

Chapter 1: Chemical Reactivity

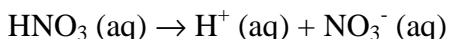
1.0 Introduction

There are two aspects of chemical reactivity:

How far does a reaction run?

How fast does a reaction run?

Some reactions progress almost completely to products, for example the dissociation of nitric acid:



Some reactions barely progress at all, for example the dissociation of acetic acid:



The degree to which a reaction progresses is called the **extent** of the reaction. When we ask “how far does a reaction run,” we are asking if the extent of the reaction lies to the right, producing large amounts of products, or to the left, with large amounts of reactants remaining. The extent of the reaction is expressed quantitatively by the equilibrium constant for the reaction. The extent of chemical reactions is one of the major subjects in **thermodynamics**. When we ask “how fast does a reaction run,” we are asking about the rate of appearance of products. The rates of chemical reactions are expressed quantitatively through rate constants. The rates of chemical reactions are studied in the field of **chemical kinetics**. Taken together, thermodynamics and kinetics answer the questions “How far?” and “How fast?”

Once we characterize a reaction, we naturally wonder why the equilibrium constant and rate constant have their particular values. To answer these questions, we need to build a molecular model of the reaction. To build molecular models, we need to understand the chemical bond. Understanding chemical bonding allows us to predict the structure of molecules and to understand bond breaking and bond making steps in reactions. **Quantum mechanics** explores the nature of the chemical bond and the interaction of light with matter. We then use **statistical mechanics** to predict chemical reactivity from our knowledge of chemical structure. Statistical mechanics is the bridge that joins the microscopic world of molecular structure with the macroscopic world of thermodynamics and kinetics. The major divisions of this text correspond to these major subdisciplines within physical chemistry: kinetics, thermodynamics, quantum mechanics, and statistical mechanics.

Biology, chemistry, geology, mathematics, psychology, and physics comprise a spectrum of overlapping sciences that are designed to solve important problems. The sciences satisfy our desire to understand the universe. The sciences are synergistic activities with no boundaries among the disciplines. However, chemistry does have a unique perspective. Chemistry seeks to use our knowledge of molecular structure to predict the function of chemical systems. The emphasis on **structure-function relationships** is the central theme of any chemistry course, and physical chemistry in particular. The functions of chemical systems include their physical properties and, most importantly, their chemical reactivity.

But why do we do chemistry? We have a drive to uncover the laws and processes that explain all physical phenomena. We just need to know. In addition, chemistry has great potential for helping us to live more prosperous and productive lives. Nano-technology, for example, is one specific area of current interest for expanding our beneficial use and control of chemical processes. Chemistry provides us the tools to face a wide array of challenges. The supply of food, clean air, clean water, and energy are in many ways chemical problems. For example, we need new materials and catalysts for direct solar energy conversion and new techniques for biomass conversion to useful fuels. Fighting disease is also a challenge, including finding new drugs to combat multiple antibiotic resistant bacteria, strategies for fighting viral and parasitic infections, preventing cancer, and finding cures for diabetes and Alzheimer's disease. Understanding processes in the environment and environmental protection are of central importance. **Biogeochemical chemistry** is an important discipline that applies physical chemical concepts to understanding the cycling of the chemical constituents of life and energy in the environment. Understanding structure-function relationships is central for finding chemical solutions to these problems. All of these challenges require the best understanding and effort that we can apply. We face many pressing problems, and chemistry can provide solutions.

1.1 Chemical Reactivity

Thermodynamics: Thermodynamics is historically the first modern branch of chemistry. The goal of thermodynamics is to provide a fundamental and concrete understanding of all aspects of our physical world, especially "How far?" Thermodynamics studies transfers of heat and work. Work includes chemical work, which we can think of as the work of chemical synthesis. But, historically thermodynamics also played another important role. We can look at science as the shared oral and written tradition of our observations of the physical world. In this context, thermodynamics was the first discipline that provided a careful and specific vocabulary for communicating our ideas. With these communication tools in hand we have continued to accumulate a vast array of ideas that help us to predict chemical phenomena. So, likewise, we begin our discussion with some necessary definitions.

The System and the Surroundings: The central concept of thermodynamics is that of the system. The **system** is the simplest part of the universe that displays the process of interest. The system is the thing that you want to study. For example, if you are interested in the properties of water, you would start by pouring some water in a beaker. However, to keep things simple, you would define your system as just the water, and you wouldn't include the beaker or the table on which it sets. On the other hand, if you were interested in how water wets glass, then you would need to define the system as the water and the beaker. So the definition of the system depends on the process you want to study. Then everything else that is not part of the system is considered part of the surroundings. We will find that the interaction of a system with its surroundings is central to the prediction of thermodynamic and quantum mechanical aspects of chemical reactivity.

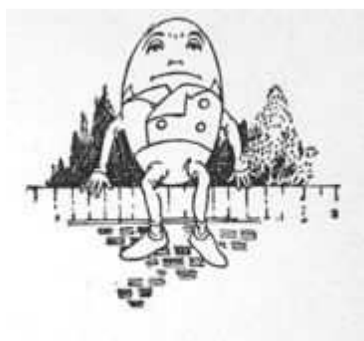
Thermodynamics is meant to be very general. We want to find the underlying form of all physical phenomena. We want to find the laws and theories that explain the behavior of all systems. So we can use any system as an example as we think about processes. To avoid unnecessary complications, we often discuss very simple systems like ideal gases or simple reactions like $\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$. Don't be put off by the simple examples. The system can be

anything that you are interested in. The system can be a polymer sample, DNA, a spinel mineral, a transition metal complex ligand exchange reaction, an SN_2 reaction, a membrane, a cell, a rat, or a human. Yes, calorimetric experiments have been done on living humans. Ecology even extends thermodynamic principles to the ecosystem level. You can consider the earth as the system.

The State of the System and Processes: The **state of a system** is specified by the volume, pressure, temperature, entropy, and mole amounts of each substance (in each phase, if more than one phase is present). These variables are symbolized by V , P , T , S , and n_i , respectively, where i indexes each chemical constituent. If electric fields are present, as in a battery, then the electric potential, ϕ , and electric charge, q , are also an important variables. We often specify the amounts of substances using their concentrations and the total volume of the system. Our goal is to predict the response of the system to a given process. A **process** is the transfer of energy to or from the system in the form of heat, work, or changes in concentration. We want to be able to predict if a given process will be spontaneous, that is, if the process will occur. We also want to be able to predict the position of equilibrium for the system. For a simple example, if we place PCl_5 in a constant volume container at 300 K will the reaction:



be spontaneous and, if so, what is the position of equilibrium? The position of equilibrium is determined by the relative amounts of products and reactants when the reaction goes to equilibrium. Let's define carefully what we mean by a spontaneous process and by equilibrium.



Humpty Dumpty sat on a wall.
Humpty Dumpty had a great fall.
All the King's horses and all the King's men
Couldn't put Humpty together again.

Figure 1.2.1: The story of a spontaneous, irreversible process.

1.2 Spontaneity and Irreversibility

Spontaneous and Equilibrium Processes: A **spontaneous process** is a process that occurs without any outside influence or intervention. A **non-spontaneous process** will not occur on its own, without energy input from the surroundings. The reverse of a spontaneous process is non-spontaneous. Humpty Dumpty is a good analogy. Humpty fell off the wall without any outside influence—eggs easily roll on their own. Rolling off the wall to make a broken mess is a spontaneous process. The reverse process won't occur without a lot of work (and a little glue), Figure 1.2.2.

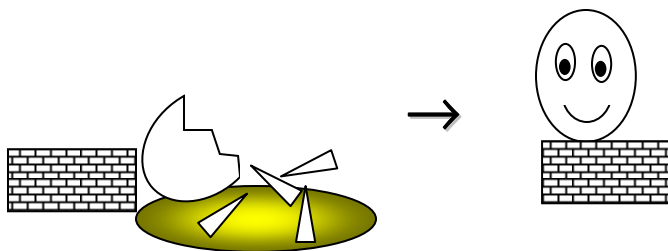
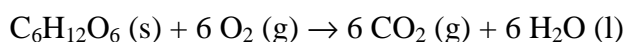


Figure 1.2.2: All the King's horses and all the King's men couldn't put Humpty together again. This process is non-spontaneous.

Consider a simple chemical example, the combustion of glucose:



The combustion of glucose is the major source of energy for your body. The combustion of glucose is a spontaneous process. The reverse process, the reaction of CO_2 and water is non-spontaneous:



Plants convert CO_2 and water into glucose through an intricate series of chemical reactions that require significant inputs of energy from the sun.

Equilibrium processes show no tendency for change. Equilibrium processes are neither spontaneous nor non-spontaneous. In other words, the reverse of an equilibrium process is also at equilibrium. The best examples of equilibrium processes are chemical reactions at equilibrium, for example the dissociation of acetic acid:



At equilibrium, the concentrations of all species show no tendency for change. You can test to see if the system is at equilibrium by applying a very small change, say a small change in H^+ concentration. If the system responds by returning to equilibrium by a small change in the opposite direction, then the system was at equilibrium. On the other hand, if we make a small change for a system that is not at equilibrium, the system evolves to a significantly different state. A very small change applied to a system is called a **perturbation**. The observations concerning perturbations on chemical reactions at equilibrium are described by the well-known LeChâtelier's rules.

We can illustrate these relationships using the potential energy of a mechanical system. Consider a ball rolling on a potential energy surface, Figure 1.2.3. The potential energy, $V(x)$, is a function of the position of the ball, x . The starting position, x_0 , for the ball is shown for three different cases. The process we wish to study is the movement of the ball in the positive x direction, $x > x_0$:

$$x_0 \rightarrow x$$

The question is, will the starting position result in a spontaneous process for an increase in x ? If the derivative of the potential energy with respect to x is negative, the potential energy will decrease with increasing x and the process is spontaneous, Figure 1.2.3a. If the derivative is zero,

the system is at equilibrium and the position won't change, Figure 1.2.3b. If the derivative is positive, the process in the direction written is non-spontaneous and the reverse process is the spontaneous direction; the ball will move to smaller x , Figure 1.2.3c. The initial states in Figure 1.2.3 a and c that correspond to spontaneous or non-spontaneous processes are said to be unstable. The equilibrium state is a stable state.

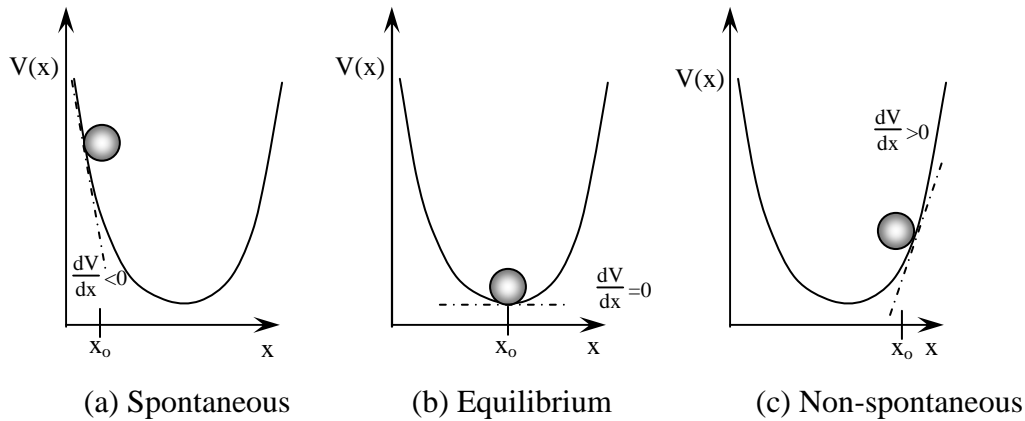


Figure 1.2.3: Potential energy changes for spontaneous, equilibrium, and non-spontaneous processes.

