same time, Faraday's constant is used to relate moles of electrons with



coulombs, as F is $96485\text{C/mol } e^-$. We can hence calculate the moles of electrons circulating in a circuit from the intensity and time. For example, an intensity of 10A circulating for 60seconds will correspond to

$$60\cancel{s} \times \frac{10\mathcal{E}}{1\cancel{s}} \times \frac{1 \text{ mol } e^-}{96485\mathcal{E}} = 6.21 \times 10^{-3} \text{ moles of } e^-$$

We can also use reaction stoichiometry to relate the moles of electrons flowing in the electrolytic cell with the moles of chemicals produced or consumed. For example, for the redox reaction behind Daniell's cell, we have that in an electrolytic cell, Zinc deposits on the cathode whereas nickel dissolves in the anode. Hence, the cathode will become heavier, whereas the anode will become lighter. We intend to calculate the number of moles of Zinc deposited after applying 10A for 60 seconds. We have that the redox reaction is:



Hence:

$$60\cancel{s} \times \frac{10\mathcal{E}}{1\cancel{s}} \times \frac{1 \text{ mol } e^-}{96485\mathcal{E}} \times \frac{1 \text{ moles of Zn}}{2 \text{ moles of } e^-} = 3.10 \times 10^{-3} \text{ moles of Zn}$$

Sample Problem 107

How much time should a 3A current be applied in order to produce 5×10^{-4} moles of Zinc in a Danielle electrolytic cell?

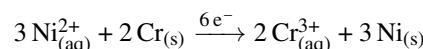
SOLUTION

We will start by using the reaction stoichiometry to convert the moles of Zn produced into moles of electrons flowing through the cell (given that two electrons are involved in the redox reaction), to then convert the moles of electrons into coulombs using Faraday's constant, and the coulombs into ampers:

$$5 \times 10^{-4} \text{ moles of Zn} \times \frac{2 \text{ moles of } e^-}{1 \text{ mole of Zn}} \times \frac{96485 \text{ C}}{1 \text{ moles of } e^-} \times \frac{1 \text{ s}}{3 \text{ C}} = 32.16\text{s}$$

❖ STUDY CHECK

How much intensity should be applied for 30 seconds to an electrolytic cell based on the reaction below in order to produce 2×10^{-5} moles of Ni.



►Answer: 0.128A

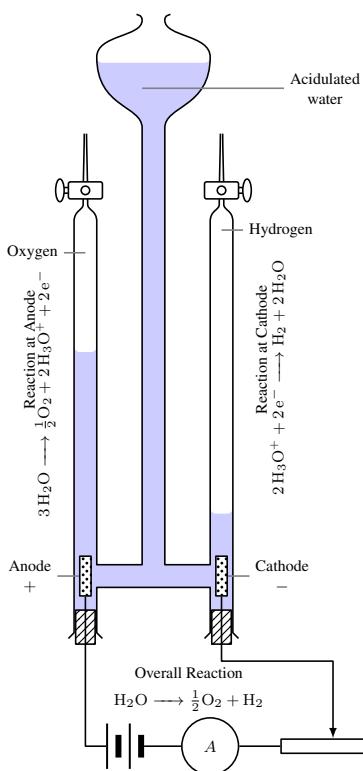
The electrolysis of water Water molecules can be split into gas hydrogen and oxygen. The oxidation of water produces oxygen,



and the reduction of water produces hydrogen,



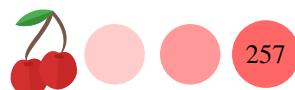
Overall, the potential needed to split water is -2.06V . However, this number is calculated at standard conditions, and at neutral PH one needs a more positive value (close



to 1.2V). Still, electrochemical processes are affected by overvoltage. That means that in order to electrolyze water we need more than 1.2V, being the difference between the needed value and the value calculated using electrochemistry the overvoltage or overpotential. This effect is due to electron transfer limitations from the solution to the electrode that increases the measured voltage needed. At the same time, pure water does not contain enough ions to conduct the electricity and in order to foster the flow of electricity, we need to add ions in the form of an acid or an electrolyte.

Electrolysis and ion mixtures Electrolysis is used to plate metal surfaces in a setup in which we have a solution containing a mixture of ions and by applying an external voltage one of the metals is deposited. Normally, the voltage is increased from zero and the first ions to deposit are those with higher-more positive-standard reduction potential. For example, in a mixture of Na^+ ($E^\circ = -2.71\text{V}$), Au^+ ($E^\circ = 1.52\text{V}$) and Pt^{2+} ($E^\circ = 1.2\text{V}$), gold would be plated first.

Electrolysis applications Electrolysis is a technique extensively used in the chemical industry to obtain metals from its ores. Metals are electron-rich elements with an excellent reducing character. In contact with the atmosphere, they are found in nature in the form of ores, a mixture of oxides, sulfides, and silicates. Electrolysis can be used to return oxidized metals into their original metallic state. Here we will describe the electrolytic production of aluminum, and chlorine, as well as other applications of electrolysis such as the electrorefining of metals and metal plating. Aluminum is a very abundant element on earth. Still, back in the 18th century, pure aluminum was a rare and expensive metal worth more than \$1000000 a pound. In nature, it is found in the form of an oxide, bauxite—the name of this mineral comes from a french region Le Baux, near Marseille in the south. This mineral is a mixture of aluminum oxide (called silica), mixed with iron oxide, silicon oxide, titanium oxide as well as other silicates. However, the production of aluminum from bauxite was proven to be very difficult. In the late nineteenth century, a french and an American scientist independently developed an electrolytic method to produce aluminum, the Hall-Heroult. On one hand, bauxite cannot be electrolyzed in water as water is more reducing than aluminum and in an aluminum solution, water would electrolyze rather than aluminum. On the other hand, in order to electrolyze bauxite, it needs to be melted first in order for the ions to migrate in the electrolytic cell, and the melting point of this mineral is close to 2050°C . The method consists first of the purification of aluminum oxide by treating bauxite with sodium hydroxide. The resulting sludge contains dissolved aluminum oxide that is then acidified with carbon dioxide. The resulting hydrated alumina is then treated with molten cryolite (Na_3AlF_6) in order to reduce the melting point of the oxide to 1000°C . The electrolysis of this melted mixture produces ultrapure—close to 100%—aluminum, that deposits on the bottom of the cell, as Al is denser than the oxide mixture. In the cell, a large current flow of 250000A is applied to a series of graphite rods. Carbon dioxide forms in the anode. Chlorine gas is used during sanitation for the disinfection of water. It is also used as a bleaching agent during the production of paper and in the manufacturing of many household cleaning products. Several electrolytic cells are used for the production of chlorine. First, the Downs cell employs a mixture of melted sodium chloride and calcium chloride to produce gaseous chlorine and solid sodium as a byproduct. Calcium chloride reduces the melting point of sodium chloride (close to 800°C) to 600°C . The generated sodium—a very reactive metal—needs to be kept under oil to avoid its oxidation. Chlorine can also be produced from brine, an aqueous solution of sodium chloride. In this process, sodium hydroxide contaminated with sodium chloride is produced as a byproduct. The mercury cell eliminated this



problem hence producing cleaner sodium hydroxide. In this cell, mercury is used as the cathode for the electrolytic treatment of brine. In the anode, chlorine is generated. In the cathode, sodium is reduced instead of water, producing a solid solution of mercury and sodium that is then treated with water producing sodium hydroxide and hydrogen gas, while recovering mercury. Other applications of electrolysis are the electrorefining of metals. Impure metals are often produced from the treatment of metal ores. A way to purify these is by using the impure slabs as anodes in electrolytic cells with an aqueous solution of the metal to be refined, where metals are dissolved into ions. Impurities and noble metals deposit on the bottom of the cell in the form of sludge. The cathode contains a slab of pure metals that grows as dissolved ions deposit in the pure metal slab forming an ultrapure metallic layer. Another useful electrolytic application is metal plating. For example, tin cans are made of tin-coated steel and car bumpers are often chrome-plated steep parts. Metals can be plated by means of an electrolytic cell in which the metal to be plated is placed in the cathode and the liquid solution contains ions of the plating materials.

