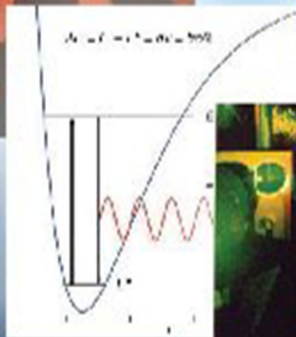
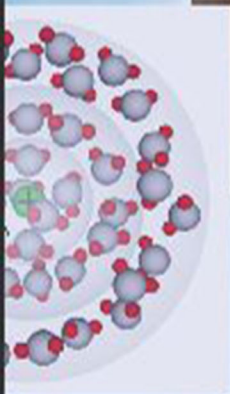
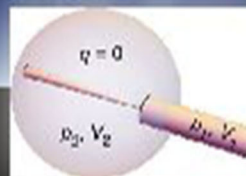
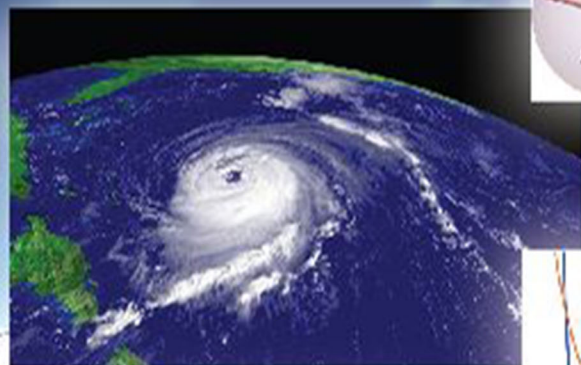
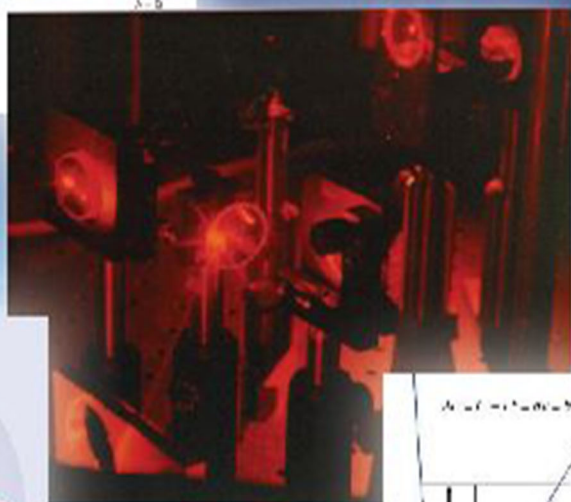
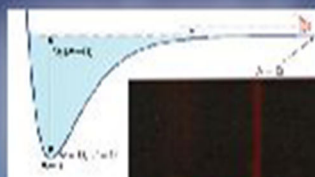


PHYSICAL CHEMISTRY

HOW CHEMISTRY WORKS

Kurt W. Kolasinski



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Physical Chemistry

Physical Chemistry

How Chemistry Works

Kurt W. Kolasinski

Department of Chemistry, West Chester University, USA

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This edition first published 2017
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John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

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Library of Congress Cataloging-in-Publication Data

Names: Kolasinski, Kurt W.

Title: Physical chemistry : how chemistry works / Kurt W. Kolasinski.

Description: Chichester, West Sussex : John Wiley & Sons, Inc., 2016. | Includes index.

Identifiers: LCCN 2016015389 | ISBN 9781118751121 (pbk.) | ISBN 9781118751206 (epub) | ISBN 9781118751213 (adobe PDF)

Subjects: LCSH: Chemistry, Physical and theoretical--Textbooks. | Chemistry--Textbooks.

Classification: LCC QD453.3 .K65 2016 | DDC 541--dc23

LC record available at <https://lccn.loc.gov/2016015389>

A catalogue record for this book is available from the British Library.

ISBN: 9781118751121

Set in 9.5/13pt Meridien by Aptara Inc., New Delhi, India

If you do not communicate your ideas, you are not doing science. You are only engaging in a hobby.

— Kurt W. Kolasinski

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Preface

This book is dedicated to my wife Kirsti, who now knows that the most frightening words in the English language are, “Yes, you’re right, I will write another book.” And to my daughter Annika, who dutifully kept asking, “How many more pages?”

To all of the readers looking at the daunting task of progressing through this tome, just keep moving one step forward every day, for the more we know, the more we seek. The more we seek, the more we find. The more we find, the more we know what to ask. No matter what new technology is ever invented, the answer to how to perform problem solving in physical chemistry (and anything else) will always be get enough sleep, eat your vegetables, make rational decisions, and do your homework.

I still crave lucidity, though this passage will be anything but lucid, and you may ask the author to explain “aber wann wird man je verstehen”? Potential overdrive, free thought and open minds. As if beams of photons lit the night. Cast adrift. Seas of rage have not yet assailed my concern for the truth. In the dark when I write, I’m sitting here by candle flame. Visions in the night. Show me what is right. Neues Glück liegt auf den Wegen. Die Welt ist groß und sie ist mein. Alte Träume die brach gelegen. Ich lass die Sorgen Sorgen sein. Thus, the “thank- you”s begin with a tip of my hat to the music of Dead Can Dance, Nick Cave, Einstürzende Neubauten, VNV Nation, Judas Priest, In Extremo, and all the Schattenreich artists.