To distinguish the different types of states, we can also apply a small finite change in position, δx , as a perturbation to check to see if the system is at equilibrium. If the potential increases for δx positive and negative, then the system is at equilibrium, Figure 1.2.4 a and b. That is if $\delta V(x \pm \delta x) > 0$, then the process is at equilibrium. This relationship is called a stability criterion.

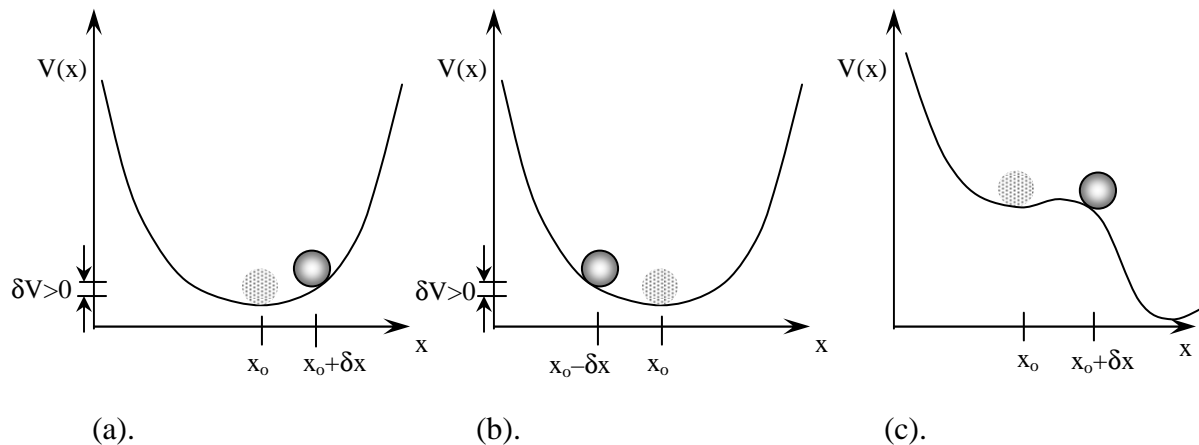


Figure 1.2.4: Stability criterion for equilibrium. (a-b). For a small perturbation in the position, a stable, equilibrium system gives $\delta V(x \pm \delta x) > 0$. (c). A meta-stable system is stable with respect to small changes and unstable for large changes.

There is another important possibility, a meta-stable state, Figure 1.2.4c. Meta-stable states are at equilibrium for very small changes, but unstable for larger changes. Meta-stable states

correspond to a local minimum. An example of a meta-stable state is a super-saturated solution. A supersaturated solution is unchanging until a bit of dust settles on the surface of the solution, or you scratch the sides of the beaker, or you add a seed crystal and then the solute suddenly precipitates out of solution. A bowl of sugar in contact with oxygen in the atmosphere is a chemical example of a meta-stable system. Meta-stable states, such as super-saturated solutions and sugar bowls, are often trapped by slow kinetic processes.

A more chemical example than a rolling ball is the expansion of a gas. Chemical reactions often involve gas phase species, so we need to account for changes in pressure and volume in the overall energy balance for chemical processes. Consider a gas confined in a cylinder by a massless, frictionless, perfectly fitting piston. The initial state of the gas is given by its pressure and volume, P_1 and V_1 . The state of the system is held constant by a stop that fixes the position of the piston. Now, consider a constant temperature expansion of the gas, $V_1 \rightarrow V_2$, with $V_2 > V_1$. This process is diagrammed in Figure 1.2.5a. Is this expansion spontaneous? If we remove the stop and the piston moves outward then the process is spontaneous. The gas will expand if the initial pressure, P_1 , is greater than the external pressure, that is, if $P_1 > P_{\text{ext}}$. The corresponding reverse process, starting at V_2 and returning to V_1 is non-spontaneous. Work must be done on the system by the surroundings that is different than the forward process to return the piston to its original position. On the other hand, if we remove the stop and the piston remains stationary, then the pressure of the system must be equal to the external pressure, $P_1 = P_{\text{ext}}$. This unchanging state with equal pressures is the equilibrium state.

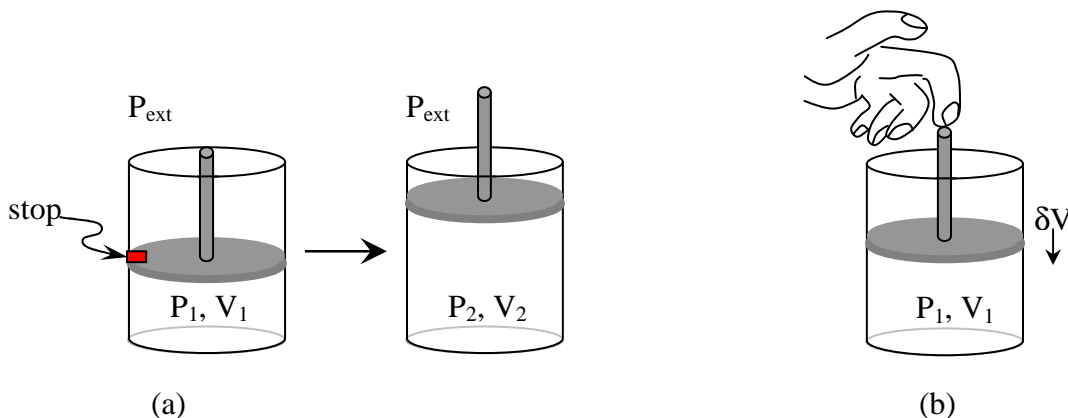


Figure 1.2.5: Spontaneity for gas expansions. (a) For $P_1 > P_{\text{ext}}$ the spontaneous direction is an expansion, $V_2 > V_1$. A system that is not at equilibrium must be held in that non-equilibrium state by a physical constraint. The physical constraint is a mechanical stop that fixes the position of the piston. (b) A small perturbation may be used to test if a system is at equilibrium. If the system returns to its original state, the system was initially at equilibrium.

The application of a small volume perturbation, δV , to our gas piston example is shown in Figure 1.2.5b. Starting with a stop on the piston at the initial volume V_1 , we remove the stop and apply a small change in volume, compressing the gas slightly. If the gas responds by returning to its initial volume V_1 , then the gas was at equilibrium. If the gas expands to a new larger volume or contracts to an even smaller volume, then the system was not initially at equilibrium.

Another example of a system that shows no tendency for change is a steady state system. **Steady states** occur for open systems that have a continual source of energy or material. A

simple example is a bucket with a hole in it, Figure 1.2.6. The level of the water in the bucket will not change if the flow of water going into the bucket is equal to the flow leaving the bucket.

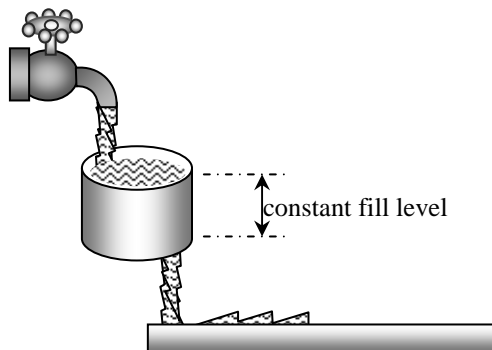
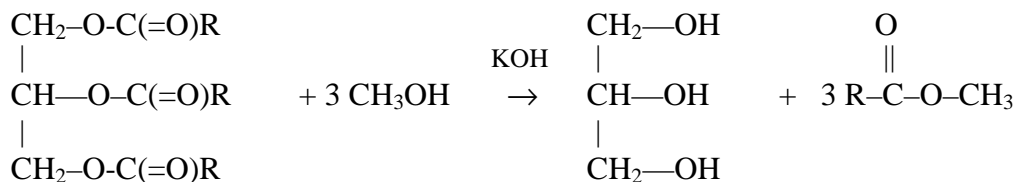


Figure 1.2.6: Steady state systems show no tendency for change, but require the continual input of energy or material. Steady state systems, such as living organisms, are not at equilibrium.

The flows can be chemical, electrical, or flows of energy caused by temperature or pressure gradients. The necessity of carefully balancing the flows makes it seem unlikely that steady state systems can be common or useful. However, living systems at rest can often be considered as being in steady states. Photosynthesis and metabolism can be usefully approximated as steady state systems. Both photosynthesis and metabolism are dependent on the formation of a steady state proton gradient across a membrane. We will use membrane systems as examples in many of the following chapters. In addition, nano-systems are often analyzed using steady state models. Separations techniques like electrophoresis and electro dialysis also operate, in certain cases, in steady states. The atmosphere and other biogeoenvironmental processes are often amenable to study using steady state models.

Flow reactors are common chemical examples of steady state systems. Flow reactors are used in research on oscillating reactions and in chemical engineering. One particular energy resource application is the production of bio-diesel from used French fryer oil. The process is the transesterification of the triglycerides in the vegetable oil with methanol to produce the fatty acid methyl esters and glycerol:



The glycerol is immiscible in the biodiesel methyl esters and is easily separated. The R-groups are $\text{C}_{14}\text{-C}_{22}$ unsaturated alkane chains. This process is efficiently run in a flow reactor with microwave heating.¹

Steady state systems are also considered meta-stable. However, it is important to recognize the difference between meta-stable equilibrium, such as super-saturation and other kinetically hindered process, and meta-stable steady states. Steady states are not at equilibrium and can only be kept in a time-invariant state away from equilibrium by the constant input of energy or material.

Irreversible and Reversible Processes: Equilibrium processes, like weak acid dissociation are **reversible**. You can make a small change in either direction, to the right or the left for the reaction as written, and the process will return to equilibrium resisting the change. Figure 1.2.4a and b show that a perturbation is a useful test for reversibility. The ball rolls forward or backward and then returns to equilibrium in response to perturbations, so the process is reversible. However, as we just discussed, spontaneous processes are not reversible; the reverse of a spontaneous process is non-spontaneous. So we see a correspondence of the concept of irreversibility with spontaneous processes and reversibility with equilibrium processes. Spontaneous processes are **irreversible**, and equilibrium processes are reversible. We can use the terms spontaneous and irreversible interchangeably and the terms equilibrium and reversible interchangeably.

Equilibrium processes are reversible. At equilibrium, the forward and the exact reverse of each process occur. For a steady state process, on the other hand, the reverse process is not the exact reverse of the forward process. In Figure 1.2.6, to be reversible, water would need to be able to flow back into the faucet from the bucket and from the trough back into the bucket.

A net process can occur for a system at equilibrium. A reversible process can occur through a sequence of equilibrium states. Gas expansions, phase transitions, mixing, and chemical reactions can all occur reversibly. Consider the decomposition of one mole of calcium carbonate, as a simple example, Figure 1.2.7.

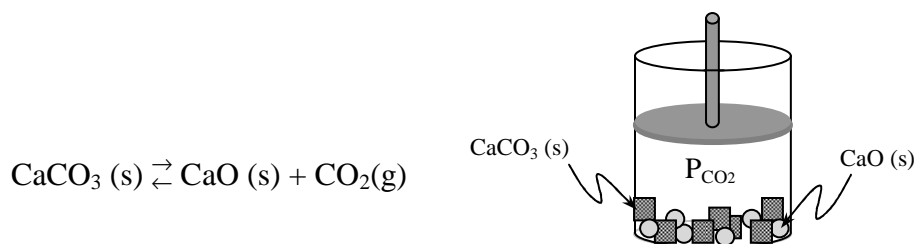


Figure 1.2.7: The decomposition of calcium carbonate is done reversibly by maintaining the system at the equilibrium decomposition pressure. The equilibrium decomposition pressure of CO_2 is constant at a given temperature (for example, 0.100 bar at $755.^\circ\text{C}$).