8.9 Corrosion

Metals corrode when returning to their original state as found in nature, in the form of oxides, sulfides, silicates, and carbonates. This complex mixture of solids is called ore. When a metal corrodes, it oxidizes. Corrosion has a severe impact on the value and properties of metals, as rusted metals often lose their integrity. Metals corrode when they oxidize, producing rust. Most structural and decorative metals (e.g. Ag, Fe, Ni, Cu, etc) spontaneously rust. They have a reduction potential lower than that of oxygen gas ($\mathcal{E}^\circ = 1.2V$), which means they have a stronger tendency to become oxidized while oxygen reduces to water—they have a strong reducing capacity. Copper forms Platina, a greenish copper carbonate. Silver forms silver tarnish, a silver sulfide (Ag_2S). Rust is a hydrated iron(II) oxide of complex composition ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$). Zinc forms a mixture of oxide and carbonate coatings. Gold is the only metal that does not oxidize under normal conditions, due to its high redox potential ($\mathcal{E}^\circ = 1.5V$). As metals oxidize very easily under atmospheric conditions, a thin layer of rust—a coating—prevents the complete oxidation of the metal as they have a higher-less negative-reduction potential. For example, metallic aluminum ($\mathcal{E}^\circ = -1.7V$) is naturally coated with aluminum oxide (Al_2O_3). This oxide ($\mathcal{E}^\circ = -0.6V$) passivates the metal preventing its further oxidation. Still, this protective effect is not infallible as natural coatings are irregular and they scale off exposing the uncorroded metal to the air. Oxygen and moisture, among other factors, are responsible for the corrosion of iron. The corrosion of iron can be understood by thinking more about the functioning of a galvanic cell than on a pure oxidation process. Some areas of an iron surface are more easily oxidized than others, due to a lack of homogeneity. These areas are called anodic areas, and metallic iron oxidizes there forming iron(II) as well as electrons, which can flow in the metal. Iron(II) ions can also migrate on the surface of iron due to moisture that acts as a salt bridge. Moisture is critical for the corrosion of iron as it is necessary for ionic migration. The presence of other electrolytes such as sodium chloride can also favor the corrosion of iron due to the formation of complex iron compounds. For example, it is well known that salt on the road favors the corrosion of cars and that cars decay faster in humid weather. In the cathodic regions, iron(II) reacts with oxygen and moisture to produce rust, iron oxide. The degree of hydration of the oxide affects the color of rust, varying from black, to yellow or red. The anodic regions and cathodic regions

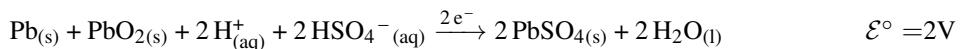


are not necessarily close to each other. That is why rust grows in remote areas from the metal pits that start the corrosion. There are several methods to prevent corrosion. The application of coatings in the form of paints, metal plating, galvanization, or alloying can help prevent corrosion. Cr and Sn are used to plate steel as they form regular and durable oxide coatings. Zn is used to galvanize iron, as Zn has a stronger tendency to be oxidized than iron. Cr and Ni are alloyed with steel to produce stainless steel. Another method to prevent corrosion is called cathodic protection. When connecting a metal that needs to be protected to a more reducing metal, a metal that can be oxidized easily, the more reducing metal acts as the anode, oxidizing first while protecting the less reducing metal. This technique is used to protect ship's hulls or steel in pipelines.

8.10 Batteries

Batteries are portable sources of electrical power. They consist of a series of galvanic cells connected in series so that the overall voltage results from the added voltage of the small cells. They are used to power a variety of essential devices, from small electric calculators to large electric cars.

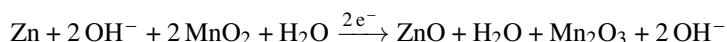
Lead batteries have been extensively used in car manufacturing since the early twenty century to self-start cars. These large and heavy batteries function under a wide range of temperatures and harsh conditions on the road, with a useful life of between 3 to 5 years. Each battery typically contains six galvanic cells, each giving about 2V, combined with an overall high voltage of about 12V. The anode is made of a lead grid, whereas the cathode is made of a metallic lead grid, coated with lead(II) oxide. Both electrodes are submerged in a sulfuric acid solution. When the battery works sulfuric acid is consumed, whereas water is being consumed as the battery charges. Traditional batteries require the periodic addition of water. The density of the sulfuric acid solutions gives an estimate of the battery conditions, as the sulfuric density decreases with use. When cars run, an alternator is used to electrolyze the battery, forcing current during recharging. One of the side reactions occurring when jump-starting the car is the electrolysis of water producing oxygen and hydrogen, which can cause battery explosions. The approximate redox reaction behind this battery is given below:



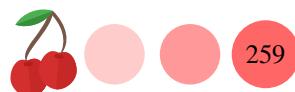
One of the drawbacks of the lab battery is its weight and the fact that contains a corrosive liquid that can leak. Dry cells are a type of battery that does not contain any liquid solution, invented more than 100 years ago. They can be found in two versions, the acid version, and the alkaline or basic version which indeed last longer. The acidic dry cell with giving an estimate of 1.5V is made of a zinc inner case acting as anode and a carbon rod in contact with a moistened mixture of MnO_2 and NH_4Cl acting as a cathode.



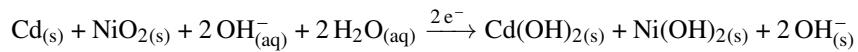
The alkali version used KOH or NaOH to replace NH_4Cl .



The zinc anode corrodes less rapidly in basic–alkaline–conditions. Other dry cells are the silver cell, the mercury cell, and the rechargeable nickel–cadmium battery. The silver cell is made of Zn anode and Ag_2O under basic conditions as a cathode. Mercury cells are made of a Zn anode and HgO in a basic environment as the cathode. The Ni–Cd batteries



are made of a Cd anode and a NiO₂ cathode. The approximate redox reaction behind this battery is given below:

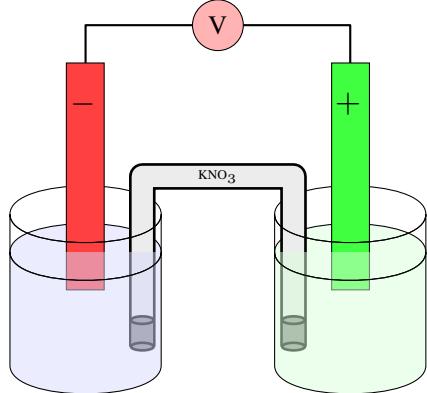


A remarkable type of battery is the lithium-ion batteries used in rechargeable cellphones and laptops. One of the first designs contained LiCoO₂ doped with numerous transition metals and LiC₆. When the battery is used—on discharge—Lithium ions (Li⁺) migrate from the anode to the cathode where they intercalate in the solid electrode, whereas electrons circulate to the anode in the external circuit. The opposite process happens during the charge. Fuel cells are a special type of battery in which reactants are continuously supplied in the form of a gas. In hydrogen fuel cells, hydrogen is being reduced in the anode to produce water and oxygen is being oxidized in the cathode.

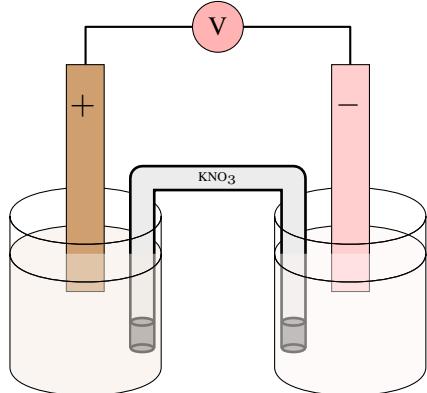
CHAPTER 8

INTRODUCTION TO GALVANIC CELLS

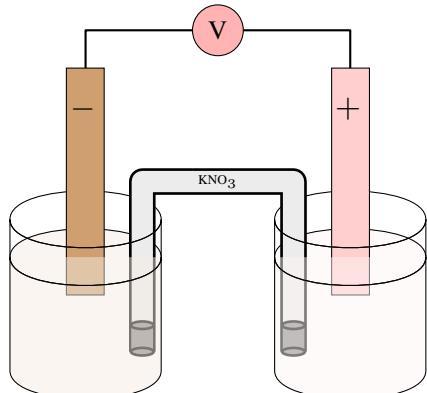
- 8.1** For the galvanic cell below, indicate: (a) the direction of flow of electrons (b) the direction of flow of cations (c) the direction of flow of anions



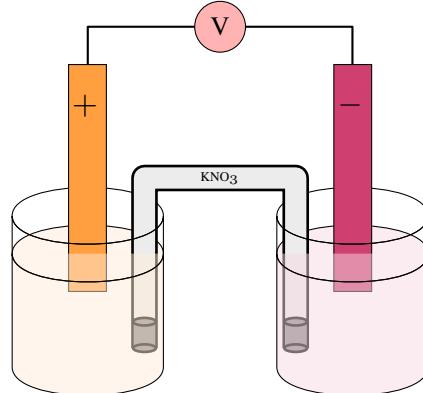
- 8.2** For the galvanic cell below, indicate: (a) the direction of flow of electrons (b) the direction of flow of cations (c) the direction of flow of anions