Concerning content I would especially like to thank to Jim Falcone, Bill Gadzuk, Wayne Itano, Eckart Hasselbrink, Erik Månsson, David Pratt, Patrik Schmuki, Greg Sitz, Pat Vaccaro, David Wineland, Dick Zare, and Ahmed Zewail for valuable discussions and comments on the text. My high-school chemistry teacher was John Spina, who proves that dedicated, inspiring teachers exist even in dire school districts. Would it were that society promoted more of the former and fewer of the latter. My high-school physics teacher was the wrestling coach. Thus, I became a physical chemist rather than a chemical physicist; though being one or the other means never having to choose. Jacob Bradley, Abbie Ganas, Paige Kogelman, Shawn Pfeil, and Mark Schuman helped with proofreading. I greatly appreciate the work of Olaf Högermeyer, animator extraordinaire, for creating several of the better-looking illustrations in this book. The sample shown in Fig. 15.2 was prepared and imaged by Abbie Ganas. Data for Fig. 16.1 were taken by William Barclay, Kyle Spivack and Devon Zimmerman. A special thanks to Laurie Butler and Matt Brynteson for providing the data for Fig. 25.16. And to Jin Cheng, Florian Libisch and Emily Carter for calculating the potential surfaces in Fig 17.12. Photos of various gems were taken with the kind assistance of Ivan Kaplan and Teresa Martin of Kaplan Fine Jewelery, West Chester, PA, USA. Dennis Tanjeloff of Astro Gallery of Gems made available the image of pyrite crystals. Many thanks are extended to the myriad students who have weathered my endless tales of burlap and monks, brandy and polar bears; but who nonetheless have asked question after question that helped me clarify what I meant to express and made those explanations more intelligible. Others who have graciously provided me with figures include Flemming Besenbacher, Fleming Crim, Cynthia Friend, Naomi Halas, Sharon Hammes-Schiffer, Marsha Lester, Anne L’Huillier, Erik Månsson, Mike McClain, Hope Michelsen, Jens Nørskov, and Geraldine Richmond.

About the companion website

This book is accompanied by a companion website:

www.wiley.com/go/kolasinski/physicalchemistry

The website hosts a variety of supplementary resources for students and instructors.

For Instructors:

- PowerPoint files of the illustrations presented within this text
- Solutions manual

For Students:

- Worked examples

CHAPTER 1

Introduction

Much of chemistry is motivated by asking ‘how’. How do I make a primary alcohol? React a Grignard reagent with formaldehyde. How do I get a solution containing phenolphthalein to change from colorless to pink? Add base. How do I make solid barium sulfate? Add enough barium chloride dissolved in water to a solution of sodium sulfate and the barium sulfate precipitates out. Physical chemistry is motivated by asking ‘why’. The Grignard reagent and formaldehyde follow a molecular dance known as a reaction mechanism, in which stronger bonds are made at the expense of weaker bonds. In acidic solutions, the protonated form of phenolphthalein absorbs light in the ultraviolet range but is transparent in the visible range. When base is added, the phenolphthalein is converted to a deprotonated form which absorbs in the green part of the visible spectrum, peaking at 553 nm. The absorption of light occurs when an electron is promoted from its ground state to an excited state. BaCl_2 and Na_2SO_4 are both highly soluble in water. BaSO_4 is less soluble in water. When enough Ba^{2+} and SO_4^{2-} are present in water, it is energetically more favorable for them to form a solid compound, which is denser than water and, therefore, precipitates to the bottom of the beaker. If you are interested in asking why and not just how, then you need to understand physical chemistry.

Introductory chemistry – general chemistry and an introduction to synthesis – has introduced all the major, sweeping, most important aspects of chemistry. In most cases you have been presented these ideas without foundations; that is, you have been told that certain phenomena occur – such as chemical bonding or phase transitions – but you have only had hints given to you about *why* these phenomena occur. You have been introduced to special cases and single-temperature results. However, you have not been given the machinery to move away from ideal cases, or to change parameters so as to predict what will happen next. Let us jog your memory about some key concepts (and perhaps add a few details I wish you would have been taught). This will illuminate where we have to go and motivate the discussion of much of our machinery building. It will also highlight some areas in which the simplifications of introductory chemistry sometimes border on myth building. The role of physical chemistry is to tear down mirages of explanation in order to construct the machinery that results in fundamental understanding. To a large extent, physical chemistry is the study and mastery of k , K , n , and ψ , (rate constant, equilibrium constant, moles, and wavefunction) and how they respond to t , T , and p (time, temperature, and pressure). That is, we want to understand the time evolution and response to experimental conditions of chemical systems. Along the way perhaps the three most important constants that we will have to understand the implications of are k_B , h and N_A (the constants of Boltzmann, Planck, and Avogadro, respectively) and how they relate to the energy, propensity for change and our ability to probe systems at the atomic level.

1.1 Atoms and molecules

Our chemical universe is made up of atoms and molecules. For the purposes of this course we are going to limit ourselves to electrons, protons and neutrons, and not worry about any internal structure of these particles (though we will mention the Higgs boson a couple of times, so don't get the blues!). Atoms are composed of a nucleus, where the protons and neutrons reside, and electrons that occupy the space outside of the nucleus. The space occupied by the electrons is called an orbital. Orbitals have specific shapes; you should recall the spherical s orbitals and dumbbell-shaped p orbitals (as usually represented in chemistry). The d orbitals and f orbitals are more complex yet. Atoms are neutral; that is, the number of negatively charged electrons exactly balances the number of positively charged protons. Neutrons carry no charge. An atom can be excited, for instance by the absorption of light. If the photons in the light are energetic enough, an electron can be removed from the atom to form a positive ion. Negative ions are formed when an atom captures an extra electron from some external source.