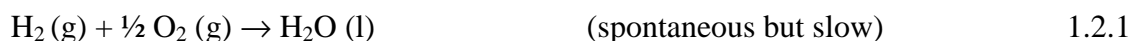
Any amount of pure CaCO_3 and CaO are at equilibrium as long as the CO_2 pressure is equal to the equilibrium pressure and both solids are present. The pressure can be maintained at a constant value if this reaction is run in a cylinder that is fitted with a piston. During the forward process the gas volume increases, but the pressure remains constant and the system remains at equilibrium. To convert a small amount of CaCO_3 into CaO , a small amount of heat is added by increasing the temperature of the surroundings by an infinitesimal amount for a short period. Because the temperature increase is infinitesimal, to convert an equal amount CaO back into CaCO_3 , the same amount of heat is removed from the system by an infinitesimal decrease in temperature for a short period. There is no net change in the surroundings for the combined forward and reverse processes. Because the decomposition of one mole of CaCO_3 can be accomplished through a sequence of such infinitesimal transfers, the net change in the surroundings for the overall combined forward and reverse process is zero, no matter how big the overall transfer. The process occurs through a sequence of equilibrium states, and is therefore reversible.

The concept of irreversible and reversible processes is useful because the description places a system within the context of its surroundings. Consider spontaneous processes; for example, Humpty Dumpty falling off the wall. The change in the system is the production of a big mess. The change in the surroundings for the process is the production of a little heat from the conversion of kinetic energy into random thermal energy from Humpty's collision with the ground. Now consider the reverse process, putting Humpty together again, Figure 1.2.2. All the King's horses and all the King's men are part of the surroundings; they attempt reassembly. The work input to rebuild Humpty is not the exact reverse of the forward process. Instead, we need all the King's horses and all the King's men—and a bit of glue.

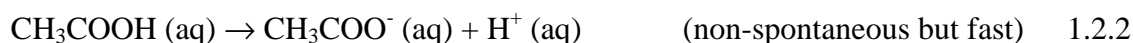
To be precise and general, a reversible process can be returned to its initial state with no net overall change in the surroundings. To reverse an irreversible process, the change in the surroundings is not the exact reverse of the change for the original, forward process. Spontaneous processes occur with exchanges of heat and work with the surroundings. Returning a spontaneous process to its initial state requires energy input from the surroundings in the form of heat and work that is not the exact reverse of the forward process. A net change in the surroundings occurs after a spontaneous process is reversed. The relationship of a system to its surroundings will be a critical part of our analysis of spontaneous processes.

Time and Equilibrium: For our initial discussion of spontaneous and equilibrium processes above, we were careful not to use time in our definitions. An equilibrium system is sometimes defined as a system that does not change macroscopically with time. However, not all time-invariant systems are at equilibrium. A spontaneous process is a process that occurs within a finite period of time, without outside influence or intervention. So, there is often a relationship between time and spontaneity.

Kinetics is the study of the time dependence of physical processes. Thermodynamics is the study of systems at equilibrium. Eventually, all non-equilibrium systems approach equilibrium, so kinetics is the study of the approach to equilibrium. However, we need to be careful about the use of time as a variable with thermodynamics. Time has no effect on thermodynamic predictions. We always wait for equilibrium before applying thermodynamics. Thermodynamics and kinetics are complementary approaches to the study of chemical reactivity. However, thermodynamics and kinetics are also disjoint. The two approaches study very different aspects of chemical reactivity, and it is important not to confuse the two. For example, spontaneous processes can be very, very slow and non-spontaneous processes can be associated with very rapid kinetic processes. For example, the reaction of H₂ and O₂ gas is very favorable thermodynamically, but H₂ and O₂ can be mixed in a flask and not react for very long periods of time:



However, add a catalyst, like platinum, or a spark and the reaction becomes so rapid an explosion results. Oxidation reactions, like the combustion of glucose, are also often in this category. Kinetic stability is one of the reasons why your cells use many enzymes to catalyze the oxidation of glucose. On the other hand, the dissociation of acetic acid is non-spontaneous from a thermodynamic perspective:



Adding one mole of acetic acid to water, the weak acid does not spontaneously dissociate into one mole of hydrogen ions and one mole of acetate ions, as written. On the other hand, proton

transfer reactions are some of the fastest chemical reactions known. The reverse of Eq. 1.2.2 is very spontaneous and changes in both directions occur in picoseconds. Table 1.1 summarizes these observations. We need to be careful not to use kinetic arguments to explain a thermodynamic process, and vice versa.

There is one point of connection, though, between thermodynamics and kinetics and that is when the system reaches equilibrium. We will find that the equilibrium constant for a reaction is given by the ratio of the overall forward and reverse reaction rate constants, $K_{eq}=k_f/k_r$.

Table 1.1: Thermodynamics and Kinetics Study Different Aspects of Chemical Reactivity. Thermodynamic reactivity and kinetic reactivity are disjoint.

	Spontaneous	Non-spontaneous
Fast	$\text{HNO}_3(\text{aq}) \rightarrow \text{H}^+ + \text{NO}_3^-$ $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \xrightarrow{\text{Pt}} \text{H}_2\text{O}(\text{l})$	$\text{CH}_3\text{COOH}(\text{aq}) \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+$ $\text{Zn}(\text{NH}_3)_2^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+} + \text{NH}_3(\text{aq})$
Slow (at 25°C)	$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ $\text{Glucose} + 6 \text{O}_2 \rightarrow 6 \text{CO}_2 + 6 \text{H}_2\text{O}$	$[\text{PtCl}(\text{H}_2\text{O})(\text{NH}_3)_2]^+ + \text{Cl}^- \rightarrow \text{PtCl}_2(\text{NH}_3)_2 + \text{H}_2\text{O}$ $2 \text{CH}_4 + 3 \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO} + \text{CO}_2 + 7 \text{H}_2$

Kinetics, Thermodynamics, and Non-equilibrium Thermodynamics: Thermodynamics is the study of systems at equilibrium. Kinetics is the study of the rates of chemical processes and the approach to equilibrium. Non-equilibrium thermodynamics combines the disciplines of thermodynamics and kinetics. The theory of non-equilibrium thermodynamics has several goals. One goal is to predict the formation of steady states. A second goal is to describe the coupling of different rate processes. One example of coupled processes is the interaction of electrical conductivity, concentration gradients, and the production of entropy in membrane systems. Non-equilibrium thermodynamics is central to understanding the emergence of order from chaos. Non-equilibrium thermodynamics is therefore very important in biochemistry, biology, complex chemical reaction mechanisms, and nano-technology. We will get a start in this important area.

1.3 Chemical Reactivity–The State of the System

As mentioned above, the state of a system is specified by V, P, T, S, and n_i for each chemical constituent. The results of a process are measured by the changes in V, P, T, S, and n_i . We need to discuss how these variables are defined and measured. Their units are also very important. In this section, we discuss V and P. We will discuss T and S in detail in later chapters on thermodynamics. The amounts of substances can alternatively be specified using moles, concentrations, or partial pressures, which is the topic of the next chapter.

Volume: Volume, mass, and time are the only direct measurements that we make. Pressure, temperature, and entropy are measured indirectly. The only comments that we need to make about volume at this point are on units. The International System of Units, or SI units, are established by international agreement and accepted worldwide. The SI base units are kg (kilograms), m (meters), and s (seconds). The corresponding units for volume are m^3 :

$$1 \text{ m}^3 = 1000 \text{ L} = 1 \times 10^6 \text{ mL} = 1 \times 10^6 \text{ cm}^3$$

Using volume in m^3 occurs when working on problems with the results in joules.

Pressure: Consider a gas confined in a rectangular container, Figure 1.3.1. Given a surface of area A , the pressure is defined as the force the gas exerts perpendicular to the surface divided by the area, $P = f/A$. The SI units for force are newtons, N. The SI units for pressure are the units of force divided by area or N m^{-2} . Expanding out the units of the newton gives $\text{N m}^{-2} = (\text{kg m sec}^{-2})/\text{m}^2 = \text{kg m}^{-1} \text{sec}^{-2}$. The **pascal** is defined as $1 \text{ Pa} \equiv 1 \text{ N m}^{-2} = 1 \text{ kg m}^{-1} \text{sec}^{-2}$. The **bar** is a convenient measure of pressure and is defined as exactly $1 \times 10^5 \text{ Pa}$:

$$1 \text{ Pa} = 1 \text{ N m}^{-2} = 1 \text{ kg m}^{-1} \text{sec}^{-2} \quad 1 \text{ bar} \equiv 1 \times 10^5 \text{ Pa} \quad 1 \text{ bar} = 100 \text{ kPa}$$

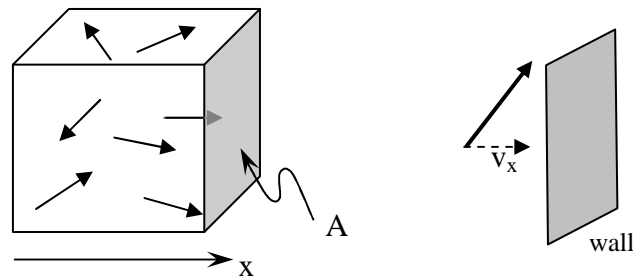


Figure 1.3.1: Pressure is the force per unit area, $P = f/A$, exerted by a gas on a surface. The force is the component perpendicular to the surface, in this case the x direction.

The pressure is measured using a manometer. Closed end manometers are used for measuring absolute pressure, Figure 1.3.2. The classic U-tube style manometer is used for measuring pressure differences. Closed end manometers are usually used to measure the barometric pressure, P_{ext} . To use a closed end manometer, the manometer tube is filled completely and then inverted. So the pressure in the internal end, P_{in} , is just the vapor pressure of the liquid. If the manometer fluid is mercury, the vapor pressure is negligible and $P_{\text{in}} = 0$, that is, a vacuum.

Consider the closed end manometer, Figure 1.3.2. The external pressure provides a force on the surface of the liquid outside the tube, pushing the liquid up the manometer tube. The column of liquid and the internal pressure inside add to provide a force downwards on the inside of the tube, $P_{\text{liq}} + P_{\text{in}}$. The level of the liquid is stationary, so the forces must balance: $P_{\text{ext}} = P_{\text{in}} + P_{\text{liq}}$.

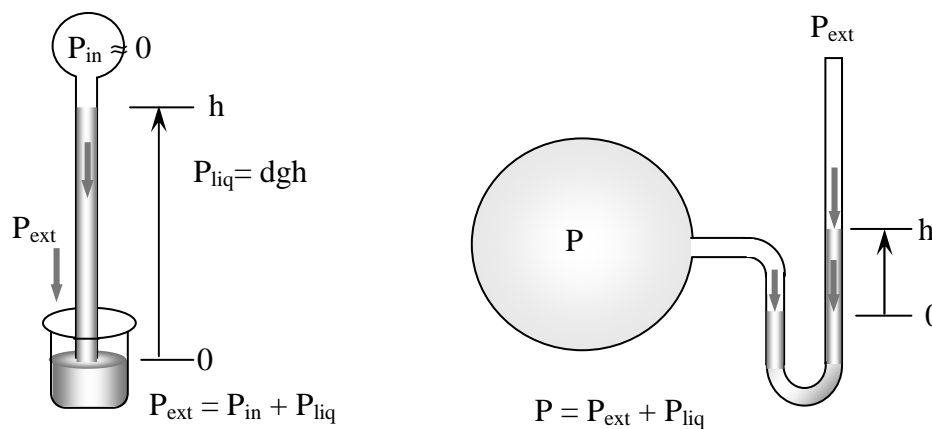


Figure 1.3.2: Closed end manometers measure absolute pressure. Open-end or U-tube manometers measure pressure differences, or differential pressure.