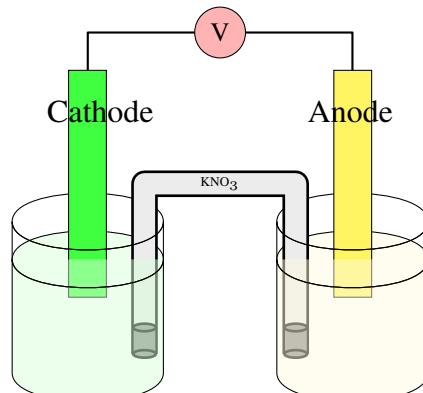
- 8.3** For the galvanic cell below, indicate: (a) label the anode (b) label the cathode



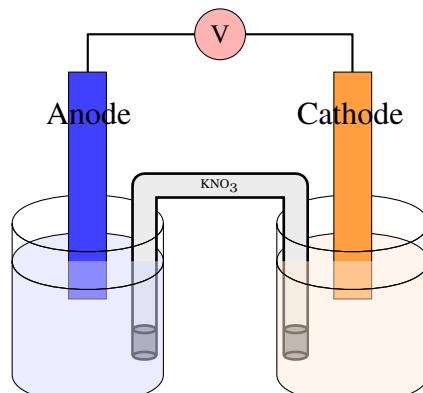
- 8.4** For the galvanic cell below, indicate: (a) label the anode (b) label the cathode



- 8.5** For the galvanic cell below, indicate: (a) label the sign (- or +) of each electrode (b) identify the flow of electrons



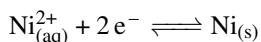
- 8.6** For the galvanic cell below, indicate: (a) label the sign (- or +) of each electrode (b) identify the flow of electrons



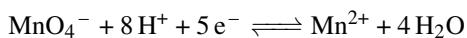


STANDARD REDUCTION POTENTIALS

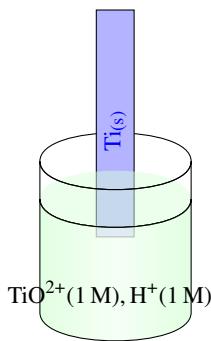
8.7 Sketch a semi-cell for the semi reaction below, indicate if the electrode is a solid-liquid electrode or gas-liquid electrode. Assume standard conditions:



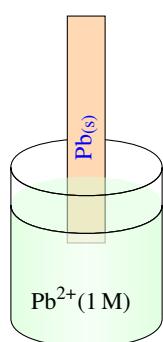
8.8 Sketch a semi-cell for the semi reaction below, indicate if the electrode is a solid-liquid electrode or gas-liquid electrode. Assume standard conditions:



8.9 Indicate the redox reaction being the following semi-cell:

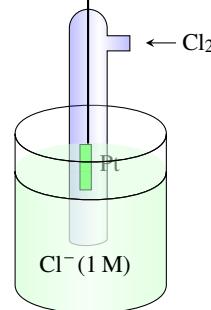


8.10 Indicate the redox reaction being the following semi-cell:

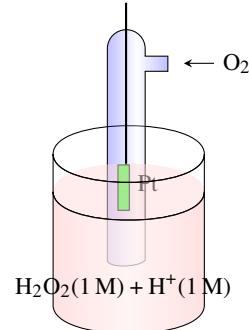


8.11 Indicate the redox reaction being the following semi-cell:

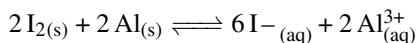
Section 8.10 • Batteries



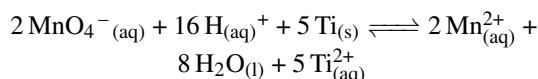
8.12 Indicate the redox reaction being the following semi-cell:



8.13 Sketch a galvanic cell based on the overall redox reaction shown below:

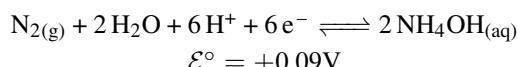
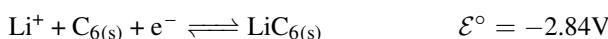


8.14 Sketch a galvanic cell based on the overall redox reaction shown below:



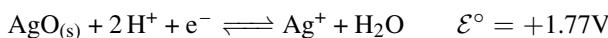
REDOX REACTIONS IN GALVANIC CELLS

8.15 We want to build up a galvanic cell based on the reactions below.

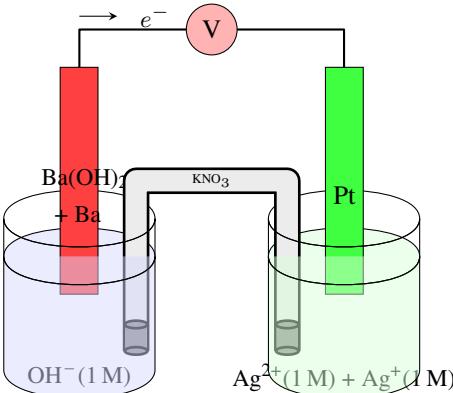


Indicate: (a) the anodic and cathodic reactions (b) the balanced overall redox (c) the number of electrons flowing (d) the overall voltage of the cell

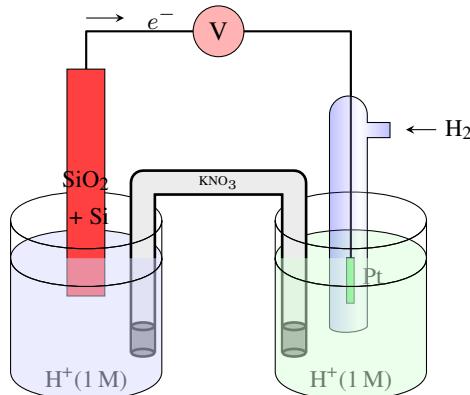
8.16 We want to build up a galvanic cell based on the reactions below.



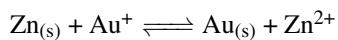
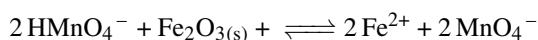
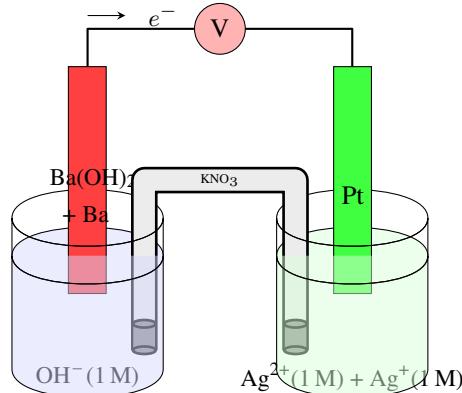
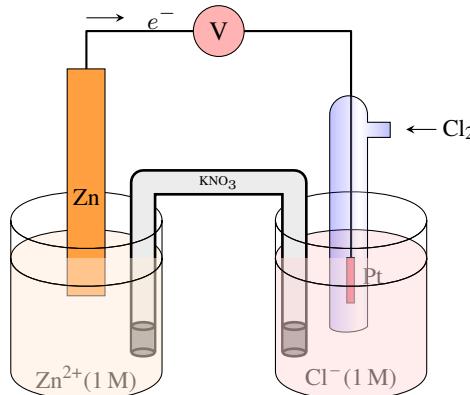
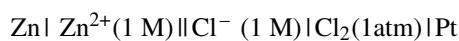
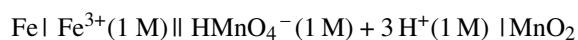
Indicate: (a) the anodic and cathodic reactions (b) the balanced overall redox (c) the number of electrons flowing (d) the overall voltage of the cell

8.17 For the galvanic cell below

Indicate: (a) Identify the anodic and cathodic reactions
 (b) Indicate the anodic and cathodic standard reduction potential
 (c) Indicate the overall potential of the cell
 (d) Indicate the number of electrons flowing

8.18 For the galvanic cell below

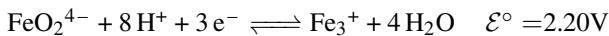
Indicate: (a) Identify the anodic and cathodic reactions
 (b) Indicate the anodic and cathodic standard reduction potential
 (c) Indicate the overall potential of the cell
 (d) Indicate the number of electrons flowing

8.19 For the unbalanced reaction below, calculate \mathcal{E}° and indicate whether the reaction is spontaneous under standard conditions. Balance the reaction.**8.20** For the unbalanced reaction below, calculate \mathcal{E}° and indicate whether the reaction is spontaneous under standard conditions. Balance the reaction.**LINE NOTATION FOR GALVANIC CELLS****8.21** Give the line notation for the galvanic cell below:**8.22** Give the line notation for the galvanic cell below:**8.23** Calculate the standard cell potential for the galvanic cell below:**8.24** Calculate the standard cell potential for the galvanic cell below:**CELL POTENTIAL, GIBBS FREE ENERGY, AND EQUILIBRIUM CONSTANT****8.25** Answer the following questions:
 (a) Calculate the standard reduction potential for the Li/Li⁺ pair given that the standard formation Gibbs free energy of formation Li⁺ is 193KJ/mol.
 (b) Calculate the standard reduction potential for the Na/Na⁺ pair given that the standard formation Gibbs free energy of formation Na⁺ is 261KJ/mol.