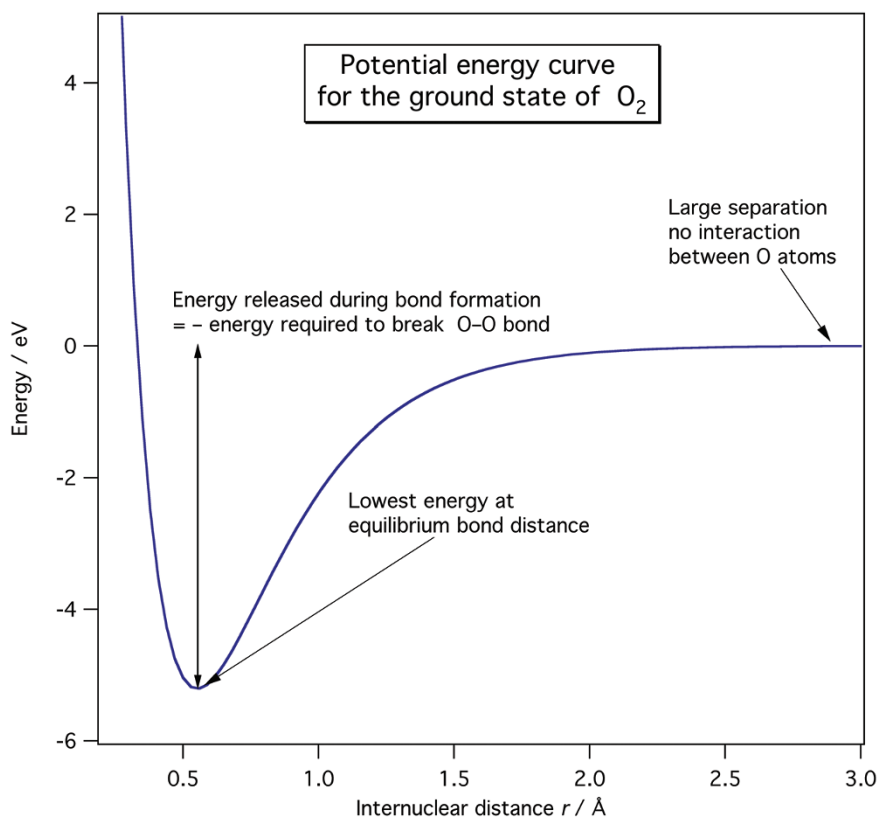


Figure 1.1 A potential energy diagram for the ground electronic state of the O_2 molecule.

Certain atoms will form molecules when they interact with each other. Molecules have well-defined stoichiometries (ratios of how many atoms combine) and well-defined geometries with characteristic bond distances and bond angles. As molecules become bigger and bigger they may be able to take on several different configurations (isomers).

A molecule is held together by chemical bonds. An especially wicked misconception held by many is that energy is released when a chemical bond is broken. As shown in Fig. 1.1, *energy is released when a chemical bond is formed*. Chemical bond formation between two atoms must be an *exothermic* process or else it would never occur. Conversely then, *it takes energy to break a chemical bond*, and this is an *endothermic* process. Chemical bonds in molecules come in two broadly defined flavors. In a covalent bond, electrons are shared. If they are shared equally, a nonpolar bond is formed, but if they are shared unequally a polar bond is formed. Unless the geometry of the molecules has a special symmetry that makes charge distributions cancel out, polar bonds lead to polar molecules, that is, molecules that exhibit dipole moments. In ionic bonds, electrostatic forces hold together the positive and negative charges on ions formed by the transfer of at least one complete electron.

The motions of subatomic particles are governed by quantum mechanics, not classical mechanics. Classical mechanics describes everyday particles: billiard balls and apples falling on the heads of drowsy natural philosophers. Quantum mechanics is different. The energy states of electrons are governed by quantum mechanics. Electrons occupy atomic orbitals in atoms and molecular orbitals in molecules. Because covalent bonding is due to electrons and their sharing by atoms, bonding is inherently quantum mechanical in nature.

1.2 Phases

Moving from a single molecule or atom to collections of particles, the influences of intermolecular forces become important. There are a number of different types of intermolecular interactions: dipole–dipole, van der Waals and hydrogen bonding are some of the most common. The three most commonly encountered phases in chemistry are gases, liquids, and solids. In this course, we will not have to worry about the other two: plasmas and Bose–Einstein condensates, which are most likely to be encountered at very high or very low temperatures, respectively.

You are already familiar with the concept of an ideal gas and its equation of state

$$pV = nRT. \quad (1.1)$$

Intermolecular interactions are absent in an ideal gas. Even in a real gas, intermolecular interactions are weak as long as the pressure and temperature are far from the conditions that induce condensation. Gas-phase molecules are free to translate, rotate, and vibrate. There are also electronic excitations, but usually these are not accessible by thermal excitations. The places where we can put energy (translations, rotations, vibrations, and electronic states) are called *degrees of freedom*.

1.2.1 Directed practice

Throughout this book you will find directed practice, short exercises for the reader to collect their thoughts and reinforce concepts. Calculate the volume in m^3 of one mole of ideal gas at *standard temperature and pressure* (STP is defined as $T = 273.15 \text{ K}$ and 100 kPa) and standard ambient temperature ($T = 298.15 \text{ K}$) and atmospheric pressure ($p = 101.325 \text{ kPa}$), denoted SATP.