For an open-end manometer, the forces also must balance. The reference level is the top of the shorter of the two columns of liquids. At this reference level the forces and pressures on both sides are equal. The measured pressure, P , is the pressure on the left-hand side, which balances with the total pressure on the right-hand side:

$$P = P_{\text{ext}} + P_{\text{liq}} \quad 1.3.1$$

The pressure of the column of liquid depends on the density of the liquid, d , and the height of the column of liquid, h , and is given by:

$$P_{\text{liq}} = d g h \quad 1.3.2$$

where g is the acceleration due to gravity, 9.80665 m s^{-2} . Calculating the pressure caused by a column of liquid is a problem that arises often, so we will show how Eq. 1.3.2 was derived. Consider a column of liquid with cross section A at height h , Figure 1.3.3. We will assume that the liquid has a constant density, in other words that the liquid is incompressible.

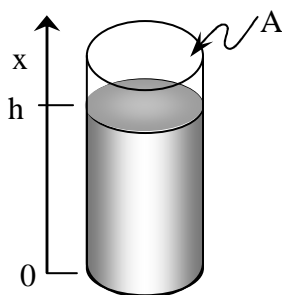


Figure 1.3.3: The pressure of a column of liquid with density d and cross sectional area A .

The volume of liquid in the column is Ah . The mass of the liquid is dAh . The force that this column exerts is $f = ma = dgAh$. The pressure is the force per unit area, $P_{\text{liq}} = f/A = dgh$, giving Eq. 1.3.2.

Because manometers are commonly used to measure pressure, pressures are often listed not in force based units, but as heights for a given manometer fluid. These units include inches of water and mm Hg. Assuming the density of Hg = $13.5951 \text{ g cm}^{-3}$ at 0°C and $g = 9.80665 \text{ m s}^{-2}$ allows the conversion to Pa using Eq. 1.3.2. The units of pressure, then, can be expressed in atmospheres (atm), torr, millimeters of mercury (mm Hg), and pounds per square inch (Psi):

$$\begin{aligned} 1 \text{ torr} &\equiv 1/760 \text{ atm} \quad (\text{exactly}) \\ 1.00000 \text{ mmHg} &= 1 \text{ torr} \quad (\text{at } 0^\circ\text{C}) \end{aligned}$$

The conversion between mm Hg and torr depends on temperature and the local acceleration of gravity. For example, the density of mercury is $13.5462 \text{ g mL}^{-1}$ at 20°C giving $1 \text{ mmHg} = 0.996 \text{ torr}$ at 20°C at sea level. Atmospheric pressure at sea level, in different units, is expressed as:

$$\begin{aligned} 1 \text{ atm} &\equiv 1.01325 \times 10^5 \text{ Pa} = 101.325 \text{ kPa} = 1.01325 \text{ bar} \\ 1 \text{ bar} &= 0.98692 \text{ atm} \\ 1 \text{ atm} &\equiv 760 \text{ torr} \cong 760 \text{ mmHg} \\ 1 \text{ bar} &= 750.06 \text{ torr} \\ 1 \text{ atm} &= 14.696 \text{ psi} \end{aligned}$$

We must be careful about significant figures. The “ \equiv ” indicates a definition, so the result is exact. For example, one atmosphere is exactly 760.000000 torr for as many significant figures as you need. In addition, when we write an integer, such as in 1 atm, the number is taken to be exact. Stoichiometric coefficients for chemical reactions are another example of this significant figure convention.

The pressure is one of many examples of a property that has been “normalized” for the size of the system. The total force on the wall of a container of gas increases with the size of the container. However, the pressure is the ratio of the force to the surface area over which the force is measured. Dividing by the area normalizes the force to unit area, which is no longer a function of the size of the system. The pressure, then, is an intrinsic measure of the properties of the system, no matter the size. The interest rate of a savings account is another example of this kind of normalization. The interest rate is given by the ratio: $(\$interest/\$principal) \times 100\%$. The interest rate is the same regardless of the amount you have in the account. The interest rate makes it easy to compare the benefits provided by different banks. The density of a substance, $d = \text{mass}/V$, is another example of an intrinsic property of the system. Such intrinsic properties are important because they show how one substance is different from another on a fundamental level. Properties that are independent of the size of the system are said to be **intensive variables**. Pressure, temperature, and density are intensive. Variables such as mass, volume, heat capacity, internal energy, and enthalpy are extensive variables. The values of **extensive variables** scale directly with the size of the system. For example, if you pour 25 mL of 20°C water into 25 mL of 20°C water, the volume doubles but the temperature stays the same. Volume is extensive and temperature is intensive. However, the ratio of two extensive variables for a system is intensive. For example, per mole quantities, like the molar volume, are intensive.

Pressure is an example of a variable that is measured indirectly. The reading from a manometer is the height of a column of liquid. To convert the height into a useful value, we need to know the density of the manometer liquid. Temperature is also an example of a property that is measured indirectly. The temperature is often measured as the height of a liquid in a thermometer. Pressure and temperature measurements are so convenient and so intuitive, based on our experience, that we sometimes forget the very indirect way they are measured. A wide variety of electronic meters and pressure gauges are available, but they must all be calibrated using measurements based on manometers.

For the tabulation of thermodynamic data, we choose a convenient standard state pressure of 1×10^5 Pa or 1 bar. Values at this standard state are indicated by a superscript “o”, as in the standard state enthalpy of formation for a substance, $\Delta_f H^\circ$. Notice that tables in older sources may use a standard state pressure of 1 atm, so make sure to pay attention to the units. One bar and 1 atm differ by only 1.3%, which is a small difference compared to ambient pressure changes caused by changing weather patterns. The choice between 1 bar and 1 atm is a small shift, and only affects the properties of gases; liquids and solids are unaffected. Because of the choice of 1 bar as the standard state pressure and the joule as the standard unit for energy, we strongly suggest that you work gas law problems in Pa. With pressure in pascals, the volume should be expressed in m^3 . The units of the PV product are $(\text{N m}^{-2})(\text{m}^3) = (\text{kg m}^{-1} \text{sec}^{-2})(\text{m}^3) = \text{kg m}^2 \text{sec}^{-2}$. The units of PV are then seen to be energy units in joules since $1 \text{ kg m}^2 \text{sec}^{-2} \equiv 1 \text{ J}$.

Ideal Gas Equation of State: The equation of state for a substance relates the variables P, V, T, and n. Under many circumstances the equation of state for gases is adequately expressed by the ideal gas law: $PV = nRT$. We will introduce more accurate equations of state in a later chapter.

The value of the constant R must be determined from experiment. The experimental value of the molar volume, V_m , of an ideal gas at a given temperature is needed. At $T = 273.15 \text{ K}$ (0°C) and 1 atm the molar volume of an ideal gas is:

$$V_m = \frac{V}{n} = 22.41410 \text{ L mol}^{-1} \quad \text{at } P = 1 \text{ atm and } T = 273.15 \text{ K} \quad (\text{ideal gas}) \quad 1.3.4^\circ$$

For equations that are specifically for an ideal gas, we will place a superscript “o” after the equation number to remind us that this is not a general result. We will also list parenthetically any restrictions for the equations. At 298.15 K and standard state pressure of 1 bar:

$$V_m^\circ = 0.0247896 \text{ m}^3 \text{ mol}^{-1} \quad \text{at } P = P^\circ = 1 \text{ bar and } 298.15 \text{ K} \quad (\text{ideal gas}) \quad 1.3.5^\circ$$

The temperature is given in kelvins, K . The PV product has units of energy. The function of R is, then, as a units conversion factor from kelvins to energy units. Using P and V in different units, R is calculated as:

$$R = \frac{PV}{nT} = \frac{1 \text{ atm} (22.41410 \text{ L})}{1 \text{ mol} (273.15 \text{ K})} = 0.08205783 \text{ L atm K}^{-1} \text{ mol}^{-1} \quad 1.3.6$$

$$R = \frac{PV}{nT} = \frac{1 \times 10^5 \text{ Pa} (0.0247896 \text{ m}^3)}{1 \text{ mol} (298.15 \text{ K})} = 8.31447 \text{ J K}^{-1} \text{ mol}^{-1} \quad 1.3.7$$

$$R = \frac{PV}{nT} = \frac{1 \text{ bar} (24.7896 \text{ L})}{1 \text{ mol} (298.15 \text{ K})} = 0.0831447 \text{ L bar K}^{-1} \text{ mol}^{-1} \quad 1.3.8$$

Even though we calculated R using the properties of an ideal gas, the definitions of the Kelvin temperature degree size (the triple point of water is defined as 273.16 K) and the joule are independent of the substance used, so R is a fundamental constant.

Example 1.3.1

Calculate the pressure of the gas in the flask in Figure 1.3.2 if the difference in height of the fluid in the manometer is 20.00 cm. The manometer liquid is water, the temperature is 25.0°C , and the atmospheric pressure is 756.2 torr. The density of water at 25.0°C is $0.99705 \text{ g mL}^{-1}$.

Answer: We need to convert everything to SI units to match the units for g in Eq. 1.3.2:

$$h = 20.0 \text{ cm} (1\text{m}/100\text{cm}) = 0.2000 \text{ m}$$

$$d = 0.99705 \text{ g mL}^{-1} (10^6 \text{ mL}/1 \text{ m}^3)(1 \text{ kg}/10^3 \text{ g}) = 997.0 \text{ kg m}^{-3}$$

$$P_{\text{ext}} = P_{\text{atm}} = 756.2 \text{ torr} (1 \text{ atm}/760 \text{ torr})(1.01325 \times 10^5 \text{ Pa}/\text{atm}) = 1.008 \times 10^5 \text{ Pa}$$

The pressure due to the column of water is:

$$P_{\text{H}_2\text{O}} = d g h = 997.0 \text{ kg m}^{-3} (9.80665 \text{ m s}^{-2})(0.2000 \text{ m}) = 1955.4 \text{ Pa}$$

Then the pressure in the flask is:

$$P = P_{\text{ext}} + P_{\text{H}_2\text{O}} = 1.008 \times 10^5 \text{ Pa} + 1955.4 \text{ Pa}$$

$$P = 1.027 \times 10^5 \text{ Pa} = 102.7 \text{ kPa} = 1.027 \text{ bar}$$

Notice that 20 cm of water corresponded to 1955.4 Pa. For a 10 cm divide by two:

$$10 \text{ cm (H}_2\text{O)} = 977.7 \text{ Pa} = 0.9777 \text{ kPa}$$

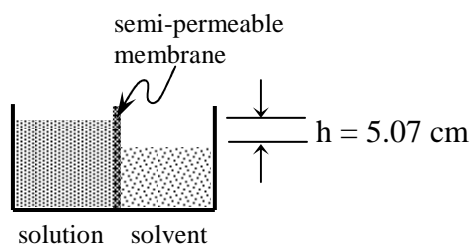
A good number to remember is that 10 cm of water corresponds to 1 kPa, to within 2%:

$$10 \text{ cm (H}_2\text{O)} \approx 1 \text{ kPa} \approx 0.01 \text{ bar}$$

This type of calculation will be very useful when we consider osmotic pressure and membrane potentials.

