

Introductory Thermodynamics

by Nathan Jones

(Revised February 18th, 2021)¹

How to Read This Document (Don't Skip This Part!)

Traditional textbooks treat their topics independently, as if they were standalone units of knowledge (which, of course, they are not!) This makes it easy for advanced students to review individual topics as needed, and for professors to select required readings, but difficult for beginning students to appreciate the dependencies and connections between things. In writing this document, I have taken a holistic approach, which I believe better serves students who have no prior knowledge of thermodynamics. Therefore, this introduction is designed to be read from start to finish, much like a novel. In the same way that events in a story follow one another chronologically, the topics covered in this introduction build on one another logically. So, I strongly encourage you to begin at the beginning and read all the way through to the end *before* returning to review individual topics, if necessary. Don't worry if you don't understand something immediately. Keep reading! I have chosen a pathway through the material that I hope makes earlier topics more salient and meaningful as later topics are introduced.

Thermodynamic concepts depend intimately on one another. For example, *work*, and *energy* are mutually interdependent ideas. Therefore, it is impossible to define either one of them *without already knowing something about the other*, which appears to be a contradiction. *Work* is the *energy* expended by a system whenever it brings about motion against an opposing force, while *energy* is the capacity to do *work*. It seems that the definition of each points at the other. Which should be discussed first, energy or work? This introduction offers one possible answer to the question. Again, my advice is: read from the beginning to the end and become comfortable with not knowing everything immediately, that is, with taking on board words that have yet to be defined, even if they appear in the definitions of other words! One of the core problems that you need to solve is how to internalize the self-referential network of definitions

¹ The most recent version of this document may be found at nathanjones.com/writing
Please send questions, comments, and corrections by email to nathanjones@langara.ca

that serves as the foundation for thermodynamics. I have done my best to treat everything in an order that I hope enables you to accomplish this task eventually.

As you read, you'll encounter words and phrases in ***bold italics***. These are core concepts that I will define and discuss in later parts of the text. Pay careful attention to them!

Introduction

When table salt (sodium chloride) is dissolved in water, does the temperature of the water go up, or down? Why? And, speaking of salts, why is sodium chloride soluble in water, while silver chloride is not? Why does ice melt at room temperature and why do puddles of rain water evaporate without boiling? Why were metals like silver and gold known to ancient peoples, while iron and copper were more recently discovered, and aluminum not known until modern times? Why is it so difficult to make ammonia (the starting material for fertilizer) from nitrogen and hydrogen, but so easy to make water from oxygen and hydrogen? How do batteries work? Why do different kinds of batteries give the voltages they do? Why do living things appear to be organized, while lifeless things tend to become disorganized? Why does time appear to travel only in one direction?

If you understand thermodynamics, you will be able to answer these questions and many more besides. Thermodynamics is *powerful*. It provides a consistent explanation for a huge variety of seemingly unrelated phenomena and is securely established as one of the foundational blocks of our scientific understanding of the fabric of reality.

Thermodynamics is the branch of physics that deals with ***heat, work, and temperature***, and their relation to ***energy*** and the physical properties of matter. In chemistry, thermodynamics is the study of the relationship between energy and chemical reactions, or between energy and physical changes of state. The behaviour of ***thermodynamic systems*** is constrained by the four ***Laws of Thermodynamics***.

Thermodynamic Systems

A thermodynamic ***system*** is the specific portion of the Universe that we have chosen to study. It is separated from its ***surroundings*** by a boundary. For example, a paper cup containing hot coffee may be considered as a thermodynamic system. In this case, the system is the coffee and the cup, the boundary is the virtual surface that is

contiguous with the exterior surface of the cup, and the surroundings are the everything in the Universe outside the cup.

Systems are classified by the permeabilities of their boundaries to matter and energy. We will consider the three types of systems shown in Figure 1.

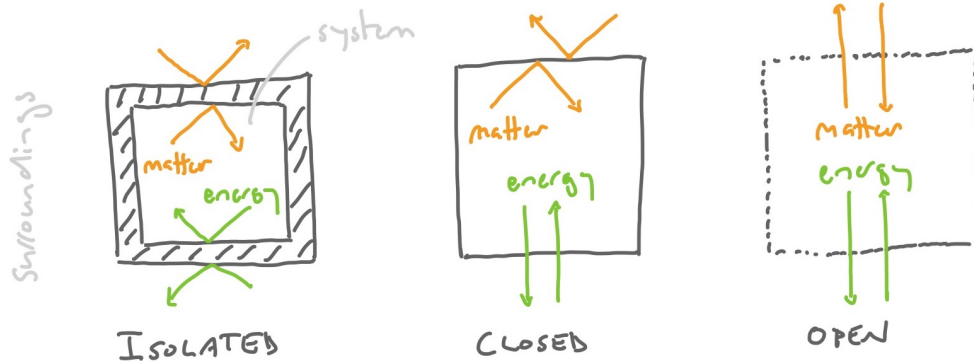


Figure 1: Three types of thermodynamic systems (isolated, closed, and open) classified by the permeabilities of their boundaries to matter and energy.

Isolated systems cannot exchange matter or energy with their surroundings. Therefore, the total energy and mass of an isolated system are constant. Closed systems can exchange energy with their surroundings, but not matter. Open systems allow both matter and energy to cross their boundaries.

If the coffee cup in our example were sealed with a plastic lid, it would be considered as a closed system. The cup could not exchange matter with its surroundings, but it would gradually cool down by losing energy in the form of heat until its temperature was equal to that of its surroundings. At this time, the system and the surroundings would be in **thermal equilibrium**.