[Answers: 0.0227 m^3 , 0.0245 m^3]

As the temperature is lowered or the pressure increased, the particles in a gas are pushed together, and eventually intermolecular interactions will lead to condensation. Most commonly, a gas will condense into a liquid. Intermolecular interactions are much more important in liquids than gases because the molecules are much closer together. That the molecules are much closer together means that their density is much higher, and that they collide with each other much more frequently than gas-phase molecules. Liquid-phase molecules are still free to translate, rotate and vibrate, but the spectra associated with these degrees of freedom look different than when they are in the gas phase. Liquids are commonly classified as to whether they are polar or nonpolar. Like tends to dissolve like, and polar solvents are capable of dissolving ionic compounds (electrolytes) into their constituent ions. Nonelectrolytes dissolve without the formation of ions. Electrolyte solutions can conduct electrical currents.

At yet lower temperature and higher pressure, liquids condense into solids. Solids are usually denser than liquids, but there is not nearly as big a change during this phase transition as the one from the gas phase to a condensed phase. The atoms and molecules in a solid can no longer translate and rotate freely. There are still vibrations and electronic excitations. Solids are often classified by their electronic structure according to their electrical conductivity properties: metals conduct well and have no band gap between their valence and conduction bands, insulators conduct poorly because they have a large band gap; semiconductors are somewhere in between.

1.3 Energy

When energy is deposited in a system it is distributed among the degrees of freedom available to it. You should recall the basic equation of calorimetry, which states that the amount of heat q required to raise the temperature by ΔT of n moles of a substance is related to the heat capacity C_m (the subscript m denotes a molar quantity)

$$q = nC_m \Delta T. \quad (1.2)$$

You may remember that C_m depends on whether the process occurs at constant volume or constant pressure; thus, we usually denote it as $C_{p,m}$ or $C_{v,m}$. You probably do not appreciate the central importance of the heat capacity to molecular and chemical properties. We will learn much more about this, learn how it is related to molecular and phase structure, and that because of this it is a temperature-dependent property. Because C_m is both temperature- and phase-dependent, we will see that Eq. (1.2) is an approximation and we will have to learn how to treat parameters that are not constant more generally. This is where calculus becomes essential.

1.3.1 Directed practice

Calculate the heat required to raise the temperature of 10.0 g water, initially at 298 K , by $1 \text{ }^\circ\text{C}$. The heat capacity of water is $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$.

[Answer: 41.8 J]

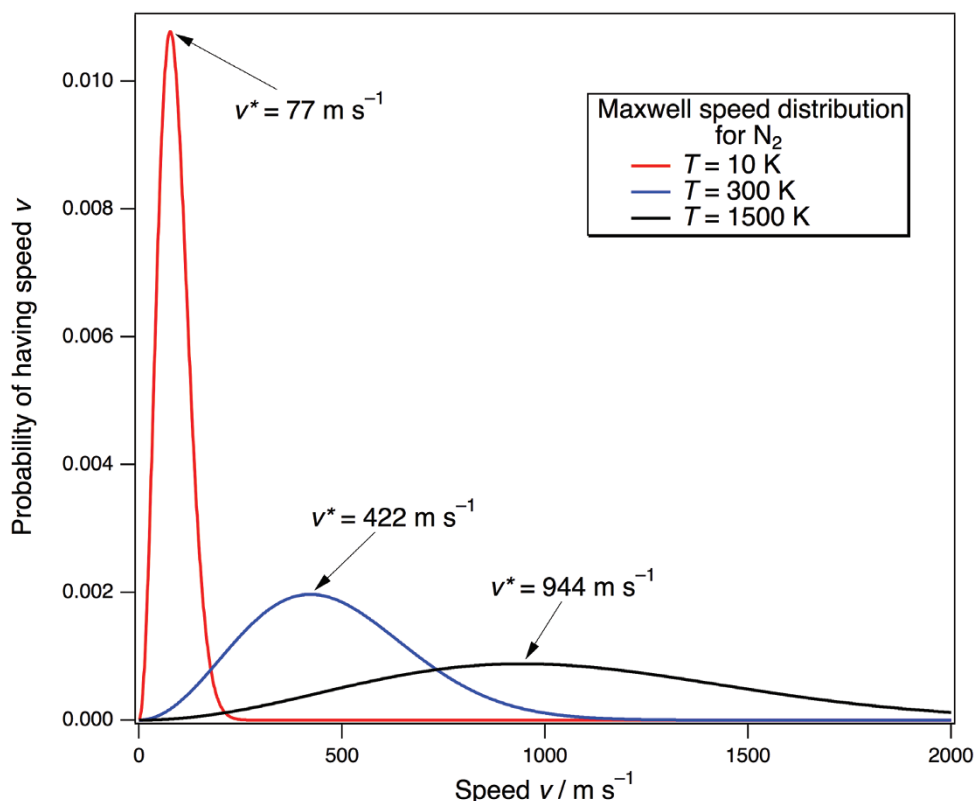


Figure 1.2 Maxwell distributions of molecular speed for gaseous N_2 at three different temperatures.

Equilibrating a sample of gas to a particular temperature leads to a partitioning of energy into the translational, rotational, and vibrational degrees of freedom. Unless we confine our molecules to very small boxes, the partitioning of energy into the translational degree of freedom is described by a continuous distribution known as the Maxwell speed distribution. A Maxwell distribution looks something like Fig. 1.2.

