

The Live Textbook of Physical Chemistry 1

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Preface

This textbook is the official textbook for the Physical Chemistry 1 Course (CHM 3001) for 2020.

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Structure of this book

How should you use this book?

Chapter 1

Systems and Variables

1.1 Thermodynamic Systems

A thermodynamic system—or just simply a system—is a portion of space with defined boundaries that separate it from its surroundings. The surroundings may include other thermodynamic systems, or physical systems that are not thermodynamic systems. A boundary may be a real physical barrier or a purely notional one. Typical examples of systems are reported in Figure 1.1 below.



Figure 1.1: Examples of Thermodynamic Systems

In the first case, a liquid is contained in a typical erlenmeyer flask. The boundaries of the system are clearly the glass walls of the beaker. The second system is represented by the gas contained in a balloon. The boundary is a physical

barrier also in this case. The third case is that of a thunder cloud, where the boundary is not a well-defined physical barrier, but rather some condition of pressure and chemical composition at the interface between the cloud and the atmosphere. Finally the fourth case is the case of an open flame. In this case the boundary is again non-physical, and possibly even harder to define than for a cloud. For example, we can choose to define the flame based on some temperature threshold, or some color criterion, or even some chemical one. Despite the lack of physical boundaries, both the cloud and the flame—as portions of space containing matter—can be defined as a thermodynamic system and studied as such.

A system can exchange exclusively mass, exclusively energy, or both mass and energy with its surroundings. Depending on the abilities of the boundaries to exchange these quantities, a system is defined as open, closed, or isolated. An open system exchanges both mass and energy. A closed system exchanges only energy, but not mass. Finally, an isolated system does not exchange mass nor energy.

Type of System:	Mass	Energy (either heat or work)
Open	Y	Y
Closed	N	Y
Isolated	N	N

When a system exchanges mass or energy with its surroundings, some of its parameters (variables) change. For example, if a system loses mass to the surroundings, the number of molecules (or moles) in the system will decrease. Similarly, if a system is absorbing some energy one or more of its variables (such as for example its temperature) increase. Mass and energy can flow into the system or out of the system. Let's consider mass exchange only. If some molecules of a substance leave the system and then the same amount of molecules flow back into the system, the system will not be modified (Fig. XXX - system losing molecules, and then gaining them back). In other words, we can count 100 molecules leaving a system and assign them the value of -100 in an outgoing process, and then observe the same 100 molecules going back into the system and assign them a value of $+100$. Regardless of the number of molecules present in the system in the first place, the overall balance will be -100 (from the outgoing process) $+100$ (from the ingoing process) $= 0$, which brings the system to its initial situation (mass has not changed). However, from a mathematical standpoint, we could have equally assigned the label $+100$ to the outgoing process, and -100 to the ingoing one, and the overall total would have stayed exactly the same: $+100-100 = 0$. Which of the two labels is best? For this case it seems natural to define a mass going out of the system as negative (the system is losing it), and a mass going into the system as positive (the system is gaining it), but is it as straightforward for energy?

Here's another example. Let's consider a system that is composed of your body. When you are exercising you are losing mass in the form of water (sweat) and CO_2 (from respiration). This mass loss can be easily measured by stepping on a scale before and after exercise. The number you observe on the scale will go down, hence you've lost weight. After exercise, you will reintegrate the lost mass by drinking and eating. If you've reintegrated the same amount you've lost, your weight is going to be exactly the same as it was before the exercise (no weight loss). But which label do you attach to the amounts that you have lost and gained? Let's say that you're running a 5km race without drinking nor eating, and you measure your weight dropping 2 kg after the race. After the race you drink 1.5 kg of water and eat a 500 g energy bar. Overall you didn't lose any weight, and it would seem normal to label the 2 kg that you've lost as negative (-2) and the 1.5 kg of water that you drank and the 500 g bar that you ate as positive ($+1.5 + 0.5 = +2$). But is it the only way? After all, you didn't gain nor lose any weight, so why not calling the 2 kg due to exercise +2 and the 2 that you've ingested as -2? It might seem silly, but mathematically it would not make any difference, the total would still be zero. Now, let's consider energy instead of mass. Let's say that in order to run the 5km race you've spent 500 kcal, which then you reintegrate exactly by eating the energy bar. Which sign would you put in front of the kilocalories that you "burned" during the race? In principle, you've lost them so if you want to be consistent you should use a negative sign. But if you think about it, you've put quite an effort to "lose" those kilocalories, so it might not feel bad to assign them a positive sign instead. After all, it's perfectly OK to say "I've done a 500 kcal run today", while it might sound quite awkward to say "I've done a -500 kcal run today." The results of our previous exercise with mass, in fact, demonstrate that it doesn't really matter which sign you put in front of the quantities. As long as you are consistent throughout the process, the signs will cancel out. That is, if you've done a +500 kcal run, then you've eaten a bar for -500 kcal, resulting in a total zero loss/gain. Alternatively, if you've done a -500 kcal run, you would have eaten a +500 kcal bar, for a total of again zero loss/gain.

