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978-1-107-00678-2 — A Life Scientist's Guide to Physical Chemistry
Marc R. Roussel
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Orientation: what is physical chemistry about?

Chemistry is traditionally divided into a small number of subfields, namely organic, inorganic, analytical and physical chemistry. It's fairly easy to say what the first three are about, but it's much harder to define physical chemistry. The problem is that physical chemistry is all of the following simultaneously:

- A discipline in its own right, with its own set of problems and techniques;
- The source of the basic theory that underlies all of the chemical sciences;
- A provider of experimental methods used across the chemical sciences.

Note that "chemical sciences" includes biochemistry and materials science, among other fields that depend on physical chemistry for at least some of their theory and methods. Physical chemistry's large mandate means that it's difficult to put a finger on what it is exactly. It's a bit like chemistry itself that way: every time you come up with a definition, you immediately think of half a dozen things done under that heading that don't fit.

Rather than trying to give a simple, neat definition of physical chemistry, I'm going to tell you about the big theories that make up physical chemistry. Hopefully, this will give you an idea of what physical chemistry is about, even if we can't wrap it up in a neat package as we can with the other subfields of chemistry.

Most physical chemists would tell you that physical chemistry has three major subdivisions: quantum mechanics, thermodynamics and kinetics (Figure 1.1). **Quantum mechanics** is the study of the properties of matter at the atomic level. In quantum mechanics, we talk about the forces that hold atoms and molecules together, and about the interaction of matter with light (spectroscopy), among other things. **Thermodynamics** is the study of matter from the other extreme: in thermodynamics, we don't worry about the microscopic details, we just deal with matter as we normally perceive it in terms of variables like temperature, pressure and volume. Chemical thermodynamics concerns itself mainly with the energetics of reactions, which sometimes allows us to say something about which reactions are possible under given conditions. Finally, **kinetics** is the study of the rate of reactions. It turns out that thermodynamics doesn't tell us anything about how fast a reaction will occur, so we need a separate set of theories to treat this important issue.

Figure 1.1 also shows some of the connections between the three major theoretical pillars of physical chemistry. **Statistical thermodynamics** allows us to calculate thermodynamic

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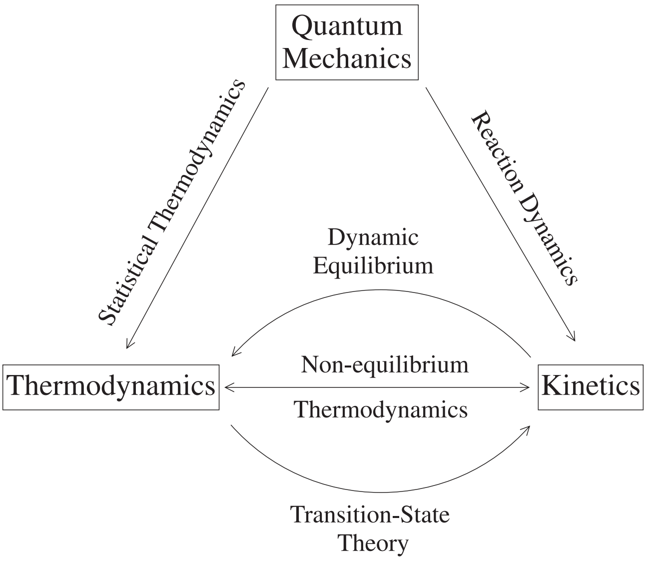

Figure 1.1 The major theories of physical chemistry and their relationships. Note that the figure only shows some of the connections between quantum mechanics, thermodynamics and kinetics.

properties from the quantum properties of matter. **Reaction dynamics** similarly lets us calculate rates of reaction from quantum mechanical principles. The classical theory of **dynamic equilibrium** connects kinetics to equilibrium and thus to a whole body of knowledge in thermodynamics. **Transition-state theory** is a theory of rates of reaction that rests on a foundation of thermodynamic reasoning. **Non-equilibrium thermodynamics** allows us to understand both the energetics and kinetics of reactions in a unified framework. These are just a few of the connections we could put into this diagram.

You will note the emphasis on theories. This is perhaps one of the defining characteristics of physical chemistry: physical chemists like to have a big theoretical umbrella that covers knowledge in the discipline. This is not to say that physical chemists aren't concerned with experiments. Most physical chemists are, in fact, experimentalists. In my experience though, almost all physical chemists ultimately want to connect their measurements to some deeper principles. This is certainly a common attitude among scientists, but perhaps a more intensely felt one among physical chemists than might be the case in other areas of chemistry.