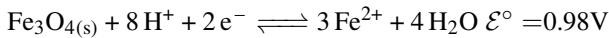


8.26 Answer the following questions: (a) Calculate the standard reduction potential for the Al/Al³⁺ pair given that the standard formation Gibbs free energy of formation Al³⁺ is 480 kJ/mol. (b) Calculate the standard reduction potential for the Ti/Ti²⁺ pair given that the standard formation Gibbs free energy of formation Ti²⁺ is 314 kJ/mol.

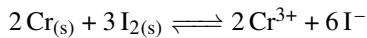
8.27 Calculate the standard Gibbs free energy for the following electrochemical reaction:



8.28 Calculate the standard Gibbs free energy for the following electrochemical reaction:



8.29 Calculate the standard Gibbs free energy for the following reaction using the given electrochemical data:



$$\mathcal{E}^\circ (\text{Cr}^{3+}/\text{Cr}_{(s)}) = -0.74 \text{ V} \text{ and } \mathcal{E}^\circ (\text{I}_{2(s)}/\text{I}^-) = 0.54 \text{ V.}$$

8.30 Calculate the standard Gibbs free energy for the following reaction using the given electrochemical data:



$$\mathcal{E}^\circ (\text{Fe}^{3+}/\text{Fe}_{(s)}) = -0.04 \text{ V} \text{ and } \mathcal{E}^\circ (\text{H}_2\text{O}_{2(aq)}/\text{H}_2\text{O}_{(l)}) = 1.78 \text{ V.}$$

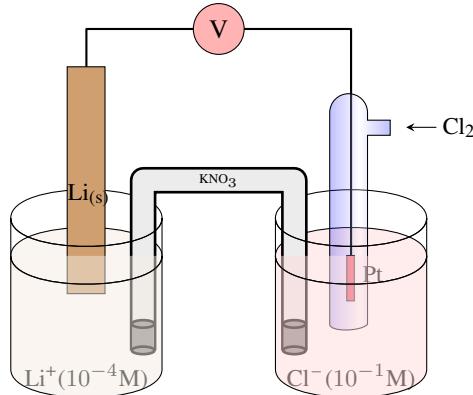
ELECTROCHEMICAL SERIES: DISSOLVING METALS IN ACID

8.31 From the following list indicate the metals that can be dissolved in HCl in standard conditions: (a) Sr (b) Ba (c) Ag (d) Pt

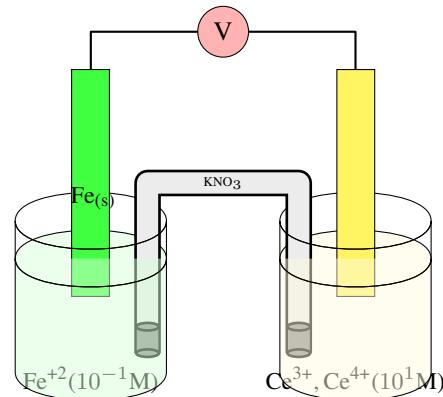
8.32 From the following list indicate the metals that can be dissolved in HCl in standard conditions: (a) Ti (b) Cr (c) Cd (d) Cu

NERNST EQUATION

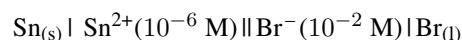
8.33 For the galvanic cell below, compute: (a) the standard potential, given $\mathcal{E}^\circ (\text{Cl}_2/\text{Cl}^-) = 1.36 \text{ V}$ and $\mathcal{E}^\circ (\text{Li}^+/\text{Li}) = -3.05 \text{ V}$ (b) the potential at the given concentrations and 298.15K



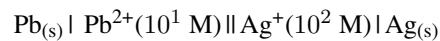
8.34 For the galvanic cell below, compute: (a) the standard potential, given $\mathcal{E}^\circ (\text{Fe}^{2+}/\text{Fe}) = -0.44 \text{ V}$ and $\mathcal{E}^\circ (\text{Ce}^{3+}, \text{Ce}^{4+}/\text{Li}) = +1.61 \text{ V}$ (b) the potential at the given concentrations and 298.15K



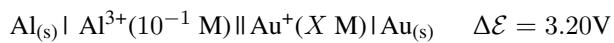
8.35 For the galvanic cell below, compute: (a) the standard potential, given $\mathcal{E}^\circ (\text{Sn}^{2+}/\text{Sn}) = -0.14 \text{ V}$ and $\mathcal{E}^\circ (\text{Br}_2/\text{Br}^-) = +1.09 \text{ V}$ (b) the potential at the given concentrations and 298.15K

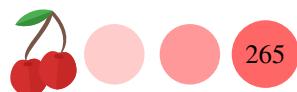


8.36 For the galvanic cell below, compute: (a) the standard potential, given $\mathcal{E}^\circ (\text{Pb}^{2+}/\text{Pb}) = -0.13 \text{ V}$ and $\mathcal{E}^\circ (\text{Ag}^+/\text{Ag}) = +0.77 \text{ V}$ (b) the potential at the given concentrations and 298.15K

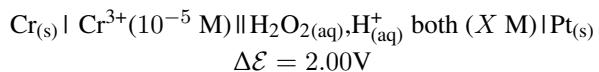


8.37 For the galvanic cell below, given the standard potential (3.35V), calculate the missing molarity X at 298.15K:





8.38 For the galvanic cell below, given the standard potential (2.52V), calculate the missing molarity X at 298.15K:



8.39 For the concentration cell below:



(a) Identify the anode and the cathode (b) calculate the cell potential at 298.15K

8.40 For the concentration cell below:



(a) Identify the anode and the cathode (b) calculate the cell potential at 298.15K

ELECTROLYSIS

8.41 We plate the following metals with an ionic solution of the same metal. Indicate how many seconds will it take to plate the objects using a 25A current: (a) 3 moles of Au^+ (b) 5 moles of Ag^+ (c) 1 moles of Sn^{2+}

8.42 We plate the following metals with an ionic solution of the same metal. Indicate how many seconds will it take to plate the objects using a 25A current: (a) 100g of Ni^{2+} (b) 200g of Zn^{2+} (c) 50g of Cu^{2+}

8.43 For the following elements, what mass can be produced by electrolysis using 10mA for an hour: (a) Mn from Mn^{2+} (b) Cr from Cr^{3+} (c) Fe from Fe^{3+}

8.44 For the following elements, what mass can be produced by electrolysis using 10mA for an hour: (a) Cu from Cu^{2+} (b) Pd from Pd^{2+} (c) Cd from Cd^{2+}

Ch. 9. Nuclear Chemistry

THE field of nuclear medicine was first established in 1934 with the production of artificial radioactive substances. This field uses the power of nuclear chemistry to cure cancer and other diseases or simply to visualize organs. In 1937, the first radioactive isotope was used to treat a person with leukemia at the University of California at Berkeley. Radioactive substances are now used to produce images of organs, such as the liver, spleen, thyroid gland, kidneys, and brain, and to detect heart disease. Today, procedures in nuclear medicine provide information about the function and structure of every organ in the body, which allows the nuclear physician to diagnose and treat diseases early. This chapter covers the basic principles of nuclear chemistry. You will learn the real meaning of radioactivity and how to quantify the effects of radiation or measure the duration of a radioactive chemical.

“ Nuclear power is one hell of a way to boil water.
Einstein”

9.1 Radiation, particles & radioisotopes

Light elements have normally stable nuclei. Differently, heavier elements with atomic numbers larger than 20 tend to often have several isotopes—remember these are atoms of the element with a different number of neutrons—that have unstable nuclei. For these unstable isotopes, the forces that keep the nucleus together are not strong enough to stabilize the nuclei. An unstable nucleus is radioactive, which means that it will spontaneously emit radiation in the form of small particles. Not all radioactivity is the same and there exist different types of radiation, which we will address in the following. Table 9.1 reports common nuclear symbols.

alpha radiation Alpha radiation—referred to as α —is a type of radiation that contains alpha particles. These particles are indeed helium nuclei, with 2 protons, 2 neutrons, and a (2+) positive charge. Alpha particles are often represented as α or ${}^4_2\text{He}$.

beta radiation Beta radiation—referred to as β —is a type of radiation that contains beta particles. These particles are indeed high-energy electrons with (−) negative charge. Beta particles are often represented as β or ${}^{-1}_0\text{e}$.

gamma radiation Gamma radiation—referred to as γ —is a type of radiation that contains high-energy photons. These particles are indeed photons with no mass or charge. Gamma particles are often represented as γ or ${}^0_0\gamma$.

protons Protons in this chapter are often referred to as p or ${}^1_1\text{H}^+$. These are positive charges.

positrons Positrons are the electron antiparticle, often referred to as β^+ or ${}^0_{+1}\text{e}$. They do have a positive charge.