The rotational and vibrational degrees of freedom are inherently quantum mechanical. The energy levels associated with these degrees of freedom are not continuous, but are quantized into discrete energy levels. Energy is partitioned into these degrees of freedom by changing the populations of these levels, that is, by changing the number of molecules in each of the energy levels. This population distribution follows a Boltzmann distribution, about which we need to learn more.

Electronic states are also quantized. The transitions between different energy levels are responsible for lines and bands observed in rotational, vibrational, and electronic spectroscopy. Nuclear magnetic resonance involves spin flips among nuclei.

1.4 Chemical reactions

When atoms and molecules are mixed together, they can react to form products. Some reactions are spontaneous and occur upon mixing, but some reactions only occur if they are given a push. All chemistry involves changes in electron-sharing arrangements. Bonds can both be made and broken during reactions. Chemical reactivity can be classified according to how the reactions proceed. Thermal chemistry occurs when the control of temperature is used to regulate reactivity and the rate of reaction. In other words, the energy that is randomly distributed among the degrees of freedom of the system is sufficient to cause electron-sharing arrangements to change. This is so common that it is usually just called 'chemistry.' Electrochemistry involves the exchange of free charge (electrons and sometimes protons). It responds to temperature but, importantly, it can also respond to voltages placed on electrodes in contact with the reacting species. Stimulated chemistry is induced by excitations caused by photon absorption, electron scattering, or ion scattering. The

most common form is photochemistry, in which electronic excitations engendered by photon/matter interactions result in the formation of products.

Reactants are often separated from products by an *activation barrier*. The height of this barrier – the activation energy – must be overcome during the course of the reaction. Higher temperatures lead to more high-energy species being present in the Maxwell–Boltzmann distribution (i.e., the tail to high velocity shown in Fig. 1.2 gets bigger); this is why we commonly see reaction rates increase with increasing temperature. The rates of reactions also depend on the concentrations of reactants, because reactants usually have to collide in order for them to react. The collision rate increases when a higher density of reactants is present. The presence of a *catalyst* can also accelerate a reaction. Catalysts lower activation energies but are not themselves consumed in reactions.

Chemical reactions occur because systems are attempting to reach a minimum in their Gibbs energy. The Gibbs energy, G , contains contributions from enthalpy H and entropy S . Enthalpy is involved with the energy of interactions (such as bonding), while entropy is involved with the randomization of energy among the degrees of freedom and disorder. A system will evolve as long as the Gibbs energy has not reached its minimum; in other words, $\Delta G = 0$ at equilibrium. At equilibrium, the Gibbs energy is no longer changing. The change in Gibbs energy is related to the change in enthalpy ΔH , the absolute temperature T and the change in entropy ΔS by

$$\Delta G = \Delta H - T\Delta S. \quad (1.3)$$

At equilibrium, the rates of forward and reverse reactions are the same and the concentrations of species involved are constant. An equilibrium constant K relates these concentrations to one another. For the reversible reaction



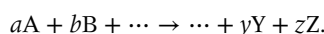
we have

$$K = \frac{[C][D]}{[A][B]}. \quad (1.5)$$

Non-ideal behavior manifests itself in both rate equations and equilibrium calculations. We deal with these deviations from ideal behavior by introducing activity in place of concentrations.

It is important to understand whether a system is in an equilibrium or nonequilibrium state. Nonequilibrium states may be characterized as being in a state of flux, in a steady state, or in a metastable state. Equilibrium is controlled by limits set by thermodynamics. Nonequilibrium states are controlled by reaction kinetics. Another way to phrase this is that thermodynamics makes certain predictions about what is allowed and what is forbidden. While what is forbidden by thermodynamics is forbidden, that which is allowed by thermodynamics is only a limit that, while it cannot be exceeded, this limit might not be approached if the reaction kinetics do not allow the system to evolve to the equilibrium state.

A balanced stoichiometric chemical reaction is written with *stoichiometric coefficients* a , b , and so forth, which are all positive numbers



The IUPAC defines *stoichiometric numbers* ν_A , ν_B , and so forth as signed quantities, which are negative for reactants and positive for products. Stoichiometric coefficients are the absolute values of the stoichiometric numbers. In other words, $a = |\nu_A| = -\nu_A$ but $z = |\nu_Z| = \nu_Z$.

1.4.1 Directed practice

Calculate the molar Gibbs energy of formation $\Delta_f G_m^\circ$ of HCl(g) at 298 K if the molar enthalpy of formation $\Delta_f H_m^\circ$ is $-92.31 \text{ kJ mol}^{-1}$ and the molar entropy of formation $\Delta_f S_m^\circ$ is $186.90 \text{ J K}^{-1} \text{ mol}^{-1}$.

[Answer: $-148.01 \text{ kJ mol}^{-1}$]

1.5 Problem solving

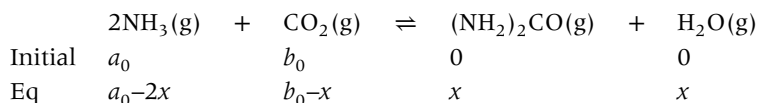
Observation is the foundation of empirical knowledge and science. There is much to be gained from description. However, if all you want is description then take an art class and don't ask questions, for artists are also looking for meaning. Therefore, we are going to go beyond the descriptive.