These simple examples clearly demonstrate that the sign that we assign to quantities that flow through a boundary is arbitrary (i.e., we can define it any way we want, as long as we are always consistent with ourselves). There is no best way to assign those signs. If you ask two different people, you might obtain two different answers. But we are scientists, and we must make sure to be rigorous. For this reason, chemists have established a convention for the signs that we will follow throughout this course. If we are consistent in following the convention, we are guaranteed to never make any sign mistake.

The chemistry convention of the sign is system-centric.

- If something (energy or mass) goes **into** the system it has a **positive** sign + (system is gaining)
- If something (energy or mass) goes **out of** the system it has a **negative** sign - (system is losing)

If you want a trick to remember the convention, use the weight loss/gain during exercise example above. You are the system, if you lose weight the kilograms will be negative (-2 kg), while if you gain weight they will be positive ($+2$ kg). Similarly, if you eat an energy bar, you are the system and you will have increased your energy by $+500$ kcal (positive), while if you burned energy during exercise, you are the system and you will have lost energy, hence -500 kcal (negative). If the system is a balloon filled with gas, and the balloon is losing mass, you are the balloon and you are losing weight, hence the mass will be negative. If the balloon is absorbing heat (likely increasing its temperature, hence increasing its volume), you are the system and you are gaining heat, hence heat will be positive.

1.2 Thermodynamic Variables

The system is defined and studied using parameters that are called variables. These variables are quantities that we are able to measure, such as pressure and temperature, but don't be surprised if in some occasion you encounter some variable that is a little harder to measure directly, such as entropy. The variables depends only on the current state of the system, and therefore they define it. In other words, if I know the values of all the "relevant variables" of a system, I know the state of the system. The relationship between the variables are described by mathematical functions that are called state functions, while the "relevant variables" are called natural variables. What are the "relevant variables" of a system? The answer to this question depends on the system, and it is not always straightforward. The simplest case is the case of an ideal gas, for which the natural variables are those that enter the ideal gas law and the corresponding equation:

$$PV = nRT \quad (1.1)$$

Therefore, the natural variables for an ideal gas are: the pressure P , the volume V , the number of moles n , and the temperature T , with R being the ideal gas constant. Recalling from the general chemistry courses, R is a universal dimensional constant which has the values of $R = 8.31$ kJ/mol in SI units.

We will use the ideal gas equation and its variables as an example to discuss about variables and functions in this chapter, and then we will analyze more complicated cases in the next chapters. Variables can be classified according to numerous criteria, each with its advantages and disadvantages. A typical classification is:

- **Physical variables (P , V , T in the ideal gas law):** independent on the chemical composition of the system.
- **Chemical variables (n in the ideal gas law):** dependent on the chemical composition of the system.

Another useful classification is:

- **Intensive variables (P, T in the ideal gas law):** independent on the physical size (extension) of the system.
- **Extensive variables (V, n in the ideal gas law):** dependent on the physical size (extension) of the system.