▼ Strawberries are normally treated with radiation



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▼ Ionization chamber smoke detectors contain a small amount of americium-241, a radioactive material



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▼ An operating nuclear power plant produces very small amounts of radioactive gases



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▼ There are radioactive gases in the air we breathe



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Section 9.1 • Radiation, particles & radioisotopes

neutrons Neutrons are nuclear particles with no charge, often referred to as n or ${}_0^1n$.

Sample Problem 108

Name or give the symbols for the following nuclear particles: beta particle, β^+ , p and ${}^0_0\gamma$.

SOLUTION

Beta particles are represented by β or ${}_{-1}^0e$. These particles are indeed simply electrons ejected during a nuclear decay. β^+ represents a positron, an anti-electron. p stands for protons, a nuclear particle with positive charge. Finally, ${}^0_0\gamma$ represents gamma radiation.

◆ STUDY CHECK

Name or give the symbols for the following nuclear particles: n , α and ${}^1_1H^+$.

► Answer: neutron; 4_2He ; Proton

Radioisotope notation Radioisotopes—atomic isotopes that produce radiation—are written as A_ZX . For example, ${}^{14}_6C$ is referred to as carbon-14. The number on the top is the mass number A , that is represented the total number of neutrons and protons in the isotope. The number on the bottom refers to the atomic number Z , that is, the total number of electrons in the atom. For example, the mass number of ${}^{14}_6C$ is 14 whereas its atomic number is 6. ${}^{14}_6C$ has 14 neutrons and protons and 6 electrons.

Sample Problem 109

Calculate the number of protons, neutrons and electrons of the following isotopes: ${}^{238}_{92}U$, ${}^{24}_{13}Al$ and ${}^{14}_6C$.

SOLUTION

According to the isotope notation (A_ZX), the number of top of the radioisotope is the mass number A that represents the number of protons plus neutrons, whereas the number of the bottom is the atomic number Z that represents the number of electrons. According to this, the number of electrons in an atom is Z . If an atom is neutral, the number of electrons and protons are the same, so the number of protons is also Z . The number of neutrons would hence be $A - Z$, as A is the number of protons+neutrons, and the number of protons is Z . We'll use a table below to obtain the electrons, protons and neutrons from A and Z .

Radioisotope	A	Z	Electrons	protons	neutrons
${}^{238}_{92}U$	238	92	92	92	146
${}^{24}_{13}Al$	24	13	13	13	11
${}^{14}_6C$	14	6	6	6	8

◆ STUDY CHECK

Calculate the number of protons, neutrons and electrons of ${}^{99}_{43}Tc$.

► Answer: 43e, 43p, 56n.

**Table 9.1 Nuclear symbols**

Particle Name		Symbol	Charge	Identity	Penetrating power	Discovery
Alpha	(α)	${}_2^4\text{He}$	2+	Helium nucleus	Minimal	1899
Beta	(β)	${}_{-1}^0\text{e}$	-1	Electrons	Short	1899
Gamma	(γ)	${}_{\gamma}^0$	0	Electromagnetic radiation	Deep	1900
Neutrons	(n)	${}_{\gamma}^1\text{n}$	0	nuclear particle	Maximal	1932
Proton	(p)	${}_{1}^1\text{H}^+$	+1	nuclear particle		1919
Positrons	(β^+)	${}_{+1}^0\text{e}$	+1	antiparticle		1932

9.2 Nuclear reactions

Isotopes—called emitters—spontaneously decompose producing new isotopes in a process called radioactive decay. In this decay, radiation is also emitted.

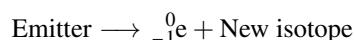


In the following, we will discuss the most important type of radioactive decay.

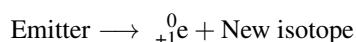
alpha decay Some isotopes produce alpha radiation, that is, they produce α particles on its decay. A nuclear reaction that produces an α particle (${}_2^4\text{He}$) is called alpha decay. In alpha decay, the emitter decreases its mass number A four units and its atomic number Z two units.



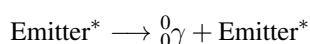
beta decay Other isotopes produce beta radiation, that is, they produce β particles on its decay. A nuclear reaction that produces a β particle (${}_{-1}^0\text{e}$) is called beta decay. In beta decay, the emitter has the same mass number A as the product isotope. However, its atomic number Z decreases by one unit.



positron emission Certain isotopes decay by producing a positron, that is, they produce ${}_{+1}^0\text{e}$ particles on its decay. A nuclear reaction that produces ${}_{+1}^0\text{e}$ is called positron emission. In a positron emission, the emitter has the same mass number A as the product isotope. However, its atomic number Z increases by one unit.



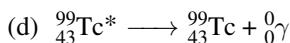
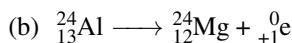
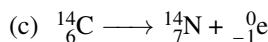
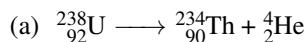
gamma decay Some other isotopes produce gamma radiation in the form of γ particles on its decay. A nuclear reaction that produces a γ particle (${}_{\gamma}^0$) is called gamma decay. In this type of decay, no new isotope is produced. Gamma emitters are normally excited, that is they have higher energy than normal; we denote this with a * symbol. Excited particles tend to lose energy to become more stable. In gamma decay, the emitter and the product isotope, both have the same mass and atomic number.





Sample Problem 110

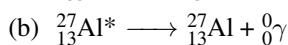
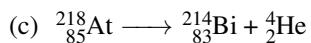
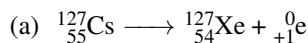
Label the following nuclear reactions as: α , β or γ decay, or positron emission:

**SOLUTION**

(a) This process produces ^4_2He and therefore is alpha emission. (b) This process generates $^0_{+1}\text{e}$ and therefore is positron emission. (c) This process produces $^0_{-1}\text{e}$ and therefore is beta emission. (d) This process produces $^0_0\gamma$ and therefore is gamma emission.

◆ STUDY CHECK

Label the following nuclear reactions as: α , β or γ decay, or positron emission:



►Answer: (a) positron emission; (b) gamma emission; (c) alpha emission.

9.3 Unknown isotopes in nuclear reactions

Sometimes one needs to identify an unknown isotope ^A_ZX in a chemical reaction. This means identifying the name X of the isotope, the atomic number Z as well as the mass number A . To do this, we will use the fact that the total mass number as well as the total atomic number should stay constant before and after the nuclear reaction. Let's break this idea down into an example.

Sample Problem 111

Identify the unknown isotope in the following nuclear reaction:

**SOLUTION**

We will solve this problem by using the fact that the total mass number as well as the total atomic number should stay constant before and after the nuclear reaction. In order to do this, we will calculate the total atomic number before the reaction (in the left) and the total atomic number after the reaction (in the right) and equal both values. We will do the same for the mass number.

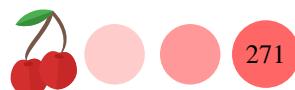
^4_2He	$^{14}_7\text{N}$	\longrightarrow	^A_ZX	^1_1H
A	4	14	A	1
Z	2	7	Z	1

Now we build up two equations, one for A and another for Z , from each of the columns (column 2 and 3) of the table:

$$4 + 14 = A + 1 \quad \text{Equation for } A \text{ from column 2 of the table}$$

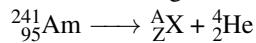
$$2 + 7 = Z + 1 \quad \text{Equation for } Z \text{ from column 3 of the table}$$

We now solve for A getting a value of $A = 17$ and for Z , getting $Z = 8$. With the atomic number Z we can go to the periodic table and identify the name of the isotope. The element with $Z = 8$ is called oxygen, and the final answer would be:



STUDY CHECK

Identify the unknown isotope in the following nuclear reaction:



► Answer: ${}_{93}^{237}\text{Np}$

Table 9.1 Half-life for various isotopes and chemicals

Americium-241	432.2 years	Lutetium-177	6.71 days	Hydrogen-3	12.35 years
Barium-133	10.74 years	Molybdenum-99	66 hours	Technetium-99	213,000 years
Bismuth-212	60.55 minutes	Nickel-63	96 years	Indium-111	2.83 days
Cadmium-109	464 days	Phosphorus-32	14.29 days	Technetium-99m	6.02 hours
Calcium-45	163 days	Potassium-40	1.28×10^9 years	Indium-113m	1.658 hours
Carbon-14	5730 years	Plutonium-239	24,065 years	Tin-113 115.1	days
Cesium-137	30 years	Polonium-210	138.38 days	Iodine-123	13.2 hours
Chlorine-36	301,000 years	Radium-226	1600 years	Tungsten-188	69.4 days
Chromium-51	27.704 days	Radon-222	3.8235 days	Iodine-125	60.14 days
Cobalt-57	270.9 days	Rhenium-188	16.98 hours	Uranium-235	703,800,000 years
Cobalt-58	70.8 days	Rubidium-81	4.58 hours	Iodine-129	15,700,000 years
Cobalt-60	5.271 years	Selenium-75	119.8 days	Uranium-238	4,468,000,000 years
Copper-62	9.74 minutes	Sodium-22	2.602 years	Iodine-131	8.04 days
Copper-64	12.701 hours	Sodium-24	15 hours	Xenon-127	6.41 days
Copper-67	61.86 hours	Strontium-85	64.84 days	Iron-55	2.7 years
Gallium-67	78.26 hours	Strontium-89	50.5 days	Xenon-133	5.245 days
Gold-195	183 days	Sulfur-35	87.44 days	Iron-59	44.529 days
Ondansetron	360 min	Capecitabine	2400s	Carmustine	0.25h

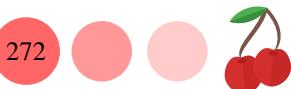
9.4 Half-life of a radioisotope

Radioisotopes—isotopes that decay producing radiation—are unstable and with time they eventually disappear given a more stable isotope. Some radioisotopes decay very quickly, such as the ones used in nuclear medicine to fight cancer. Other radioisotopes take longer to disappear.

The concept of half-life The half-life of an isotope represented as $t_{1/2}$ is the time it takes for an isotope to disappear reducing the sample mass to half the initial value. For example, $t_{1/2}$ for chromium-51 is 28 days and that means that after 28 days a sample of 1 gram of the radioisotope will indeed weigh 0.5 g. Table 9.1 reports half-lives of numerous isotopes. Samples of radioisotopes weigh less and less with time as they decompose producing more stable isotopes. Similarly, $t_{1/2}$ for strontium-90 is 38 years which means that a one-gram sample will take 38 years to reduce its mass to 0.5g. We can use the concept of half-life to compare the speed of decomposition of different radioisotopes. For example $t_{1/2}$ for strontium-90 is 38 years whereas $t_{1/2}$ for chromium-51 is 28 years. Hence, strontium-90 will exist longer than chromium-51. The activity of an isotope is indeed its rate of the decomposition r which depends on the amount of radioactive isotope you have in the sample n ,

$$r = kn$$

where k is the rate constant for the decomposition. At the same time this rate constant



is related to half-life, as decomposition is a first order reaction:

$$t_{1/2} = \frac{0.693}{k}$$

Sample Problem 112

On one hand, Docetaxel is a chemotherapy medication used to treat a number of types of cancer with a half-life of 309600 seconds. On the other hand, Vandetanib is an anti-cancer medication that is used for the treatment of certain tumors of the thyroid gland with a half-life of 1641600 seconds. Which medication will remain longer in the body?

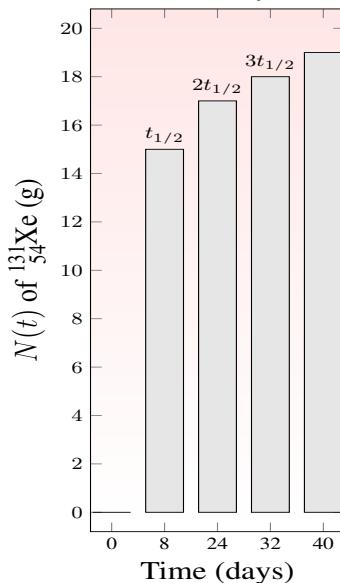
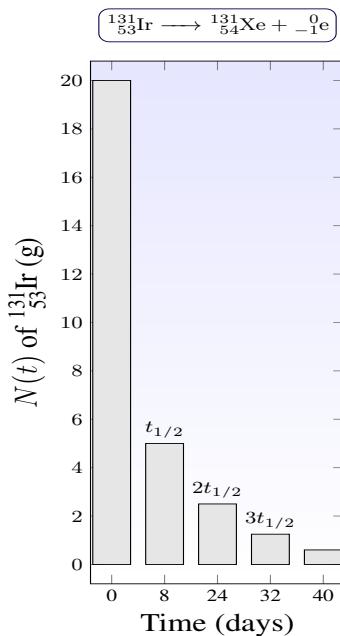
SOLUTION

We will compare the half-lives of both medication using scientific notation to express the numbers so that we can clearly see how the numbers compare. $t_{1/2}$ for Docetaxel is 3.096×10^5 seconds, whereas $t_{1/2}$ for Vandetanib is 1.6416×10^6 seconds. We have that Vandetanib has a larger half-life and hence it will remain longer in the body.

◆ STUDY CHECK

On one hand, Methadone is a synthetic Opioid agonist used for opioid maintenance therapy in opioid dependence and for chronic pain management with a half-life of 2×10^5 seconds. On the other hand, Fluoxetine, sold under the brand names Prozac, is an antidepressant with a half-life of 4 days. Which medication will remain longer in the body and how many time is the half-life of the largest remaining drug in comparison with the other?

►Answer: Fluoxetine, 384



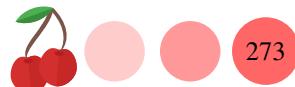
Quantifying half-life The formula that related the amount of radioisotope with $t_{1/2}$ is:

$$N(t) = N_o \cdot 0.5^{\left(\frac{t}{t_{1/2}}\right)} \quad (9.1)$$

where $N(t)$ is the amount of isotope at a given time t , N_o is the initial amount of isotope, t is the time and $t_{1/2}$ is the half-life. $N(t)$ is often referred to as the activity of the radioisotope at a given time t . At the same time, while the radioisotope disappears, a new isotope—this time more stable than the radioisotope—starts forming. The amount of product formed $F(t)$ at a given time is:

$$F(t) = N_o \cdot \left[1 - 0.5^{\left(\frac{t}{t_{1/2}}\right)} \right] \quad (9.2)$$

After several half-lives So if the half-life is the time it takes for a radioisotope to decompose in half, what would happen after several half-lives? For example, imagine we have 20 grams of iridium-131 with a half-life of 8 days. When we prepare or hypothetically unseal the sample, we will have 20 grams of ^{131}Ir . After one half-life (8 days) we'll have 10 grams of ^{131}Ir . After two half-lives (16 days), we'll have 5 grams of ^{131}Ir . Similarly, after three half-lives (22 days), we'll have 2.5 grams.



Sample Problem 113

$^{131}_{53}\text{I}$ has a half-life of 8 days. How many milligrams of a 50mg sample will remain after 10 days.

SOLUTION

We will follow these steps to solve this problem:

- 1 **Step one:** list of the given variables.

- 2 **Step two:** use the half-life formula $N(t) = N_0 \cdot 0.5^{\frac{t}{t_{1/2}}}$ to obtain the mass remaining of the radioisotope

$$N(t) = N_0 \cdot 0.5^{\frac{t}{t_{1/2}}}$$

10d t
 8d t_{1/2}

- 3 **Step three:** solve for $N = 50 \cdot 0.5^{\frac{10}{8}} = 50 \cdot 0.5^{1.25} = 21\text{mg}$. The result means that after 10 days from the 50mg sample of radioisotope, only 21mg will remain due to radioactive decay.

◆ **STUDY CHECK** $^{222}_{86}\text{Rn}$ has a half-life of 3.8 days. How many milligrams of a 25mg sample will remain after 15 days?

► Answer: 1.6mg.

9.5 Radiation measurement, units and radiation effects

Beta and gamma radiation can be detected with a Geiger counter, which consists of a detector tube with a specific ionizing gas. When radiation enters the Geiger counter, it generates charged particles that produce a detectable electrical current. The larger the current the stronger the radioactive source. In the following, we will address the different units of radioactivity—activity, adsorbed dose, and biological damage—reported in Table 9.2 as well as the effects of radiation.

Activity units The radioactivity of an isotope often referred to as *activity*, can be measured in two different units: Curies (Ci) or becquerel (Bq). Curie was somehow the original unit employed to measure the radioactivity of radium and becquerel is a more modern unit of radioactivity. Bq is the SI unit of activity. Both units are related by:

$$1\text{Ci} = 3.7 \times 10^{10} \text{Bq} \quad \text{or} \quad \frac{1\text{Ci}}{3.7 \times 10^{10} \text{Bq}} \quad \text{or} \quad \frac{3.7 \times 10^{10} \text{Bq}}{1\text{Ci}} \quad (9.3)$$

Activity refers to the isotope and is also measured in disintegration per minute (cpm).