Example 1.3.2

A semi-permeable membrane allows some species to pass but not others. Consider a membrane that is permeable to water but not ionic substances (cellophane candy wrappers are an example). The membrane is placed between two compartments; one is filled with $1.00 \times 10^{-4} \text{ M NaCl}$ and the other pure water, as shown in the Figure below. A pressure difference builds between the two compartments as evidenced by a difference in the height of the solution as compared to the pure solvent. The pressure difference is called the osmotic pressure. Assume the density of this very dilute NaCl solution is the density of water at 25.0°C , 0.997 g mL^{-1} . Calculate the osmotic pressure, π , if the height difference is 5.07 cm.



Answer: The density of water is $0.997 \text{ g mL}^{-1} = 977. \text{ kg m}^{-3}$. The osmotic pressure is:

$$\pi = dgh = (977 \text{ kg m}^{-3}) (9.80665 \text{ m s}^{-2})(0.0507 \text{ m}) = 485.8 \text{ Pa}$$

To help you get used to pascals, convert this result to other common pressure units:

$$\pi = 485.8 \text{ Pa} \quad (1 \text{ atm}/1.01325 \times 10^5 \text{ Pa}) = 4.79 \times 10^{-3} \text{ atm}$$

$$\pi = 4.79 \times 10^{-3} \text{ atm} \quad (760 \text{ torr}/1 \text{ atm}) = 3.64 \text{ torr}$$

The Barometric Formula Describes the Variation of Pressure with Height: Two important application areas for physical chemistry are atmospheric environmental chemistry and meteorology. The barometric formula gives the pressure for a gas as a function of height. This problem is similar to the pressure for a column of liquid, Figure 1.3.3, except that we can no longer assume that the density is constant. Consider a column of air of cross-sectional area A , Figure 1.3.4. The pressure at $h = 0$ is the full atmospheric pressure caused by the column up to infinite height. The pressure at height h is caused by the air above that point. To calculate the pressure at height h , we start at $h = 0$ with pressure P_0 and then subtract the pressure of the gas in thin slices up to height h , leaving the gas above.

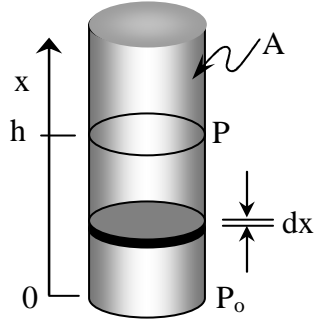


Figure 1.3.4: The pressure of a column of liquid with density d and cross sectional area A .

Consider a thin slice of the column at height x . The mass of a thin slice of the gas of thickness dx is $d A dx$. The force that this slice exerts on the column is $df = - d g A dx$ and the corresponding change in pressure is the force per unit area, $dP = df/A = - d g dx$. The negative sign is necessary, to do the subtraction of the slices from $x = 0$ to h . Because the pressure decreases with height, the density of the gas also decreases. Assuming that the gas behaves as an ideal gas,

$$d = \frac{\mathcal{N}_{\text{gas}} n}{V} = \frac{\mathcal{N}_{\text{gas}} P}{RT} \quad (\text{ideal gas}) \quad 1.3.9^\circ$$

where \mathcal{N}_{gas} is the molar mass of the gas. The change in pressure for a change in height is then:

$$dP = - \frac{\mathcal{N}_{\text{gas}} P}{RT} g dx \quad (\text{ideal gas}) \quad 1.3.10^\circ$$

The right-hand side of this last equation is difficult to integrate because P changes with x . To avoid this problem, we divide both sides of Eq. 1.3.10 $^\circ$ by P :

$$\frac{dP}{P} = - \frac{\mathcal{N}_{\text{gas}} g}{RT} dx \quad (\text{ideal gas}) \quad 1.3.11^\circ$$

Now assuming that the temperature is constant (cst. T), the integrand on the right in this equation is constant. The pressure at height h is given by the integral from 0 to h . The pressure at $h=0$ is P_0 and at height h is P :

$$\int_{P_0}^P \frac{dP}{P} = - \int_0^h \frac{\mathcal{N}_{\text{gas}} g}{RT} dx \quad (\text{ideal gas}) \quad 1.3.12^\circ$$

The integral on the left is in the form of $\int \frac{dx}{x} = \ln x$ and the constants $\mathcal{N}_{\text{gas}} g / (RT)$ factor out in front of the integral on the right:

$$\left(\ln P \right)_{P_0}^P = - \frac{\mathcal{N}_{\text{gas}} g}{RT} \left(x \right)_0^h \quad (\text{ideal gas, cst. } T) \quad 1.3.13^\circ$$

For a quick review of calculus, please see the addendum, Section 1.5. Evaluating at the endpoints of the integral gives:

$$\ln P - \ln P_0 = - \frac{\mathcal{N}_{\text{gas}} g h}{RT} \quad (\text{ideal gas, cst. } T) \quad 1.3.14^\circ$$

Combining the ln terms gives:

$$\ln \frac{P}{P_0} = -\frac{\mathcal{M}_{\text{gas}} g h}{RT} \quad (\text{ideal gas, cst. T}) \quad 1.3.15^\circ$$

We can solve for P by exponentiating both sides of this equation and multiplying by P_0 :

$$P = P_0 e^{\left(\frac{-\mathcal{M}_{\text{gas}} g h}{RT}\right)} \quad (\text{ideal gas, cst. T}) \quad 1.3.16^\circ$$

The pressure decreases exponentially with height. The rate at which the pressure decreases is dependent on RT. We will find that RT is a measure of the available thermal kinetic energy of the gas. The greater the thermal kinetic energy, the greater is the pressure at a given altitude. The effective molar mass of air is just the weighted average of the molar masses for O_2 and N_2 , which is 20.9 mole % O_2 and 79.1% N_2 and other trace gases:

$$\mathcal{M}_{\text{air}} \approx 0.209(32.0 \text{ g mol}^{-1}) + 0.791(28.0 \text{ g mol}^{-1}) = 28.8 \text{ g mol}^{-1} \quad 1.3.17$$

The pressure as a function of altitude is plotted in Figure 1.3.5 assuming the temperature is 20°C , 293 K and the sea level atmospheric pressure, P_0 , is 1 bar. Of course, the temperature in the atmosphere also decreases with altitude, $-6^\circ\text{C}/1000\text{m}$, through the troposphere, so this plot is a rough approximation.

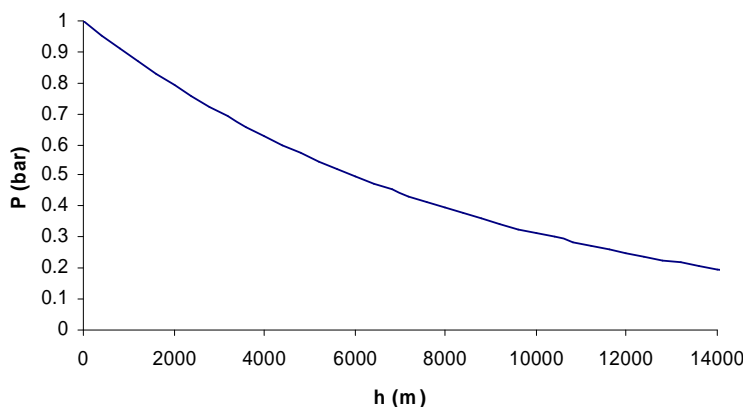


Figure 1.3.5: The pressure as a function of altitude at 293 K.

§1

Our First General Pattern: Simple Exponential Processes, First-Order Homogeneous Differential Equations with a Constant Coefficient: The barometric formula, Eq. 1.3.15°-16°, is certainly an important formula, especially for environmental applications. But, we have to admit that we had an ulterior motive. The general form for the differential in Eq. 1.3.10° is very common. Solving this differential equation gave you some practice in integration and practice in dealing with equations of this form. We always want to move quickly from pure mathematics to the chemical understanding of the underlying ideas. If you can recognize the form of an equation, then solving the equation becomes straightforward and we don't need to dwell on the

mathematical details. We can get to the chemistry faster. In this text, when we introduce a particularly useful general form, we will highlight the material as a “General Pattern” that we can use repeatedly throughout the text. Let’s summarize the steps we took in general form. The differential was in the form:

$$df = - a f dx \quad 1.3.18$$

where a is a constant. This general form is officially called a first-order homogeneous differential equation with a constant coefficient. Since f is a variable and not constant, we then divided both sides of the equation by f :

$$\frac{df}{f} = - a dx \quad 1.3.19$$

This step is called the separation of variables. Now f appears only on the left-hand side of the equation and x and constants appear only on the right. Next we determined the integral limits. As x varies from x_1 to x_2 then f will vary from f_1 to f_2 . The integral limits are then specified:

$$\int_{f_1}^{f_2} \frac{df}{f} = - \int_{x_1}^{x_2} a dx \quad 1.3.20$$

The constant, a , factors out in front of the integral on the right. Then integrating:

$$\left(\ln f \right) \Big|_{f_1}^{f_2} = - a \left(x \right) \Big|_{x_1}^{x_2} \quad 1.3.21$$

Evaluating at the endpoints of the integral gives:

$$\ln f_2 - \ln f_1 = - a (x_2 - x_1) \quad 1.3.22$$

Combining the \ln terms gives:

$$\ln \frac{f_2}{f_1} = - a (x_2 - x_1) \quad 1.3.23$$

Exponentiation both sides and multiplying by f_1 gives:

$$f_2 = f_1 e^{-a(x_2 - x_1)} \quad 1.3.24$$

For the special case that $x_1 = 0$, no confusion results if rename $x_2 = x$, $f_1 = f_0$ and $f_2 = f$ to give from Eq. 1.3.23:

$$\ln \frac{f}{f_0} = - a x \quad 1.3.25$$

Solving for f gives:

$$f = f_0 e^{-ax} \quad 1.3.26$$

which we recognize as an exponentially decreasing function, Figure 1.3.6.

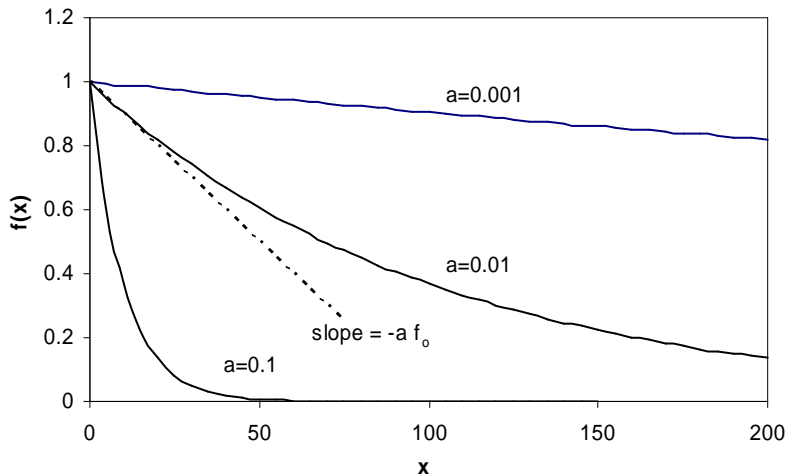


Figure 1.3.6: An exponentially decreasing function, $f_0 e^{-ax}$, for $f_0 = 1$. The limiting slope at $x = 0$ is: slope = $-a f_0$.