When we deal with thermodynamic systems, it is more convenient to work with intensive variables. Luckily, it is relatively easy to convert extensive variables into intensive ones by just taking the ratio between two of them. For an ideal gas, by taking the ratio between V and n , we obtained the intensive variable called molar volume:

$$V_m = \frac{V}{n}. \quad (1.2)$$

We can then recast eq. (1.1) as:

$$PV_m = RT, \quad (1.3)$$

which is the preferred equation that we will use for the remainder of this course. The ideal gas equation connects the 3 variables pressure, molar volume, and temperature, and reduces the number of independent variables to just 2. In other words, once 2 of the 3 variables are known, the other one can be easily obtained using these simple relations:

$$P(T, V_m) = \frac{RT}{V_m}, \quad (1.4)$$

$$V_m(T, P) = \frac{RT}{P}, \quad (1.5)$$

$$T(P, V_m) = \frac{PV_m}{R}. \quad (1.6)$$

These equations define three state functions, each one expressed in terms of two independent natural variables. For example, eq. (1.4) defines the state function called “pressure”, expressed as a function of temperature and molar volume. Similarly, eq. (1.5) defines the “molar volume” as a function of temperature and pressure, and eq. (1.6) defines the “temperature” as a function of pressure and molar volume. When we know the natural variables that define a state function, we can express the function using its total differential, for example for the pressure $P(T, V_m)$:

$$dP = \left(\frac{\partial P}{\partial T} \right) dT + \left(\frac{\partial P}{\partial V_m} \right) dV_m \quad (1.7)$$

Recalling Schwartz's theorem, the mixed partial second derivatives that can be obtained from eq. 1.2.7 are the same:

$$\frac{\partial^2 P}{\partial T \partial V_m} = \frac{\partial}{\partial V_m} \frac{\partial P}{\partial T} = \frac{\partial}{\partial T} \frac{\partial P}{\partial V_m} = \frac{\partial^2 P}{\partial V_m \partial T} \quad (1.8)$$

Which can be easily verified considering that:

$$\frac{\partial}{\partial V_m} \frac{\partial P}{\partial T} = \frac{\partial}{\partial V_m} \left(\frac{R}{V_m} \right) = -\frac{R}{V_m^2} \quad (1.9)$$

and

$$\frac{\partial}{\partial T} \frac{\partial P}{\partial V_m} = \frac{\partial}{\partial T} \left(\frac{-RT}{V_m^2} \right) = -\frac{R}{V_m^2} \quad (1.10)$$

While for the ideal gas law all the variables are “well-behaved” and always satisfies Schwartz's theorem, we will encounter some variable for which Schwartz's theorem does not hold. Mathematically, if the Schwartz's theorem is violated (i.e., if the mixed second derivatives are not equal), then the corresponding function cannot be integrated, hence it is not a state function. The differential of a function that cannot be integrated cannot be defined exactly. For this reason, these functions are called path functions, that is, they depend on the path rather than the state. The most typical example of path functions that we will encounter in the next chapters are heat (Q) and work (W). For these functions we cannot define exact differentials dQ and dW, and we must introduce a new notation to define their “inexact differentials” δQ and δW .

We will return on exact and inexact differential when we discuss heat and work, but for this chapter it is important to notice the difference between a state function and a path function. A typical example to understand the difference between state and path function is to consider the distance between two geographical locations. Let's for example consider the distance between New York City and Los Angeles. If we fly straight from one city to the other there are roughly 4,000 km between them. This “air distance” depends exclusively on the geographical location of the two cities and it stays constant regardless of the method of transportation that I have accessibility to travel between them. Since the positions of the cities depend uniquely on their latitudes and longitudes, the “air distance” is a state functions, i.e., it is uniquely defined from a simple relationship between measurable variables. However, the “air distance” is not the distance that I will practically have to drive when I go from NYC to LA. Such “travel distance” depends on the method of transportation that I

decide to take (airplane vs. car vs. train vs. boat vs. ...), and it will depend on a plentiful amount of other factors such as the choice of road to be traveled (if going by car), the atmospheric conditions (if flying), and so on. A typical “travel distance” by car is, for example, about 4,500 km, which is about 12% more than the “air distance”. Certainly we could even design a very inefficient road trip that avoids all highways and will result in a “travel distance” of 8,000 km or even more (200% of the “air distance”). The “travel distance” is a clear example of a path function because it depends on the specific path that I decide to travel to go from NYC to LA. See Figure 1.2.