Up to this point in your academic career, you have primarily used only the two most basic levels of learning: (1) *remembering*; and (2) *understanding*. To perform well in physical chemistry you will need to become proficient in the next three levels of learning, namely (3) *applying*, (4) *analyzing*, and (5) *evaluating*. Mastering all of these will set you up to perform research, which requires the highest level of learning: (6) *creating*. This course is about *problem solving* – that is, solving the problem of how chemical species react with each other, how they respond to changes in conditions such as temperature and pressure, and what is the basis of a number of their physical properties. I am attempting to teach you methods of chemical problem solving: Applying what you are taught to new situations to analyze variations on problems and evaluate the results. In your future careers you will need to learn a variety of things. It is unlikely that there is a textbook written for most of the things you will encounter. In your professional life you will never find a real problem to solve in which exactly all of the right information is given to you, in the right units. You will always be faced with either too much information or too little information, and have to decide which parts are necessary. Being able to tackle problems under these circumstances is an important skill. It is the foundation of the ability of physical chemists/chemical physicists to tackle problems ranging from atomic physics to thermodynamics, to reaction dynamics in all phases, through nanoscience and beyond biochemistry into astrochemistry. Learning problem solving is one of the most important skills you will acquire in this course.

There is no single method for problem solving. The best way to solve a problem is the one that gives the right answer. If you see the path to an answer, take it. There are often multiple avenues. But if you are stuck, how do you get started? Let me outline the four basic steps for problem solving. These may not always all be applicable, but checking each will help you get past the writer's block of staring at a blank page.

- 1 Start with a balanced reaction (including phases).
- 2 Draw a diagram.
- 3 Draw a straight line.
- 4 Answer the question asked with appropriate units.

These are obviously oversimplifications for impact and ease of remembrance; but let's consider this distillation. Always start by identifying the system and how it is changing. Organize the information you have available. Evaluate the physical processes that occur. If there is not a diagram to draw, then, for example, chart the amount of substance in moles and how it changes. I call this a *reaction chart*. For the gas-phase reaction of ammonia (initial concentration a_0) with carbon dioxide (initial concentration b_0) to form an equilibrium with urea and water (not initially present), it has the form



Note that a properly balanced reaction also includes all phase designations.

Next, determine what equations relate to the data given and answers sought. If you do not communicate your results then you are partaking in a hobby, not performing science. Thus, we are forever presenting graphs or constructing tables. Drawing a straight line (or otherwise presenting results appropriately) for interpretation and clarity is an important part of analysis, evaluating models, and drawing conclusions. In the first instance, you always need to identify what question is being asked and what data you have available. But problem solving does not always start at the beginning and take a linear path to the last step. Sometimes, you need to work backwards: look at the final result you want and find the step that would lead to it. Sometimes, looking at the end is the most important step in showing you where you need to start.

To engage in effective problem solving you need to stop thinking solely of the correct *answer* and start thinking about the correct *method* of finding the answer. A revealing recurring comment on student evaluations of my teaching is "stop doing derivations and show us the answer." Performing derivations is one of the primary means of teaching you the techniques you need to apply to perform effective problem solving. The 'Directed practice' exercises are intended to reinforce this. Directed practices are intended to get you into the habit of interrupting your reading, stopping to think about what you have just read, performing a simple calculation (or filling in missing steps in a derivation), and enhancing comprehension of what you just read. Get into this habit, perform it often – even when a Directed practice is not indicated – and your comprehension and problem-solving prowess will increase. Make your own Directed practices to get you used to and comfortable with manipulating equations and ideas. If you don't understand a Directed practice, ask a question in the lecture.

1.5.1 Directed practice

If $a_0 = b_0 = a$, set up the algebraic equation required to find the value of x for the reaction of ammonia and carbon dioxide to produce urea and water.

Hint: you will have to set up an equation similar to Eq. (1.5) and then collect terms to find a third-order polynomial that you set equal to zero.

[Answer: $4x^3 - \left(8a - \frac{1}{K}\right)x^2 + 5a^2x - a^3 = 0$]

1.5.2 Performing calculations

A calculation a day keeps ignorance away. All calculations were once done by hand. You should look at performing calculations with only a calculator as outdated as using only tables of logarithms and a slide rule. At this point in your scientific education and career it is time to use computers for calculations and the presentation of data. Spreadsheet software is okay for calculating grades. It can be a good introduction to scientific computing but a spreadsheet is hardly sufficient for proper data analysis. You should consider introducing yourself to real data analysis software. There are many options such as Igor Pro, Origin, and SigmaPlot. This type of software allows you to handle large data sets, perform calculations, present data and perform curve fitting. If you are considering further study in physical chemistry then you should also consider learning software that is capable of algebraic and symbolic computing as well as calculus, such as Mathematica, MathCAD, and MATLAB.

1.5.3 Units and reporting data

A number reported without the appropriate units is the scientific equivalent of nihilistic relativism. Forty-two is the answer to everything, we just do not know what the conversion factor is to the units that actually have meaning. This is a dramatic way of saying, no answer is correct without the correct units. Many of your errors will have their basis in not using the right units or the right conversion factors. It is not always easy, but it is always something that you have to check, and a check of the units is one of the surest ways to determine if your calculation has gone astray. Numerical values and units, just like the symbols that represent these physical quantities, can be manipulated with the usual rules of algebra. Let algebra be your friend and use it constantly.