Let's make some general observations on exponentially decreasing functions. From the figure, notice that the decay is faster for larger values of a . Now look at the small x and large x limits.

$$x \rightarrow 0 \quad \text{then} \quad e^{-ax} \rightarrow e^0 = 1 \quad \text{so that } f \rightarrow f_0 \quad 1.3.27$$

$$x \rightarrow \infty \quad \text{then} \quad e^{-ax} = \frac{1}{e^{ax}} \rightarrow \frac{1}{e^\infty} = 0 \quad \text{so that } f \rightarrow 0 \quad 1.3.28$$

In other words f drops from f_0 , the initial value, to zero, asymptotically. We can also get a rough approximation for f by expanding in a Taylor series and keeping the first few terms. Hopefully, approximating the exponential function this way will give you a better feel for the properties of this important function.

Remember that the Taylor series allows us to approximate the value of any function, near a given point x_0 , arbitrarily well through the power series:

$$f \approx f(x_0) + \left(\frac{df}{dx}\right)_{x=x_0} (x - x_0) + \left(\frac{d^2f}{dx^2}\right)_{x=x_0} \frac{(x - x_0)^2}{2} + \left(\frac{d^3f}{dx^3}\right)_{x=x_0} \frac{(x - x_0)^3}{3!} + \dots \quad 1.3.29$$

For a quick review of Taylor series, please see the addendum, Section 1.5. Keeping just the first two terms corresponds to approximating the function as a straight line. The Taylor expansion for an exponentially decreasing function for small x is:

$$e^{-ax} \approx 1 - a x + a^2 \frac{x^2}{2} - a^3 \frac{x^3}{6} + \dots \quad 1.3.30$$

Using the Taylor Series expansion for e^{-ax} and keeping only the first two terms gives the approximation for Eq. 1.3.26 as:

$$f \approx f_0 - f_0 a x \quad (\text{small } x) \quad 1.3.31$$

and for Eq. 1.3.24, expanding around x_1 , as

$$f_2 \approx f_1 - f_1 a (x_2 - x_1) \quad (x_2 \approx x_1) \quad 1.3.32$$

To summarize, for small x , $f = f_0 e^{-ax}$ decreases linearly with x with a slope of $(-f_0 a)$. If you look at Figure 1.3.6, you will notice that for small x , the curve approaches f_0 linearly with a negative slope as expected from Eq. 1.3.31. Alternatively, you can just evaluate the derivative at $x = 0$, to determine the limiting slope:

$$\frac{df}{dx} = \frac{d(f_0 e^{-ax})}{dx} = -f_0 a e^{-ax} \Big|_{x=0} = -f_0 a \quad 1.3.33$$

Hopefully, recognizing the general form of Eq. 1.3.18, and having a good appreciation for the general behavior of e^{-ax} will make life simpler later on.

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Example 1.3.3

Calculate the pressure at a height of 400.0 m in the atmosphere using the exact equation and using the Taylor series approximation, keeping just the first two terms to give a linear approximation. Assume that the sea level pressure is 1 bar and the temperature is 20.0°C.

Answer: Applying the linear form of the Taylor series expansion for e^{-ax} , Eq. 1.3.31, to Eq. 1.3.16:

$$P = P_0 e^{\left(\frac{-\mathcal{M}_{\text{gas}} g h}{RT}\right)} \approx P_0 - P_0 \left(\frac{\mathcal{M}_{\text{gas}} g h}{RT}\right)$$

Substituting with $\mathcal{M}_{\text{gas}} = 28.8 \text{ g mol}^{-1}$ ($1 \text{ kg}/1000\text{g}$) = $28.8 \times 10^{-3} \text{ kg mol}^{-1}$ and $T = 293.2 \text{ K}$ gives:

$$\left(\frac{\mathcal{M}_{\text{gas}} g h}{RT}\right) = \frac{28.8 \times 10^{-3} \text{ kg mol}^{-1} (9.807 \text{ m s}^{-2})(400.0 \text{ m})}{8.314 \text{ J mol}^{-1} \text{K}^{-1} 293.2 \text{ K}} = 0.04634$$

Substitution into the exact formula gives: $P = 1 \text{ bar } e^{-0.04634} = 0.9547 \text{ bar}$
and the linear approximation gives: $P = 1 \text{ bar} - 1\text{bar} (0.04634) = 0.9537 \text{ bar}$
or only 0.1% error.

1.4 Summary – Looking Ahead

The Reach of Chemistry: From the Beaker to Interacting Global Systems: The written form of the chemical reaction:



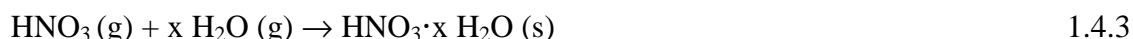
describes processes on a single molecule level, on a mole scale, or on a scale of millions of kilograms. Chemical reactions are inherently scale independent. Chemical insights can therefore be extended from the molecular level to the scale of global systems. This scale independence is the basis for the utility of structure-function relationships.

Scale independence has two different forms. One type of scale independence is simply based on the physical size of the system: from molecules to grams to tons. However, another aspect of the scale of a system is the possibility of interactions. One example is the coupling of the oxidation of NO, Eq. 1.4.1, with the production of NO and the consumption of NO₂ through the reactions:



This sequence of reactions is responsible for the nitric acid that forms in raindrops, which contributes to acid rain. New types of interactions and behavior result from increasing the scale of systems. Another example arises from biochemistry: metabolism results from the interactions of proteins and small molecules, metabolism drives processes in living cells, living cells comprise organisms, organisms form communities, communities interact within ecosystems, and ecosystems interact to form global systems. The perspective of chemistry is that the functioning of complex systems is a result of molecular interactions. We can design and synthesize compounds to manipulate and control the interactions within complex systems.

The various theories of chemistry have different scale dependence. Quantum mechanics is applicable at all chemical scales. However, quantum methods become intractable beyond the level of a few biopolymers. Thermodynamics and classical chemical kinetics don't apply to the single-molecule level, but are scale independent for macroscopic systems. Thermodynamics applies at the level of picomolar enzyme-substrate interactions and to the scale of global climate change. The scale independence of thermodynamics with increasing system complexity includes expanding hierarchies of molecular and system interactions. For example, the concepts of temperature, pressure, and chemical equilibrium do not apply to single molecules. However, starting with small systems containing billions of molecules, temperature, pressure, and equilibrium relationships are well defined. Small systems tend to have a uniform temperature and pressure. As the scale enlarges, systems become more complex. For an example of a complex system, processes in the stratosphere occur with a decrease in temperature and pressure with altitude. The temperature of the atmosphere also changes with latitude and the seasons. The extreme cold in the stratosphere during the Antarctic winter allows solid nitric acid hydrates to form, which act as a sink for reactive nitrogen species:



In the Antarctic spring, the nitric acid hydrates release a pulse of nitric acid into the gas phase, which through photochemical reactions catalyze the spontaneous destruction of ozone. Quantum mechanics, statistical mechanics, thermodynamics, and chemical kinetics allow the characterization of the interrelationships that drive processes across multiple scales.

You are encouraged to think across multiple scales as you learn more about chemistry. Even if your interests are primarily on the single-molecule level, the motivation and context for your work lie in more complex systems. Even if your interests lie in global processes, structure-function relationships at the quantum level are the key to understanding the interactions that govern all chemical processes. Our study of physical chemistry begins with chemical kinetics and thermodynamics, which explore the interrelationships within and between systems of any macroscopic scale.

Our example of the formation of nitric acid in rain combines gas phase, solution phase, and mass transport processes. In the next chapter we discuss concentration measures, concentration determination, and transport processes.

1.5 Addendum: A Very Brief Review of Calculus

Derivatives: In many ways, the calculus that we will use is fairly basic; you just need to practice your calculus skills so that you can do problems quickly. Do keep your calculus text handy for reference. A basic table of derivatives is given in Table 1.5.1. The basic derivatives are straight forward. The difficulty often comes with using the product rule and the chain rule.

Table 1.5.1 Basic Derivatives and Integrals (reading backwards).

$f(x)$	$\frac{df}{dx}$
x^n	$n x^{n-1}$
$\frac{1}{x^n}$	$\frac{-n}{x^{n+1}}$
$\ln x$	$\frac{1}{x}$
$x \ln x - x$	$\ln x$
e^x	e^x
$\sin x$	$\cos x$
$\cos x$	$-\sin x$

Example 1.5.1:

Find the derivative of $\frac{1}{x^m}$ with respect to x , using the fact that $\frac{dx^n}{dx} = n x^{n-1}$.

Answer: Rewrite the function as x^{-m} then use the normal rule for powers of x , $\frac{dx^n}{dx} = n x^{n-1}$:

$$\frac{d x^{-m}}{dx} = -m x^{-m-1} = \frac{-m}{x^{m+1}}$$

Notice that you just proved the second relationship in Table 1.5.1.

Product Rule: For two functions f and g :

$$\frac{d(fg)}{dx} = f \frac{dg}{dx} + g \frac{df}{dx} \tag{1.5.1}$$

Quotient Rule: For the quotient of two functions f and g , consider $f/g = f g^{-1}$ and use the product rule to find the derivative. From Table 1.5.1 note that the derivative of $1/g = -1/g^2$:

$$\frac{d(f/g)}{dx} = \frac{d(fg^{-1})}{dx} = f \frac{dg^{-1}}{dx} + g^{-1} \frac{df}{dx} = f \left(\frac{-1}{g^2} \right) \frac{dg}{dx} + \frac{1}{g} \frac{df}{dx} \quad 1.5.2$$

To add the two terms, use g^2 as the common denominator:

$$\frac{d(f/g)}{dx} = \frac{-f \frac{dg}{dx} + g \frac{df}{dx}}{g^2} \quad 1.5.3$$

In other words, you can just use Eq. 1.5.3 as a separate rule for the quotient or you can always use the product rule for both products and quotients as we did in deriving Eq. 1.5.3.

Example 1.5.2:

Find the derivative of $h(x) = x \ln x - x$, with respect to x .

Answer: The derivative of the sum is the sum of the derivatives:

$$\frac{dh}{dx} = \frac{d(x \ln x - x)}{dx} = \frac{d(x \ln x)}{dx} - \frac{dx}{dx}$$

Use the product rule for the $(x \ln x)$ term:

$$\frac{d(x \ln x)}{dx} = x \frac{d \ln x}{dx} + \ln x \frac{dx}{dx} = x \frac{1}{x} + \ln x = 1 + \ln x$$

Now substituting:

$$\frac{dh}{dx} = \frac{d(x \ln x - x)}{dx} = \frac{d(x \ln x)}{dx} - \frac{dx}{dx} = 1 + \ln x - 1 = \ln x$$

Notice that you just proved the fourth relationship in Table 1.5.1

Example 1.5.3:

Find the derivative of $h(x) = \frac{e^x}{cx^2}$, with respect to x , for c a constant.

Answer: We'll factor out the constant and then use the product rule with $f = e^x$ and $g = x^{-2}$:

$$\frac{dh}{dx} = \frac{1}{c} \frac{d(e^x/x^2)}{dx} = \frac{1}{c} \frac{d(e^x x^{-2})}{dx} = \frac{1}{c} \left(e^x \frac{dx^{-2}}{dx} + x^{-2} \frac{de^x}{dx} \right)$$

Using Table 1.5.1, $de^x/dx = e^x$ and $dx^{-2}/dx = -2/x^3$ gives:

$$\frac{dh}{dx} = \frac{1}{c} \left(e^x \frac{-2}{x^3} + x^{-2} e^x \right) = \frac{e^x}{cx^2} - \frac{2e^x}{cx^3}$$

or you could use the quotient rule to get the same result.