Figure 1.2: State Functions vs. Path Functions

Chapter 2

Zeroth Law of Thermodynamics

2.1 What is Thermodynamics?

Thermodynamics is the branch of science that deals with heat and work, and their relation to energy. As the definition suggests, thermodynamics is concerned with two types of energy: heat and work. A definition of these forms of energy is as follow:

- Work is exchanged if external parameters are changed during the process.
- Heat is exchanged if only internal parameters are changed during the process.

As we saw in Chapter 1 though, heat and work are not “well-behaved” quantities because they are path functions. While on the one hand it might be simple to measure experimentally the amount of heat and/or work, these measured numbers cannot be used to define the state of a system. Since heat and work are path functions, their values depend directly on the methods that are used to transfer them (their paths). Understanding and quantifying these energy transfers is the reason why thermodynamics was developed in the first place. The origin of thermodynamics dates back to the XXXX century, a time when people began to use heat and work for technological applications. These early scientists needed a mathematical tool to understand how heat and work were related with each other, and how they were also related with the other variables that they were able to measure, such as temperature and volume. XXX some more XXX

Before we even discuss the definition of energy and how it relates to heat and work, it is important to introduce the important concept of temperature. Tem-

perature is an intuitive concept that has a surprisingly complex definition. In fact with this course we will not even arrive at a rigorous definition of temperature, so you will not see it in this book. However, for all our purposes, it is not important to have a microscopic definition of temperature, as long as we have guarantee that this quantity can be measured in an unambiguous manner. In other words, we need a mathematical definition of temperature that will agree with the physical existence of thermometers.

2.2 Thermometers

2.3 The zeroth law of thermodynamics

The mathematical definition that guarantee that the thermal equilibrium is an equivalence relation is called the zeroth law of thermodynamics. The zeroth law of thermodynamics states that if two thermodynamic systems are each in thermal equilibrium with a third one, then they are in thermal equilibrium with each other. The law might appear trivial and possibly superfluous, but it is a fundamental requirement for the mathematical formulation of thermodynamics, so it needs to be stated. The zeroth law can be summarized by the following simple mathematical relation:

$$\text{If } T_A = T_B \text{ , and } T_B = T_C \text{ , then } T_A = T_C \quad (2.1)$$

Notice that when we state the zeroth law, it appears intuitive. However, this is not necessarily the case. Let's, for example, consider a pot of boiling water at $P = 1$ atm. Its temperature, T_{H_2O} , is about 373 K. Let's now immerse in this water a coin made of wood and another coin made of metal. After some sufficient time, the wood coin will be in thermal equilibrium with the water, and its temperature $T_W = T_{H_2O}$. Similarly, the metal coin will also be in thermal equilibrium with the water, hence $T_M = T_{H_2O}$. According to the zeroth law the temperature of the wood coin and that of the metal coin are exactly the same $T_W = T_M$, even if they are not in direct contact with each other. Now here's the catch: since wood and metal transmit heat in different manners, if I take the coins out of the water and put them immediately in your hands, one of them will be very hot, but the other will burn you. So, if you had to guess the temperature of the two coins without a thermometer, and without knowing that they were immersed in boiling water, would you guess that they have the same temperature? Probably not.

Chapter 3

First Law of Thermodynamics

Chapter 4

Thermochemistry

Chapter 5

Thermodynamic Cycles

Chapter 6

Second and Third Laws of Thermodynamics

Chapter 7

Chemical Potentials

Chapter 8

Chemical Equilibrium

Chapter 9

Introduction to Gases

Chapter 10

Real Gases

Chapter 11

Phase Equilibrium

Chapter 12

Multi-Component Phase Diagrams

Chapter 13

Solutions

Chapter 14

Kinetic Theory of Gas

Chapter 15

Chemical Kinetics