Given the complexity implied by Figure 1.1, how can we proceed to learn physical chemistry? Fortunately, the major theories are coherent entities that can be studied one at a time. Because of the connections between the theories, a knowledge of one will enhance our appreciation of the others, but we can still study kinetics, for example, as a thing in itself. In this book, we will study all three of the major theories, as well as some of the bridges between them. The intention is to provide you with a core of chemical theory that can be applied to a wide variety of problems in the chemical sciences.

A note on graph axis labels and table headings

We can only graph pure numbers. We could put numbers with units in a table, but to avoid repeating the units, we typically just put them in the table heading, leaving just numbers in the table itself. Throughout this text, you will see graph axis labels and table headings that look like "λ/nm." The logic behind this notation is as follows: λ is a physical observable that has both a value and units. The pure number in the table or graph is what you get by dividing out the units of λ, in this case nm.

This way of labeling axes and tables may not seem like a huge improvement over just writing "λ (nm)." The advantage appears when you have numbers that all share a common multiple of a power of 10 that you want to avoid writing down over and over again. For example, molar absorption coefficients are often a multiple of $10^5\,\text{L}\,\text{mol}^{-1}\text{cm}^{-1}$. If I'm typing a table of these coefficients, I might not want to repeat '$\times 10^5$' for every entry. I would then label the table heading as "$\varepsilon/10^5\,\text{L}\,\text{mol}^{-1}\text{cm}^{-1}$," meaning that the number in the table is what you get when you divide ε by $10^5\,\text{L}\,\text{mol}^{-1}\text{cm}^{-1}$. For example, if one of the numbers in the table is 1.02, then that means that $\varepsilon/10^5\,\text{L}\,\text{mol}^{-1}\text{cm}^{-1} = 1.02$, or that $\varepsilon = 1.02 \times 10^5\,\text{L}\,\text{mol}^{-1}\text{cm}^{-1}$. Once you get used to this way of writing table headings, you will find that it's much clearer than any of the alternatives you routinely run across.

Part One

Quantum mechanics and spectroscopy

2

A quick tour of quantum mechanical ideas

The objective of this chapter is to go over a few of the basic concepts of quantum mechanics in preparation for a discussion of spectroscopy, which is in many ways the business end of quantum mechanics, at least for chemical scientists. We will also need a few quantum mechanical ideas from time to time in our study of thermodynamics and of kinetics.

Why should we learn quantum mechanics at all? Atoms and molecules are small, and their constituent parts, electrons, protons and neutrons, are even smaller. Early in the twentieth century, we learned that small things don’t obey the laws of classical mechanics. A different kind of mechanics, quantum mechanics, is required to understand chemistry on a fundamental level. In fact, we need different mechanical theories to treat extremes of both size and speed. Figure 2.1 summarizes the situation. There isn’t a sharp cut-off between the various sectors of this diagram. Also note that some of the theories are more general than others. We could in principle use quantum mechanics or general relativity to predict the trajectories of tennis balls, but it just isn’t worth the effort, given that classical mechanics works perfectly well in this range of masses and speeds. On the other hand, classical mechanics doesn’t give very good results for things that are either extremely large, or small, or fast.

Like it or not, to discuss phenomena on an atomic scale, we need quantum mechanics. Ordinary (non-relativistic) quantum mechanics is generally adequate, although electrons in heavy atoms sometimes reach relativistic speeds (approaching the speed of light, c), requiring relativistic quantum mechanics. We can get away with using classical mechanics to treat large-scale motions of molecules (e.g. motions of domains of proteins). However, many molecular phenomena will remain mysterious to us if we don’t arm ourselves with at least a little bit of quantum mechanical theory.