Adsorbed dose Whereas activity refers to the isotope, the adsorbed dose refers to the body that receives radiation. The unit for adsorbed dose is called rad (radiation adsorbed



dose). This unit refers to the amount of radiation adsorbed per gram of material. The SI unit for adsorbed dose is called the gray (Gy).

Radiation equivalent in humans, rem Not all radiations have the same impact on the human body. The radiation equivalent in humans takes into account the different types of radiation to adjust the biological damage of radiation. The rem is the number of rads times a factor that depends on the radiation. This factor is one for beta and gamma radiation, being 20 for alpha particles. The following formula related REM with RAD:

$$\text{rem} = \text{rad} \times \text{Factor} \quad (9.4)$$

Exposure to radiation We are all somehow exposed to radiation every day. The reason for this background radiation is that many natural radioisotopes form the atoms of many materials such as brick, concrete, water, or even the air. Still, the daily exposure is very low and you should not be concerned by the effect of this background radiation.

Table 9.2 Radiation Measurement

Activity	curie (Ci) Becquerel (Bq) = 2.7×10^{-11} Ci $1\text{Ci} = 2.22 \times 10^{12}$ dpm
Dosage (D)	rad gray (Gy) = 100rad
Damage (H)	rem Sievert (Sv) = 100rem

Dangers of radiation Radiation units different than Ci or Bq are used to measure the impact of radiation on humans. The rem (radiation equivalent in humans) is a radiation unit that measures the direct biological effects of different kinds of radiation. The number of rems a person receives would determine the impact of the radiation on this person's health. As an example, radiation exposure under 25 rem is harmless and they cannot be detected. If a victim is exposed to 100 rem or higher, the person will suffer the symptoms of radiation sickness and will feel nausea, vomit, fatigue, and a reduction in white cell count. If a person is exposed to a dosage greater than 300 rem, that can lower the white-cell count to zero; the victim will suffer diarrhea, hair loss, and infection. Exposure to radiation of about 500 rem is expected to cause death in half of the people receiving that dose. Radiation dosages of about 600 rem would be fatal to all humans within a few weeks.

Sample Problem 114

Ioflupane is a radiopharmaceutical that helps visualize the brain of Parkinson patients. An injection of this drug has a 5mCi activity. Convert this value to MBq.

SOLUTION

▼An old Geiger counter used to measure radiation



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▼Nurses expose to radiation wear film badges to detect radiation exposure

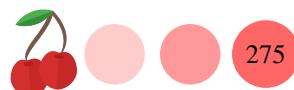


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▼New Geiger counters



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You need to use the conversion factor between Bq and Ci, $\frac{1Ci}{3.7 \times 10^{10} Bq}$, as well as the conversion factor between mCi and Ci $\frac{1mCi}{1 \times 10^{-3} Ci}$, and Bq and MBq $\frac{1MBq}{1 \times 10^6 Bq}$.

$$5mCi \times \frac{1 \times 10^{-3} Ci}{1mCi} \times \frac{3.7 \times 10^{10} Bq}{1Ci} \times \frac{1MBq}{1 \times 10^6 Bq} = 185MBq$$

STUDY CHECK

Quadramet is a radiopharmaceutical used treat pain when cancer has spread to the bone. A injection of this drug has a 740 MBq activity. Convert this value to mCi.

►Answer: 20mCi.

9.6 Radiation protection

Radioactivity results from the emission of very energetic and small particles. It can be extremely harmful when no proper protection is used. Therefore, all hospital personnel working with radioactive isotopes—radiologists, doctors, and nurses—need to be protected against radiation. Table 9.3 reports some useful information regarding radiation protection.

alpha particles Alpha radiation is made of very heavy particles (He nuclei) that can only travel between 2-4cm in the air before disappearing. Inside your body they can penetrate only 0.05mm. A simple piece of thin clothing, a lab coat, gloves, or even our skin can protect us against alpha particles.

beta particles Beta radiation is made of lighter particles (electrons) that move much faster than alpha particles. Beta particles travel between 200-300cm in the air and between 4-5mm in body tissue. Heavy clothing such as lab coats or gloves is needed to protect you against this radiation.

gamma particles Gamma radiation can pass through many materials including body tissues. Gamma rays travel around 500 m in the air and more than 50cm in tissue. Only very dense shielding, such as lead or concrete, will protect you from this radiation.

Table 9.3 Radiation protection

Particle	Travels in air	Travels in tissue	Protected with
α	2-4cm	0.05mm	thin clothing
β	200-300cm	4-5mm	heavy clothing
γ	500m	50cm	lead or concrete

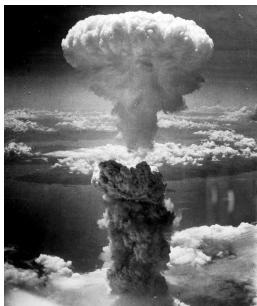
9.7 Radioactive gases: radon

Radon is a colorless, odorless radioactive gas produced by the radioactive decay of uranium. It is present in nearly all soils and very small levels of radon are found in the air we breathe every day. The problem occurs when radon gas enters our home and gets trapped. If you are breathing in too much radon, you will not feel sick right away. Only long-term exposure



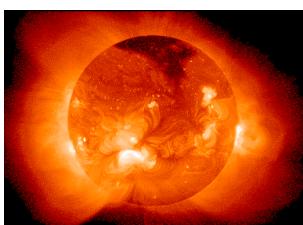
to high levels of radon can cause lung cancer and the risk is higher for those who smoke. While questions remain over the quantities and length of exposure, radon concerns are a fact of homeownership. Most residential real estate transactions require radon testing, and many states require radon mitigation for new construction. The recommended reference radon level is $100 \text{ Bq} \cdot \text{m}^3$ in dwellings. Testing your home for radon is easy and doesn't cost very much. You can test for radon yourself or hire a professional to do it for you. There are relatively simple tests for radon gas. Radon detection devices are commercially available. Digital radon detectors provide ongoing measurements giving daily, weekly, short-term and long-term average readouts via a digital display. Short-term radon test devices used for initial screening purposes are inexpensive, in some cases free.

▼ Nuclear weapons are based on the principles of fission



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▼ The Sun generates its energy by nuclear fusion of hydrogen nuclei into helium.

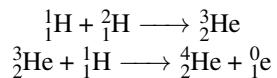


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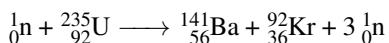
9.8 Fusion and fission

This section will address nuclear fusion and fission. These two processes involve the liberation of a very large amount of energy and are the base for using nuclear processes as a source of energy.

Nuclear fusion Large energy quantities are released when two light isotopes combine to produce a heavier isotope. Nuclear fusion is the mechanism of energy production in the stars. Very high temperatures are required to initiate nuclear fusion and that is the reason why this source of energy has not been exploited on the earth yet. An example of fusion reactions found in the stars are:



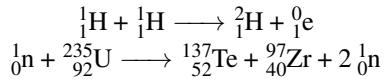
Nuclear fission Nuclear fission was discovered before the second world war when ${}_{92}^{235}\text{U}$ was bombarded with neutrons. The result is the split of the atom into two different isotopes and the release of more neutrons:



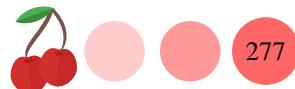
This process releases 26 million times more energy than the combustion of methane. As neutrons are produced in a fission process, they can already activate another uranium atom producing more neutrons. This is the essence of a chain reaction: a self-sustained fission process. If less than one neutron causes a new fission process the fission process will stop and the reaction is said to be subcritical. Differently, when exactly one neutron from each fission even produces another fission the process will sustain and the reaction is known as critical. When more than one neutron produced generates a new fission the fission process will escalate and the reaction is known as supercritical. During World War II, the Manhattan project was a united states research project to build a bomb based on the principles of fission. A fission bomb operates by suddenly combining subcritical masses of uranium, producing an enormous explosion.

Sample Problem 115

Identify the following reactions as fusion or fission:



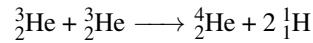
SOLUTION



The first nuclear reaction combines two hydrogen isotopes and hence it will be a fusion reaction. The second reaction results of the fragmentation–fission–of uranium and it will be fission.

 **STUDY CHECK**

Identify the following reaction as fusion or fission:



►Answer: fusion.