Another basic topic that often causes confusion is the reading of data in tables and figures. Always label column and axes with units. Shorthand is often used to avoid the repetition of orders of magnitude. Best practice is to divide out the units and appropriately and clearly include indications of orders of magnitude. Note the equivalence of the following. Note further that units are in Roman type while variables are italicized, and that a space appears between numbers and units. Manipulation of the magnitudes and units of physical quantities is known as *quantity calculus*. For more on this see the IUPAC Green Book.

T / K	T^{-1} / K^{-1}	K / T	$10^3 \text{ K} / T$	$T^{-1} / (10^{-3} \text{ K}^{-1})$
300	3.33×10^{-3}	3.33×10^{-3}	3.33	3.33

p / Pa	$p / (10^6 \text{ Pa})$	p / MPa	$\ln(p/\text{Pa})$	$\ln(p/\text{MPa})$
1.45×10^6	1.45	1.45	14.19	0.3716

1.6 Some conventions

This section includes some conventions on notation contained in Tables 1.1 through 1.5 that will be used throughout this book. All recommendations are in line with the IUPAC Green Book. There are several different types of reaction that we will encounter, and we will use symbols to help differentiate these. Reactions that occur on the molecular level in one step are elementary reactions. These reactions are differentiated from one another on the basis of how many species are involved as reactants. *Elementary reactions* may involve one, two or three species, and are termed unimolecular (or monomolecular), bimolecular or trimolecular (termolecular), respectively. An arrow going from left to right is used to show the direction of reaction.

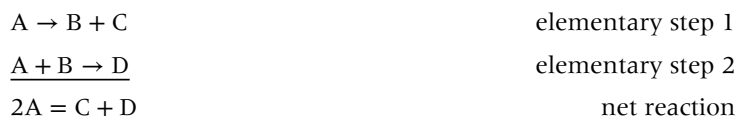


Thus, the number of species on the left determines the *molecularity* of the reaction. If the elementary step is reversible, it can proceed in either the forward or reverse directions and this is indicated with two double-headed arrows.



A *reaction mechanism* is the set of elementary steps that occurs during a net reaction. If the mechanism contains two or more steps, it is a *composite mechanism*. The *net reaction* is the sum of the elementary steps (some of which may have to be

counted more than once), and it has the proper stoichiometry for the overall reaction. The net reaction has its reactants and products separated by an equal sign. Thus, the net reaction to form C and D from 2A by a two-step composite mechanism is shown below



A is a reactant, C and D are products, B is an intermediate. A net reaction is not described by molecularity, only an elementary reaction is. A net reaction is also indicated by opposing arrows with only a single stroke in their heads; the convention used throughout this book.



Table 1.1 States of aggregation.

Symbol	State	Symbol	State
a or ads	species adsorbed on a surface	am	amorphous solid
aq	aqueous solution	aq, ∞	aqueous solution, infinite dilution
cd	condensed phase, i.e. liquid or solid	cr	crystalline
f	fluid phase, i.e. liquid or gas	g	gas or vapor
l	liquid	lc	liquid crystal
mon	monomeric form	n	nematic phase
pol	polymeric form	s	solid
sat	saturation or saturated	sat l	saturated liquid
sln	solution	vit	vitreous

Table 1.2 SI base units.

Base quantity	Name	Symbol
length	meter	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
thermodynamic temperature	kelvin	K
amount of substance	mole	mol
luminous intensity	candela	cd

Table 1.3 SI derived units.

Derived quantity	Name	Symbol	Expressed in terms of other SI units
plane angle	radian	rad	$\text{m m}^{-1} = 1$
solid angle	steradian	sr	$\text{m}^2 \text{m}^{-2} = 1$
frequency	hertz	Hz	s^{-1}
force	newton	N	m kg s^{-2}
pressure, stress	pascal	Pa	$\text{N m}^{-2} = \text{m}^{-1} \text{kg s}^{-2}$
energy, work, heat	joule	J	$\text{N m} = \text{m}^2 \text{kg s}^{-2}$
power, radiant flux	watt	W	$\text{J s}^{-1} = \text{m}^2 \text{kg s}^{-3}$
electric charge	coulomb	C	A s
electric potential	volt	V	$\text{J C}^{-1} = \text{m}^2 \text{kg s}^{-3} \text{A}^{-1}$
electromotive force			
electric resistance	ohm	Ω	$\text{V A}^{-1} = \text{m}^2 \text{kg s}^{-3} \text{A}^{-2}$
electric conductance	sieman	S	$\omega^{-1} = \text{m}^{-2} \text{kg}^{-1} \text{s}^3 \text{A}^2$
electric capacitance	farad	F	$\text{C V}^{-1} = \text{m}^{-2} \text{kg}^{-1} \text{s}^4 \text{A}^2$
magnetic flux	weber	Wb	$\text{V s} = \text{m}^2 \text{kg s}^{-2} \text{A}^{-1}$
magnetic flux density	tesla	T	$\text{Wb m}^{-2} = \text{kg s}^{-2} \text{A}^{-1}$
inductance	henry	H	$\text{V A}^{-1} \text{s} = \text{m}^2 \text{kg s}^{-2} \text{A}^{-2}$
catalytic activity ^[1]	katal	kat	mol s^{-1}

[1] Should replace the (enzyme) unit, $1 \text{ U} = \mu\text{mol min}^{-1} \approx 16.67 \text{ nkat}$.

Table 1.4 SI prefixes.