2.1 Light

From the seventeenth to the nineteenth century, there were two competing theories on the nature of light. Some evidence (diffraction, refraction etc.) suggested that light was a wave phenomenon. On the other hand, a particle theory was attractive to many workers due to the linear propagation of light rays. Although the wave theory of light was more

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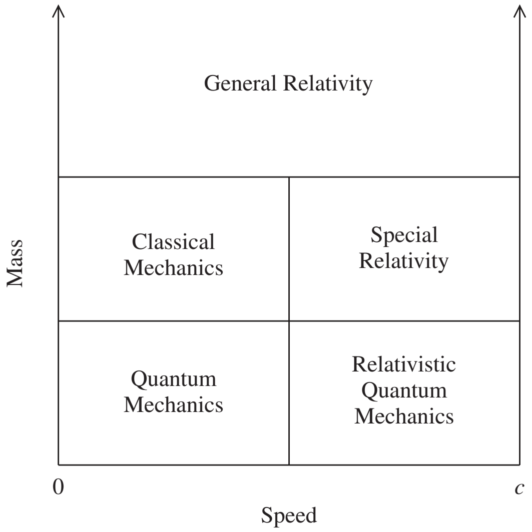

Figure 2.1 Sketch of the domains of validity of different mechanical theories (not to scale). The speed of light (c) sets an upper limit on the speeds that can be reached by material objects. Relativistic theories are required for objects whose speeds are close to the speed of light. Classical mechanics is appropriate to objects of moderate size moving at speeds well below c. Quantum mechanics is required to treat phenomena on an atomic scale.

broadly successful in this period, there was no clear resolution of the matter until the 1860s.

James Clerk Maxwell's contributions to physics are among the most important and beautiful of the nineteenth century. His crowning achievement was perhaps the unification of the laws of electricity and magnetism into a set of consistent equations which together describe all electrical and magnetic phenomena. As he studied these equations, he made a startling discovery: the equations suggested the possibility of electromagnetic waves. Furthermore, the wave speed, which could be computed from the equations, was extremely close to the best estimate then available of the speed of light. Very soon, everyone became convinced that a final explanation of the nature of light had been discovered: light is an electromagnetic wave, i.e. a traveling wave of oscillating electric and magnetic fields. Figure 2.2 shows a schematic drawing of an electromagnetic wave.

If light is a wave phenomenon, then it obeys the usual laws of wave dynamics. For instance, its frequency (ν) and wavelength (λ) are related by

$$c = \lambda\nu, \tag{2.1}$$

where c is the wave speed, in this case the speed of light. The SI unit of frequency is the hertz (Hz). One hertz is one cycle per second.

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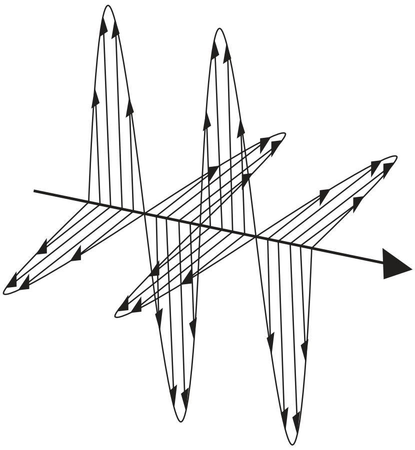

Figure 2.2 Schematic diagram of an electromagnetic wave. The wave is made up of oscillating electric and magnetic fields, represented here by vectors. The vertical vectors (say) represent the electric field at different points along the wave propagation axis, while the horizontal vectors represent the magnetic field. The direction of propagation of the wave is indicated by the large arrow. The wave amplitude is the height of the wave (measured in electric field units). The wavelength is the distance between two successive maxima. The frequency is the number of cycles of the wave observed at a fixed position in space divided by the observation time.

Example 2.1 Wavelength and frequency The shortest wavelength of light visible to us is approximately 400 nm. The corresponding frequency is

$$\nu = \frac{c}{\lambda} = \frac{2.997\,924\,58 \times 10^{8}\,\mathrm{m\,s^{-1}}}{400 \times 10^{-9}\,\mathrm{m}} = 7.49 \times 10^{14}\,\mathrm{Hz}.$$

Instead of the wavelength or frequency, we sometimes use the **wavenumber** $\tilde{\nu}$ to describe light waves. The wavenumber is just the inverse of the wavelength, so $\tilde{\nu} = \lambda^{-1}$. If the wavelength is the length of one wave, the wavenumber is the number of waves per unit length. Wavenumbers are mostly used in spectroscopy, which we will study in the next chapter, and are usually given in reciprocal centimeters ($\mathrm{cm^{-1}}$). This unit is so commonly used that spectroscopists often read values like 1000 $\mathrm{cm^{-1}}$ as “one thousand wavenumbers,” although this is a bad habit which should be discouraged.