CHAPTER 9

RADIATION, PARTICLES & RADIOISOTOPES

9.1 Indicate the name of the following nuclear symbols:

- (a) ${}_{+1}^0 e^+$ (b) ${}_{0}^0 \gamma$ (c) ${}_{1}^1 H$

9.2 Indicate the name of the following nuclear symbols:

- (a) ${}_{2}^4 He$ (b) ${}_{0}^1 n$ (c) ${}_{-1}^0 e$

9.3 Indicate the nuclear symbol for (a) Oxygen-18
(b) Magnesium-24 (c) Lithium-7

9.4 Indicate the nuclear symbol for (a) Iodine-134
(b) Lithium-4 (c) Carbon-14

9.5 Calculate the number of electrons for the following isotopes: (a) ${}_{17}^{24} Mg$ (b) ${}_{53}^{129} I$

9.6 Calculate the number of electrons for the following isotopes: (a) ${}_{19}^{40} K$ (b) ${}_{37}^{87} Rb$

NUCLEAR REACTIONS

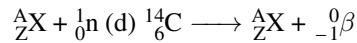
9.7 Classify the following nuclear reactions as: (a) α decay (b) β decay (c) γ decay (d) positron emission (e) electron capture (i) ${}_{92}^{238} U \longrightarrow {}_{90}^{234} Th + {}_{2}^{4} He$ (ii) ${}_{19}^{42} K \longrightarrow {}_{20}^{42} Ca + {}_{-1}^0 e$ (iii) ${}_{8}^{15} O \longrightarrow {}_{7}^{15} N + {}_{+1}^0 e$ (iv) ${}_{88}^{228} Ra \longrightarrow {}_{89}^{228} Ac + {}_{-1}^0 e$ (v) ${}_{6}^{13} C + {}_{1}^1 H \longrightarrow {}_{7}^{14} N + {}_{0}^0 \gamma$

9.8 Classify the following nuclear reactions as: (a) α decay (b) β decay (c) γ decay (d) positron emission (e) electron capture (i) ${}_{6}^{14} C \longrightarrow {}_{7}^{14} N + {}_{-1}^0 \beta$ (ii) ${}_{6}^{11} C \longrightarrow {}_{5}^{11} B + {}_{+1}^0 \beta^+$ (iii) ${}_{26}^{55} Fe + {}_{-1}^0 \beta \longrightarrow {}_{25}^{55} Mn + X-ray$ (iv) ${}_{88}^{234} Th^* \longrightarrow {}_{88}^{234} Th + {}_{0}^0 \gamma$ (v) ${}_{88}^{226} Ra \longrightarrow {}_{86}^{222} Rn + {}_{2}^4 \alpha$

UNKNOWN ISOTOPES IN NUCLEAR REACTIONS

9.9 Identify the unknown radioactive particle involved in the following nuclear equations: (a) ${}_{6}^{11} C \longrightarrow {}_{Z}^A X + {}_{+1}^0 \beta^+$ (b) ${}_{Z}^A X + {}_{-1}^0 \beta \longrightarrow {}_{25}^{55} Mn + X-ray$ (c) ${}_{88}^{234} Th^* \longrightarrow {}_{Z}^A X + {}_{0}^0 \gamma$ (d) ${}_{88}^{226} Ra \longrightarrow {}_{86}^{222} Rn + {}_{Z}^A X$

9.10 Identify the unknown radioactive particle involved in the following nuclear equations: (a) ${}_{4}^9 Be + {}_{Z}^A X \longrightarrow {}_{6}^{12} C + {}_{0}^1 n$ (b) ${}_{15}^{31} P + {}_{1}^1 H \longrightarrow {}_{16}^{31} S + {}_{Z}^A X$ (c) ${}_{1}^3 H + {}_{1}^2 H \longrightarrow$



HALF-LIFE OF A RADIOISOTOPE

9.11 The following organic chemicals are used in chemotherapy. Indicate the chemical that will last longer in the body. (a) Ondansetron ($t_{\frac{1}{2}} = 360\text{min}$) (b) Capecitabine ($t_{\frac{1}{2}} = 2400\text{s}$)

9.12 The following organic chemicals are used in chemotherapy. Indicate the chemical that will last longer in the body. (a) Carmustine ($t_{\frac{1}{2}} = 0.5\text{h}$) (b) Capecitabine ($t_{\frac{1}{2}} = 2400\text{s}$)

9.13 Research the half-life of the following isotopes: (a) Chlorine-36 (b) Cadmium-109 (c) Copper-64 (d) Chromium-51 (e) Carbon-14 (f) Gold-195 (g) Calcium-45

9.14 Research the half-life of the following isotopes: (a) Potassium-40 (b) Cesium-137 (c) Cobalt-57 (d) Bismuth-212 (e) Gallium-67 (f) Americium-241

9.15 Xenon-133, which is used for lung imaging, has a half-life of 5.2 days. If 50.0 mg of Xe-133 were prepared at 8:00 A.M. on Monday, how many mg remain at 8:00 A.M. on the following day?

9.16 Gold-198, which is used for liver disease diagnosis, has a half-life of 2.7 days. If 100.0 mg of Au-198 were prepared at 8:00 A.M. on Monday, how many mg remain at 8:00 A.M. on Wednesday? And at 2:00 P.M. on Wednesday?

9.17 The half-life of bromine-74 is 25 min. How much of a 100 mg sample is still active after 100 min?

9.18 Technetium-99m has a half-life of 6 h, being used to image the skeleton and heart muscle in particular. How much of a 5 mg sample is still active after 50 min?

9.19 The half-life of bromine-74 is 25 min. 20mg of the isotopes remain after 10 minutes of preparing the sample.



Calculate the initial mass of the bromine-74 sample.

9.20 The half-life of Au-198 is 2.7 days. 100mg of the isotopes remain after 5days of preparing the sample. Calculate the initial mass of the isotope sample.

RADIATION MEASUREMENT, UNITS AND RADIATION EFFECTS

9.21 $^{199}\text{Tc}^*$ is a radioisotope used for liver disease diagnosis. The administered activity of the isotope is 740MBe. How much is this activity in mCi?

9.22 $^{201}\text{TI}^*$ is a radioisotope used for myocardial scan. The administered activity of the isotope is 110MBe. How much is this activity in mCi?

9.23 The measured activity of an isotope in the lab is 100 counts per minute. Calculate this measurement in counts per second.

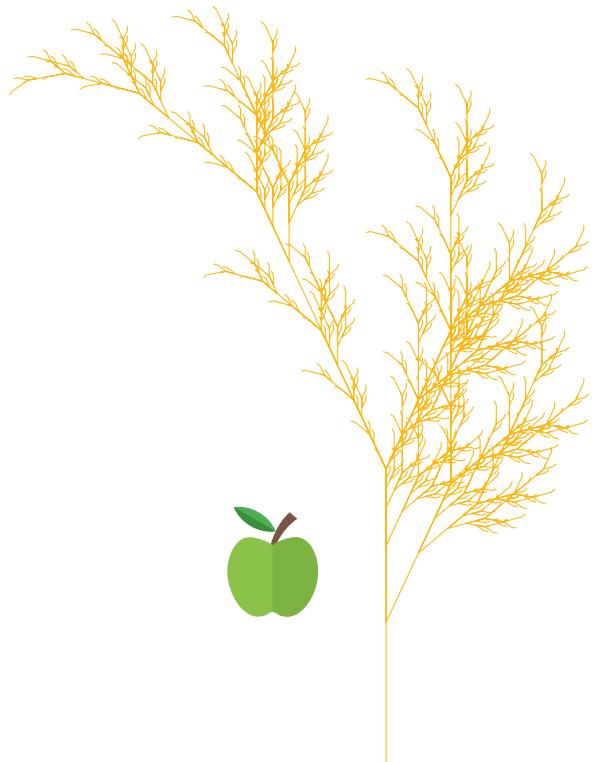
9.24 The measured activity of an isotope in the lab is 20 counts per second. Calculate this measurement in counts per minute.

9.25 Select a symptom of mild radiation sickness from the list below: (a) a lowered white cell count. (b) a lowered red blood cell count. (c) a raised white cell count. (d) a raised red blood cell count. (e) a white cell count of zero.

9.26 Select a symptom that does not result from acute radiation sickness from the list below: (a) permanent hair loss. (b) loss of appetite. (c) fatigue. (d) fever. (e) nausea. (f) diarrhea.

9.27 Alpha radiation is the most damaging because alpha particles (a) have the largest charge. (b) have the greatest energy. (c) have the greatest mass. (d) consist of high energy electrons.

9.28 Gamma radiation is the most penetrating because gamma particles (a) have the largest charge. (b) have the greatest energy. (c) have the greatest mass. (d) consist of high energy electrons.



College Chemistry

A Comprehensive Set of Imperfect Notes

This set of lectures present content in a simple and clear way, while including numerous worked examples and many problems with solution. In particular, this current version of the manuscript contains more than 90 solved problems and more than 200 problems with solution. It also contains numerous diagrams and graphs specifically developed to clarify the content. The organization of the note intends to help the reader digest the large content typically covered in a GOB or college Chemistry class. Every part ends with a review quiz that assesses content.