Submultiple	Name	Symbol	Multiple	Name	Symbol
10^{-1}	deci	d	10^1	deca	da
10^{-2}	centi	c	10^2	hector	h
10^{-3}	milli	m	10^3	kilo	k
10^{-6}	micro	μ	10^6	mega	M
10^{-9}	nano	n	10^9	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f	10^{15}	peta	P
10^{-18}	atto	a	10^{18}	exa	E
10^{-21}	zepto	z	10^{21}	zetta	Z
10^{-24}	yocto	y	10^{24}	yotta	Y

Table 1.5 Symbols, operators, and functions.

Description	Symbol
Signs and Symbols	
left-hand side of equation	LHS
right-hand side of equation	RHS
equal to	=
not equal to	\neq
identically equal to	\equiv
equal to by definition	$\stackrel{\text{def}}{=}$ or $:=$
approximately equal to	\approx
asymptotically equal to	\simeq
corresponds to	$\hat{=}$
proportional to	\sim, \propto
tends to, approaches	\rightarrow
infinity	∞
less than	$<$
greater than	$>$
less than or equal to	\leq
greater than or equal to	\geq
much less than	\ll
much greater than	\gg
Operations	
magnitude of a	$ a $
mean value of a	$\langle a \rangle, \bar{a}$
n factorial	$n!$
sum of a_i	$\sum a_i, \sum_i a_i, \sum_{i=1}^n a_i$
product of a_i	$\prod a_i, \prod_i a_i, \prod_{i=1}^n a_i$
Functions	
base of natural logarithms	e
exponential of x	$\exp x, e^x$
logarithm to the base a of x	$\log_a x$
natural logarithm of x	$\ln x$
logarithm to the base 10 of x	$\lg x$
change in x	$\Delta x = x(\text{final}) - x(\text{initial})$
infinitesimal variation of f	δf
limit of $f(x)$ as x tends to a	$\lim_{x \rightarrow a} f(x)$
first derivative of f	$df/dx, f', (d/dx)f$
second derivative of f	$d^2f/dx^2, f''$
partial derivative of f	$\partial f/\partial x$

(continued)

Table 1.5 (Continued)

Description	Symbol
total differential of f	df
inexact differential of f	δf
integral of $f(x)$	$\int f(x) dx, \int dx f(x)$
Kronecker delta	$\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}$
Dirac delta function	$\delta(x), \int f(x) \delta(x) dx = f(0)$
unit step function, Heaviside function	$\epsilon(x), H(x), h(x),$ $\epsilon(x) = 1 \text{ for } x > 0, \epsilon(x) = 0 \text{ for } x < 0$
gamma function	$\Gamma(x) = \int_0^{\infty} t^{x-1} e^{-t} dt$ $\Gamma(n+1) = n!$ for positive integers n
convolution of functions f and g	$f * g = \int_{-\infty}^{\infty} f(x-x') g(x') dx'$
Complex Numbers	
square root of $-1, \sqrt{-1}$	i
real part of $z = a + ib$	$\text{Re } z = a$
imaginary part of $z = a + ib$	$\text{Im } z = b$
modulus of $z = a + ib$	$ z = (a^2 + b^2)^{1/2}$
argument of $z = a + ib$	$\arg z; \tan(\arg z) = b/a$
complex conjugate of $z = a + ib$	$z^* = a - ib$
Vectors	
vector \mathbf{a}	\mathbf{a}, \vec{a}
Cartesian components of \mathbf{a}	a_x, a_y, a_z
unit vectors in Cartesian coordinate system	$\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$ or $\mathbf{i}, \mathbf{j}, \mathbf{k}$
scalar product	$\mathbf{a} \cdot \mathbf{b}$
vector or cross product	$\mathbf{a} \times \mathbf{b}$
nabla operator, del operator	$\nabla = \mathbf{e}_x \frac{\partial}{\partial x} + \mathbf{e}_y \frac{\partial}{\partial y} + \mathbf{e}_z \frac{\partial}{\partial z}$
Laplacian operator	$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$
Matrices	
matrix with elements A_{ij}	\mathbf{A}
product of matrices \mathbf{A} and \mathbf{B}	\mathbf{AB} , where $(\mathbf{AB})_{ik} = \sum_j A_{ij} B_{jk}$
unit matrix	\mathbf{E}, \mathbf{I}
inverse of a square matrix \mathbf{A}	\mathbf{A}^{-1}
transpose of matrix \mathbf{A}	$\mathbf{A}^T, \vec{\mathbf{A}}$
complex conjugate of matrix \mathbf{A}	\mathbf{A}^*
conjugate transpose (adjoint) of \mathbf{A} (hermitian conjugate of \mathbf{A})	$\mathbf{A}^H, \mathbf{A}^\dagger$, where $(\mathbf{A}^\dagger)_{ij} = A_{ji}^*$
trace of a square matrix \mathbf{A}	$\sum_i A_{ii}, \text{tr } \mathbf{A}$
determinant of a square matrix \mathbf{A}	$\det \mathbf{A}, \mathbf{A} $

SUMMARY OF IMPORTANT EQUATIONS

You should already be familiar with these equations from your previous introduction to chemistry. We will learn much more about them, their limitations and their derivations but you should be prepared to use them now.

$$m = M/N_A$$

Mass per molecule m is the molar mass M divided by the Avogadro constant N_A .

$$n = m/M = N/N_A$$

Amount of substance (moles) n is equal to mass divided by molar mass as well as number of molecules N divided by the Avogadro constant.