Example 2.2 Wavelength and wavenumbers Wavenumbers are most commonly encountered in infrared (IR) spectroscopy. The infrared part of the electromagnetic spectrum ranges from about 750 nm to 1 mm. Let us convert this into a wavenumber range. Let’s start with the lower end of the wavelength range. That wavelength, converted to cm, is

$$\frac{(750\,\mathrm{nm})(10^{-9}\,\mathrm{m\,nm^{-1}})}{10^{-2}\,\mathrm{m\,cm^{-1}}} = 7.5 \times 10^{-5}\,\mathrm{cm}.$$

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This corresponds to a wavenumber of $(7.5 \times 10^{-5}\,\text{cm})^{-1} \approx 13\,000\,\text{cm}^{-1}$. If we do the same calculation for the other end of the infrared range, we get $10\,\text{cm}^{-1}$, so the infrared ranges from 10 to $13\,000\,\text{cm}^{-1}$.

Maxwell's electromagnetic theory of light was thought for a few decades to answer all questions about the nature and behavior of light. However, as so often happens in science, an anomaly cropped up. The photoelectric effect, the ejection of electrons from a metal surface when irradiated with light of a sufficiently high frequency, resisted explanation by Maxwell's theory. In a nutshell, the problem was that the energy of a classical electromagnetic wave should be related to its amplitude. Cranking up the intensity should eventually provide enough energy for any desired process, including removing electrons from matter. The frequency shouldn't have anything to do with it.

It was Einstein who provided the resolution of this puzzle in 1905: he postulated that light is made up of particles he called photons. Each photon has an energy related to the frequency of the light by an equation originally proposed by Max Planck to explain blackbody radiation (wherein lies a whole other tale):

$$E = h\nu, \tag{2.2}$$

where h is Planck's constant. This innocent-looking equation revolutionized physics; it links the energy of a *particle* to a *wave* property, the frequency ν. Einstein had thus provided a completely original and unexpected solution to the old debate about the nature of light: light is *both* a particle *and* a wave. Light propagates in space like a wave, but in its interactions with matter, light behaves as if it were made of particles which are absorbed as individual units. This ability of light to behave either like a particle or like a wave, depending on the situation, is called **duality**.

This solves the puzzle of the photoelectric effect: assuming that only one photon is absorbed at a time (an idea known as the law of photochemical equivalence, to which we shall shortly return), then an individual photon either does or does not have enough energy to eject an electron from a metal surface. Since the energy of a photon is proportional to its frequency, it is easy to see that the frequency must be sufficiently high in order to cause a photoelectric effect. In the photon theory, increasing the intensity of a light beam only increases the number of photons delivered by the beam per unit time, and not the energies of the photons.

Example 2.3 Photon energy We calculated earlier that the highest frequency of visible light is approximately 7.49×10^{14} Hz (Example 2.1). The energy of a single photon with this frequency is

$$E = h\nu = (6.626\,068\,8 \times 10^{-34}\,\text{J}\,\text{Hz}^{-1})(7.49 \times 10^{14}\,\text{Hz}) = 4.96 \times 10^{-19}\,\text{J}.$$

The energy of a mole of photons of this frequency is

$$\bar{E} = (4.96 \times 10^{-19}\,\text{J})(6.022\,142\,0 \times 10^{23}\,\text{mol}^{-1}) = 299\,\text{kJ}\,\text{mol}^{-1}.$$

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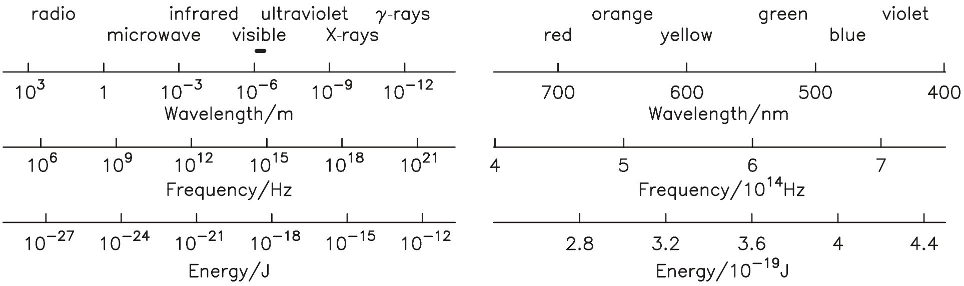

Figure 2.3 Electromagnetic spectrum. The full spectrum is shown on the left, plotted on a logarithmic scale. The visible part of the spectrum (marked by the heavy dash under the word visible) represents only a tiny fraction of the range of wavelengths commonly observed in the natural environment. On the right, we see a blowup of the visible part of the spectrum. The labels (γ-ray, X-ray etc.) only name an approximate region of the spectrum. The color labels of the visible spectrum are particularly unreliable as there is wide variation in color perception among people.