The Chain Rule: The chain rule is based on finding a simplifying substitution for a complex derivative. For example, to find the derivative of $f = e^{-c\epsilon^2}$ with respect to ϵ , we can make the substitution $z = -c\epsilon^2$. After substitution $f = e^z$. Then the chain rule for differentiation is:

$$\frac{df}{dx} = \frac{df}{dz} \frac{dz}{dx} \quad 1.5.4$$

For our specific problem:

$$\frac{d e^{-c\epsilon^2}}{dx} = \frac{de^z}{dz} \frac{dz}{dx} \quad 1.5.5$$

The derivative de^z/dz is just e^z and also substituting back in $z = -c\epsilon^2$ gives:

$$\frac{d e^{-c\epsilon^2}}{dx} = e^z \frac{dz}{dx} = e^{-c\epsilon^2} \frac{d(-c\epsilon^2)}{dx} = -2 c\epsilon e^{-c\epsilon^2} \quad 1.5.6$$

You can even make multiple substitutions, for example find the derivative of:

$$f(x) = \frac{1}{1-e^{-cx}} \quad 1.5.7$$

Let $q = -cx$ and $r = 1 - e^q$, then the chain rule would be:

$$\frac{df}{dx} = \frac{df}{dr} \frac{dr}{dq} \frac{dq}{dx} \quad 1.5.8$$

Effectively, on the right-hand side, you can think of dr or dq as a kind of variable, and these terms cancel to give just df/dx . For our example, Eq. 1.5.7:

$$\frac{df}{dx} = \frac{d\left(\frac{1}{1-e^{-cx}}\right)}{dx} = \frac{d\left(\frac{1}{r}\right)}{dr} \frac{d(1-e^q)}{dq} \frac{d(-cx)}{dx} = \frac{-1}{r^2} (-e^q) (-c) = \frac{-c e^{-cx}}{(1-e^{-cx})^2} \quad 1.5.9$$

Of course, we often don't bother to do explicit substitutions; rather, we just do the chain rule "in our heads." For example, the derivative of e^{-ax} can be taken as the result of the substitution $z = -ax$, with $de^z/dz = e^z$. More colloquially,

$$\frac{df}{dx} = \frac{d e^{\text{whatever}}}{dx} = e^{\text{whatever}} \left(\frac{d(\text{whatever})}{dx} \right) = e^{-ax} \left(\frac{d(-ax)}{dx} \right) = -a e^{-ax} \quad 1.5.10$$

Example 1.5.4:

Find the derivative of $m = \frac{c}{q - v b}$ with respect to b , for c , q , and v constants.

Answer: We'll use the chain rule using explicit substitution. Let $z = q - v b$, then $m = c(1/z)$ and using the chain rule:

$$\frac{dm}{db} = c \left(\frac{d(1/z)}{dz} \right) \left(\frac{dz}{db} \right) = \frac{-c}{z^2} \left(\frac{d(q-vb)}{db} \right) = \frac{-c}{(q-vb)^2} (-v) = \frac{cv}{(q-vb)^2}$$

Substitution: The substitution trick we used in discussing the chain rule is also generally useful. For example, find the derivative of j^2 with respect to $1/j$:

$$\frac{dj^2}{d(1/j)} = ?$$

This derivative looks tough, until you make the substitution $z = 1/j$. Rewriting j^2 in terms of z gives $j^2 = 1/z^2$:

$$\frac{dj^2}{d(1/j)} = \frac{d(1/z^2)}{dz} = \frac{-2}{z^3} \quad 1.5.11$$

Doing the substitution $z = 1/j$ into Eq. 1.5.11 gives the final result:

$$\frac{dj^2}{d(1/j)} = \frac{-2}{z^3} = -2j^3 \quad 1.5.12$$

Inversion: For the derivative:

$$\frac{dV}{d(1/V)} = ? \quad 1.5.13$$

The substitution trick, $z = 1/V$, also works well. Inverting z gives $V = 1/z$ and substitution into 1.5.13 gives:

$$\frac{dV}{d(1/V)} = \frac{d(1/z)}{dz} = \frac{-1}{z^2} = -V^2 \quad 1.5.14$$

Notice however, we could have just inverted the whole derivative, done the differentiation, and then inverted the result:

$$\frac{dV}{d(1/V)} \xrightarrow{\text{invert}} \frac{d(1/V)}{dV} = \frac{-1}{V^2} \xrightarrow{\text{invert}} \frac{V^2}{-1} = -V^2 \quad 1.5.15$$

The agreement between Eq. 1.5.14 and 1.5.15 shows this shortcut to be valid. You can show that this inversion trick is always valid for any derivative. Inversion can be useful whenever you want to take the derivative of something easy with respect to something difficult. The derivative with respect to $1/V$ will occur when working with the Ideal Gas law and other equations of state.

Integrals: By the Fundamental Theorem of Calculus, Table 1.5.1 is also a table of integrals. We just read from right-to-left. For example,

$$\int \frac{1}{x} dx = \ln x \quad \int e^x dx = e^x \quad \int \ln x dx = x \ln x - x$$

There are extensive tables of integrals in handbooks like the *Handbook of Chemistry and Physics*,² and many Internet sites. You can save a lot of time by becoming familiar with these

resources. You are also encouraged to use symbolic computational programs like *Mathematica* or *Maple*.

Taylor Series: The Taylor series expansion allows us to approximate the value of any function, near a given point x_0 , arbitrarily well through the power series:

$$f \approx f(x_0) + \left(\frac{df}{dx}\right)_{x=x_0} (x - x_0) + \left(\frac{d^2f}{dx^2}\right)_{x=x_0} \frac{(x - x_0)^2}{2} + \left(\frac{d^3f}{dx^3}\right)_{x=x_0} \frac{(x - x_0)^3}{3!} + \dots + \left(\frac{d^n f}{dx^n}\right)_{x=x_0} \frac{(x - x_0)^n}{n!} \quad 1.5.16$$

Keeping just the first two terms corresponds to approximating the function as a straight line. Keeping the first three terms corresponds to a quadratic approximation. We will rarely need terms beyond the cubic term. For example, find the Taylor expansion for the exponential function in Eq. 1.3.26, e^{-ax} . We first need to find the derivatives using the chain rule. Using Eq. 1.5.10 as a guide:

$$\left(\frac{df}{dx}\right) = \left(\frac{d e^{-ax}}{dx}\right) = e^{-ax} \left(\frac{d(-ax)}{dx}\right) = -a e^{-ax} \quad 1.5.17$$

For the second derivative, starting from the first derivative:

$$\left(\frac{d^2f}{dx^2}\right) = \left(\frac{d -a e^{-ax}}{dx}\right) = a^2 e^{-ax} \quad 1.5.18$$

Expanding around $x_0=0$, we note that:

$$\left(\frac{df}{dx}\right)_{x=x_0} = -a e^{-ax_0} = -a \quad \left(\frac{d^2f}{dx^2}\right)_{x=x_0} = a^2 e^{-ax_0} = a^2 \quad \left(\frac{d^3f}{dx^3}\right)_{x=x_0} = -a^3 e^{-ax_0} = -a^3 \quad 1.5.19$$

Then substituting into Eq. 1.5.16 gives:

$$e^{-ax} \approx 1 - a x + a^2 \frac{x^2}{2} - a^3 \frac{x^3}{6} + \dots \quad 1.5.20$$

Let's check to see how well the approximation works; refer to Table 1.5.2, where for convenience we have chosen $a = 1$. The underlined values correspond to 2-3% error.

Table 1.5.2. Taylor Series Approximation for e^{-x} . Underlined entry gives $\leq 3\%$ error.

x	e^{-x} exact	$1-x$	$1-x+x^2/2$	$1-x+x^2/2-x^3/6$
0.1	0.9048	0.9	0.905	0.9048
0.2	0.8187	0.8	0.820	0.8187
0.5	0.6065	0.5	0.625	0.6042
0.8	0.4493	0.2	0.520	0.4347
1.0	0.3679	0	0.500	0.3333

As you can see, the Taylor Series does very well with only a few terms. For 3% error, for $e^{-x} \approx 1 - x$ we can go up to $x = 0.2$ and for $e^{-x} \approx 1 - x + x^2/2$, x can be as large as 0.5.

Taylor series expansions for functions that we will use are listed in Table 1.5.3. The infinite series $e^x \approx 1 + x + x^2/2 + x^3/6 + \dots + x^n/n!$, as you might remember, is actually the definition of the exponential function. Handheld calculators and computers use this Taylor series to calculate the value of e^x .

Example 1.5.5:

The “e” in e^{-x} is just a number, 2.7183. Use the Taylor series expansion of e^{-x} to calculate the value of “e”. You can work with just four terms in the expansion.

Answer: To use the Taylor series expansion of e^{-ax} , just set $a = -1$ and $x = 1$. Then up to the cubic term, the expansion gives:

$$\begin{aligned} e^{-ax} &\approx 1 - a x + a^2 \frac{x^2}{2} - a^3 \frac{x^3}{6} = 1 - (-1)(1) + (-1)^2 \frac{1^2}{2} - (-1)^3 \frac{1^3}{6} \\ &\approx 1 + 1 + \frac{1}{2} + \frac{1}{6} = 2 + 0.5 + 0.167 = 2.667 \end{aligned}$$

which isn't too far off from 2.7183 given that we only used four terms.

Table 1.5.3. Taylor Series Expansions

expand around	for $x \approx x_0$	for x very close to x_0
$x_0 = 0$	$e^x \approx 1 + x + \frac{x^2}{2} + \frac{x^3}{6}$	$e^x \approx 1 + x$
$x_0 = 0$	$e^{-ax} \approx 1 - a x + a^2 \frac{x^2}{2} - a^3 \frac{x^3}{6}$	$e^{-ax} \approx 1 - a x$
$x_0 = 0$	$\ln(1 - x) \approx -x - \frac{x^2}{2}$	$\ln(1 - x) \approx -x$
$x_0 = 1$	$\ln x \approx (x - 1) - \frac{(x-1)^2}{2}$	$\ln x \approx (x - 1)$
$x_0 = 0$	$\frac{1}{1-x} \approx 1 + x + x^2$	$\frac{1}{1-x} \approx 1 + x$
$x_0 = 0$	$\sqrt{1-x} \approx 1 - \frac{x}{2} - \frac{x^2}{8}$	$\sqrt{1-x} \approx 1 - \frac{x}{2}$
$x_0 = 0$	$\frac{1}{1 - e^{-ax}} \approx \frac{1}{ax - (ax)^2/2}$	$\frac{1}{1 - e^{-ax}} \approx \frac{1}{ax}$
$x_0 = 0$	$\sin x \approx x - \frac{x^3}{6} + \frac{x^5}{5!}$	$\sin x \approx x$
$x_0 = 0$	$\cos x \approx 1 - \frac{x^2}{2} + \frac{x^4}{4!}$	$\cos x \approx 1 - \frac{x^2}{2}$

Example 1.5.6

Give the Taylor series expansion for $\ln(1-x)$, where x is a small number. Just use the first two terms in the expansion. Test your approximation on $x = 0.100$. We will use this approximation often.

Answer: We need to do the expansion around $x_0 \approx 0$. The first derivative using the chain rule is:

$$\frac{d \ln(1-x)}{dx} = \frac{1}{1-x} \frac{d(1-x)}{dx} = \frac{-1}{1-x}$$

Evaluating the derivative at $x_0 = 0$ gives just -1 . Substitution into the Taylor Series gives:

$$\ln(1-x) = \ln(1-0) + (-1)(x) = -x \quad (\text{small } x)$$

For $x = 0.100$, the exact value for $\ln(1 - 0.100) = -0.105$ and our approximation gives -0.100 , for a 5% error.