It turns out that this energy is similar to chemical reaction energies. This observation is of considerable importance in photochemistry and photobiology.

Equations (2.1) and (2.2) can be combined to give a relationship between photon energy and wavelength, or, since the wavenumber is the reciprocal of the wavelength, between energy and wavenumber:

$$E = \frac{hc}{\lambda} = hc\tilde{\nu}. \tag{2.3}$$

While we can only see electromagnetic radiation in a very restricted range, there is neither an upper nor a lower limit to the possible wavelengths of light. Figure 2.3 shows the electromagnetic spectrum. The labels are not to be taken too seriously; there is no exact dividing line between, for instance, γ-rays and X-rays. However, these labels are convenient identifiers of the spectral region to which a given radiation belongs.

Einstein is of course most famous for his work on relativity. One of the central equations of relativity theory is

$$E^2 = c^2 p^2 + m_0^2 c^4, \tag{2.4}$$

where E is the energy of a particle, p is its momentum and m_0 is the rest mass (the mass at zero velocity) of the particle. (In relativity, the mass varies with speed.) If we take the case of a particle at rest ($p = 0$), we recover the most famous version of this equation: $E = m_0 c^2$. Photons represent the opposite extreme. They have a rest mass of zero, so for photons

$$E = cp. \tag{2.5}$$

In other words, a photon has a momentum proportional to its energy. This momentum can be related to the wavelength by

$$E = cp = hc/\lambda;$$
$$\therefore\ p = h/\lambda. \tag{2.6}$$

Before we proceed to some examples, it is worth recalling that the SI unit of mass is the kilogram, not the gram. Thus, if we consistently work in SI units, the units of momentum obtained from Equation (2.6) will be $\mathrm{kg\,m\,s^{-1}}$.

Example 2.4 Momentum of a mole of photons What is the momentum of a mole of 400 nm photons?

$$p = \frac{6.626\,068\,8 \times 10^{-34}\,\mathrm{J\,Hz^{-1}}}{400 \times 10^{-9}\,\mathrm{m}} = 1.66 \times 10^{-27}\,\mathrm{kg\,m\,s^{-1}}$$

per photon or

$$(1.66 \times 10^{-27}\,\mathrm{kg\,m\,s^{-1}})(6.022\,142\,0 \times 10^{23}) = 9.98 \times 10^{-4}\,\mathrm{kg\,m\,s^{-1}}$$

for a mole of photons.

Example 2.5 Photon pressure and solar sailing While the momentum of a photon is quite small, the Sun just keeps producing photons so that, away from a planet's gravitational field, this is sufficient to accelerate a spacecraft equipped with a large sail, i.e. a thin sheet of reflective material, to respectable speeds. Solar sailing is made possible by the near-vacuum conditions present in interplanetary space (which minimize frictional losses) and by the microgravity environment (which makes it possible to deploy very large, thin sails). Photon pressure has been used for attitude control on a number of spacecraft. The first spacecraft to actually be propelled by a solar sail is the Japanese craft IKAROS. IKAROS is a 315 kg craft carrying out a variety of science experiments. It has deployed a square solar sail with a 20 m diagonal, corresponding to an area of $200\,\mathrm{m}^2$. As of this writing, IKAROS is near Venus, where the solar flux is[1] $\phi_E = 2563\,\mathrm{J\,m^{-2}s^{-1}}$. This is the amount of electromagnetic radiation from the Sun that would be received on a one-square-meter surface every second near the orbit of Venus. Equation (2.5) allows us to transform this energy flux into a momentum flux:

$$\phi_p = \frac{\phi_E}{c} = \frac{2563\,\mathrm{J\,m^{-2}s^{-1}}}{2.997\,924\,58 \times 10^{8}\,\mathrm{m\,s^{-1}}} = 8.549 \times 10^{-6}\,(\mathrm{kg\,m\,s^{-1}})\mathrm{m^{-2}s^{-1}}.$$

By multiplying by the surface area of the sail, we get the momentum of the photons passing through that area every second. The maximum push is provided when the sail is perpendicular to the solar flux. In this case, the photons are reflected straight back so the

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[1] *CRC Handbook of Chemistry and Physics*, 66th edn.; Boca Raton: CRC Press, 1985, p. F-129.