Chapter Summary

1. The system is the simplest part of the universe that displays the process of interest.
2. The surroundings are everything that is not part of the system.
3. The state of a system is specified by V , P , T , S , and moles, n_i , or concentrations, c_i , for each chemical constituent i .
4. A process is the transfer of energy to or from the system in the form of heat, work, or changes in concentration.
5. A spontaneous process is a process that occurs without any outside influence.
6. A non-spontaneous process will not occur, without work input from the surroundings.
7. The reverse of a spontaneous process is a non-spontaneous process.
8. Equilibrium processes show no tendency for change.
9. The reverse of an equilibrium process is also at equilibrium.
10. Equilibrium processes are reversible. Reversible processes are at equilibrium.
11. An equilibrium state is a stable state.
12. For a given perturbation, δx , if $\delta V(x \pm \delta x) > 0$ the state is at equilibrium.
13. Meta-stable systems are at equilibrium for small changes, but unstable for large changes.
14. Steady states are time-invariant, but not at equilibrium, and can only be kept in a steady state away from equilibrium by the constant input of energy or material.
15. Spontaneous processes are irreversible. Irreversible processes are spontaneous.
16. A reversible process occurs through a sequence of equilibrium states.
17. A reversible process can be returned to its initial state with no net change in the surroundings.
18. Kinetics is the study of the approach to equilibrium. Thermodynamics applies only to systems at equilibrium.
19. Thermodynamics and kinetics are complementary and disjoint (except that $K_{eq} = k_f/k_r$).
20. Kinetically favorable processes are not necessarily thermodynamically favorable. Thermodynamically favorable processes are not necessarily kinetically favorable.
21. Non-equilibrium thermodynamics combines thermodynamics and kinetics.

22. Pressure is defined as f/A , which is normalized for the size of the system.
23. The pressure of a column of liquid is: $P_{liq} = d g h$, where d is the density and h the height.
24. Intensive variables are independent of the size of the system. Examples are P , T , and d .
25. Extensive variables scale directly with the size of the system. Examples are mass, V , S (entropy), ΔU (internal energy), and ΔH (enthalpy).
26. The ratio of two extensive variables for a given system is intensive. Examples are per mole quantities like the molar volume, $V_m = V/n$, and enthalpy per mole, $\Delta H_m = \Delta H/n$.
27. The ideal gas equation of state is $PV = nRT$, with $R = 8.31447 \text{ J K}^{-1} \text{ mol}^{-1}$, using P in pascals and V in m^3 .
28. $e^{-ax} \approx 1 - ax$ for small x .
29. The function $f = f_0 e^{-ax}$ approaches f_0 as $x \rightarrow 0$ with a constant negative slope $= -af_0$.
30. $\ln(1-x) \approx -x$ for small x .

¶1. The general solution of a differential equation in the form $df = -af dx$ is:

$$f_2 = f_1 e^{-a(x_2-x_1)} \quad \text{or} \quad f = f_0 e^{-ax}, \text{ if the initial } x = 0.$$

Literature Cited

1. N. E. Leadbeater, L. M. Stencel, "Fast, Easy Preparation of Biodiesel Using Microwave Heating," *Energy & Fuels*, **2006**, *20*, 2281-2283.
2. D. R. Lide, Ed., *Handbook of Chemistry and Physics*, The Chemical Rubber Co., Cleveland, OH., 2007.

Problems: Chemical Reactivity

1. Consider a bowl of sugar. Sugars are our primary source of energy, so the oxidation of sucrose in our body must be thermodynamically favorable. How can a bowl of sugar exist in the open atmosphere for very long times?
2. Consider a salt shaker balanced on one edge, Figure P1.1. This state is often possible if a few salt grains are sprinkled on the table. Characterize the state of the system with respect to change in position. If the system is not at equilibrium, state the equilibrium position. Describe any spontaneous processes that might occur if the salt grains were gently blown away.

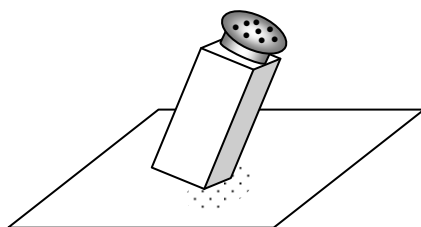


Figure P1.1: A balanced salt shaker.

3. Our bodies, at rest, can be considered as being in a steady state. Describe the incoming flows that keep us away from equilibrium. What are the outgoing flows? What is the equilibrium state for our bodies?

4. Are spontaneous processes always irreversible? Explain.
5. (a). In what way is a steady state and an equilibrium system similar? (b). In what ways are a steady state and an equilibrium system different?
6. Determine if the following processes are spontaneous, non-spontaneous, or reversible.
- 1 J of heat is transferred from a hot cup of coffee to the table top.
 - Sugar is added to a cup of coffee and the sugar dissolves.
 - Water decomposes into H_2 and O_2 from a cup of coffee.
 - A small amount of ice melts in a cup of iced coffee at $0^\circ C$.
 - A small amount of ice melts in a cup of coffee at $5^\circ C$.
 - A small amount of water freezes in a cup of iced coffee at $0^\circ C$.
 - A small amount of water freezes in a cup of coffee that is placed outdoors at $-10^\circ C$.
 - Too much sugar is added to a cup of coffee producing a super-saturated solution. After bumping the cup on the table, some of the sugar crystallizes out of solution.
7. Prove that if the reverse of a spontaneous process is also spontaneous, it is possible to construct a perpetual motion machine.^{1,2}
8. Calculate the molar density, in mol m^{-3} , and the mass density, in kg m^{-3} and g L^{-1} , for an ideal gas at standard pressure, $P^\circ = 1.00 \text{ bar}$, and 298.15 K . Assume the gas is air with an effective molar mass given by Eq. 1.3.17.
9. Calculate the number of moles of an ideal gas in a volume of 1.000 L for a pressure of 1.000 bar and a temperature of 298.15 K . Do this problem using three different sets of units and the corresponding value for R : (a) using L atm , (b) using Pa m^3 , and (c) using L bar .
10. The density of a mixture of H_2 and O_2 is 0.982 g L^{-1} at 298.2 K and 1.00 bar pressure. Calculate the mole fraction of H_2 in the mixture.
11. Two containers, which are separated by a stopcock, are held in a constant temperature bath at 298.2 K , Figure P1.2. The first container has a volume of 24.80 L and the second 12.39 L . The two containers are filled with 2.00 mol and 1.00 mol of ideal gas, respectively. Calculate the initial pressures. After the stopcock is opened, calculate the final volume and pressure. Of P , V , and n , which are intensive and which are extensive?

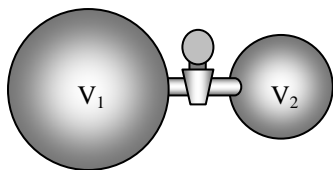


Figure P1.2: Two closed containers are opened to form a combined system.

12. Classify the following variables as intensive or extensive:
- molar concentration of a solution.
 - molar density.
 - density (mass density).

- (d). surface area of an interface between two dissimilar phases. The air-water, olive oil-water, and olive oil-glass interfaces are three examples. The interface can be the planar interface between two bulk samples or the surface of a droplet.
- (e). surface tension, which is defined as the change in surface energy of an interface divided by the change in surface area: $\gamma = dU/d\sigma$.
- (f). temperature.
- (g). coefficient of thermal expansion at constant pressure, which is defined as:

$$\alpha = -\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

where $(\partial V/\partial T)_P$ is the rate of change of the volume of a sample with temperature, while holding the pressure constant.

13. Calculate the pressure inside your mouth that would be necessary to drink a soft drink through a straw of length 20.0 cm. Assume the drink has the density of water at 20.0°C, 0.9982 g mL⁻¹ and the atmospheric pressure is 1.000 bar.
14. Calculate the height of a column of water at 20.0°C in a closed end manometer for an atmospheric pressure of 1.000 bar. Assume the liquid has a constant density. The density of water at 20°C is 0.9982 g mL⁻¹. The vapor pressure of water at 20.0°C is 2.338 kPa.
15. Long's Peak in the Colorado Rocky Mountains is 3962. m high. What is the predicted pressure on the top of Long's Peak? Assume a constant temperature of 20.0°C. Compare the molar density on top of Long's Peak with the molar density of air at sea level.
16. Calculate the altitude in the atmosphere that corresponds to a pressure of 0.500 bar if the surface pressure is 1.000 bar. Assume the temperature is constant at 18°C.
17. For liquids with moderate changes in pressure, the density is given by:

$$d = d_o [1 + \kappa_T (P - P_o)]$$

where κ_T is the isothermal compressibility, d_o is the density of the liquid at the surface pressure P_o and d is the density at final pressure P . (a). Show that the formula for the pressure as a function of depth is given by:

$$\frac{1}{\kappa} \ln(1 + \kappa_T (P - P_o)) = d_o g h$$

- (b). Calculate the pressure in the Mariana Trench at a depth of 10911 m (35798 ft) given $\kappa_T = 4.587 \times 10^{-10} \text{ Pa}^{-1}$ at 20°C. Use the density of pure water, 0.9982 g mL⁻¹ at 1 bar, for this problem, instead of the density of sea water. Assume the surface pressure is 1.000 bar.
18. (a). Find the derivative of the atmospheric pressure with respect to altitude from the barometric formula, Eq. 1.3.16°. (b). Show that this derivative satisfies the original differential equation, Eq. 1.3.10°.
19. Chemical kinetic equations are good examples of first-order homogeneous differential equations with a constant coefficient. The rate of change of the concentration of a substance A with time in a first-order chemical reaction is given as:

$$\frac{d[A]}{dt} = -k [A]$$

where k is the rate constant. (a). Show that this expression is a first-order homogeneous differential equation with a constant coefficient. (b). Integrate the equation from an initial concentration of $[A]_0$ at time $t = 0$ to a final concentration of $[A]$ at time t .

20. Do the Taylor expansion for $\sqrt{1-x}$ for $x \approx 0$, keeping terms up to x^2 .
21. Using a Taylor series expansion, what is the linear approximation for $\ln(f_2/f_1)$ for $f_2 \approx f_1$.
22. Determine the number of terms in the Taylor series expansion of $\ln(1-x)$ that are necessary for 1% and 0.1% accuracy, if $x = 0.100$.
23. Calculate the derivative of $h(x) = e^{-cx}/(1-e^{-cx})$, with respect to x for c equal to a constant.
24. Find the derivative of $P = \frac{nRT}{(V-nb)} - a \frac{n^2}{V^2}$, with respect to V . Assume that n , R , T , a , and b are all equal to a constant.
25. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true. If the statement is true, but too restrictive, give the more general statement.
- For a spontaneous process, no work can be done by the surroundings on the system.
 - Fast processes are spontaneous.
 - On an average day at sea level, supporting a column of mercury in a closed tube higher than 760 mm requires more force per unit area than the atmosphere can provide.
 - Your mouth provides a partial vacuum that pulls a soft drink into your mouth through a straw.
 - The derivative of the potential energy with respect to a displacement in a system is zero for a system at equilibrium.
26. (*Challenge Problem*) Three definitions of a reversible process are:
- A reversible process is one in which the system never deviates from equilibrium by more than an infinitesimal amount.
 - A reversible process is not a real process, but a hypothetical succession of equilibrium states.
 - A reversible process is one for which the system can be returned to its initial state with no net change in the surroundings.

Consider the melting of 1 mole of ice at 0°C as an example. Show how each of the three definitions is equivalent.

Literature Cited:

- A. M. Lesk, *Introduction to Physical Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1982, Ch. 5.
- P. T. Landsberg, *Thermodynamics with Quantum Statistical Illustrations*, Wiley-Interscience, New York, NY, 1961, p. 95.