The Zeroth Law of Thermodynamics

A system is at equilibrium when there are no further changes in its macroscopic properties, such as pressure, volume, and temperature. Two systems are in thermal equilibrium if the net transfer of heat between them is zero when they are connected via a path permeable to heat. Under these conditions, they will have the same temperature. An isolated system is in thermal equilibrium with itself when the temperature inside the system is spatially and temporally uniform.

The Zeroth Law of Thermodynamics asserts that *if two thermodynamic systems are independently in thermal equilibrium with a third system, then they are in thermal*

equilibrium with each other. This law is analogous to Transitive Law, which is the mathematical and logical assertion that if $a = c$ and $b = c$, then $a = b$.

Work

The fundamental physical parameter in thermodynamics is **work**. Work is the energy expended by a system whenever it brings about motion against an opposing force, for example, when an electric motor lifts a weight against gravity. Work is a *scalar quantity*, that is, it has magnitude, but no direction.

The basic equation relating work (w), force (F), and distance moved (d) is:

$$w = Fd \quad (1)$$

The SI unit of work is the joule, J. One joule is the work done by the system to move a force of 1 N through a distance of 1 m. ($1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$.)

Consider a gas confined to a cylinder capped at one end by an immovable wall and at the other by a moveable piston (Figure 2.) We assume that the piston is massless, frictionless, rigid, and perfectly fitting.

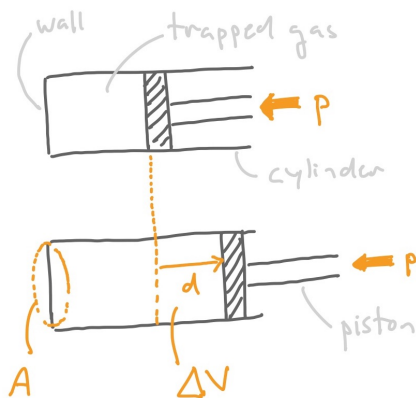


Figure 2. Expansion of a gas against an external pressure.

If the gas expands against an external pressure p so that the piston is pushed outwards by a distance d , then the work done is given by:

$$w = -pAd \quad (2)$$

where A is the cross-sectional area of the cylinder. Equation (2) proceeds directly from Equation (1) because pressure is defined as force per unit area; therefore, the force

against which the gas expands is given by $F = pA$. The product Ad is the change in volume of the gas, ΔV . So, Equation (2) may be re-written as:

$$w = -p\Delta V \quad (3)$$

The change in volume can also be calculated by:

$$\Delta V = V_{final} - V_{initial} \quad (4)$$

where V_{final} and $V_{initial}$ are the final and initial volumes of the gas, respectively. Generally, when a gas expands, $\Delta V > 0$, and when it is compressed, $\Delta V < 0$.

Thermodynamics takes a system-centric view. Therefore, when a system expands against an external pressure, that is, does work on its surroundings, its **internal energy** must be depleted. This is the reason for introducing a negative sign into Equation (2). When $\Delta V > 0$, w is < 0 ; when $\Delta V < 0$, w is > 0 .

State Variables and Functions

The delta notation is used frequently in thermodynamic calculations to describe *changes* that a system undergoes. Generally, for any quantity, x , $\Delta x = x_{final} - x_{initial}$. When thermodynamic quantities are expressed in this manner, we do not care about the particular pathway that the quantity traversed from its initial to its final value; all we care about is the difference, or “delta,” between the final and initial values. Another way of saying this is that we don’t care *how* the change happened; all we care about is *that* it happened.

Consider the ideal gas equation:

$$PV = nRT \quad (5)$$

Here, the pressure P , volume V , quantity n , and temperature T of the gas are **state variables** (R is the universal gas constant.) The combination of their values uniquely specify the “state” of the gas, that is, they describe its particular, current configuration without saying anything about how it came to be in that configuration.

Equation (5) demonstrates that if the quantity and temperature of an ideal gas are held constant, then we can calculate its volume if we know the pressure. That is, V is a *function of P* ($V = f(P) = \frac{k}{P}$, where $k = nRT$). Therefore, V may be considered a **state function**. Likewise, each of the other variables describing the state of an

ideal gas may be expressed as a function of one of the others (if the remaining variables are held constant.) Therefore, all of them can be expressed as state functions.

State functions have the characteristic that they can be written using the delta notation. For example, $\Delta V = f(P_{final}) - f(P_{initial}) = k\left(\frac{1}{P_{final}} - \frac{1}{P_{initial}}\right)$. This, as we

have said previously, signifies that it is sufficient for us to know only their initial and final values, not the particular path traversed by the system in moving from its initial to final state. State functions are said to be *path-independent*.

The following is a list of common thermodynamic state functions together with their symbols and units. Note well that heat and work are NOT state functions. That is, heat and work are path-dependent.

- Amount of substance, n (mol)
- Pressure, P (atm)
- Temperature, T (K)
- Volume, V (L)
- Internal Energy, U (J)
- Enthalpy, H (J)
- Gibbs free energy, G (J)
- Entropy, S (J K⁻¹)

Don't worry if you don't know what all of these words mean. We will get to them in time. Keep reading!

Heat

Heat involves two systems; it is NOT a property of any one system. Thus, the thermodynamic conception of heat must be distinguished from the common sense idea of "heat." We typically think of "heat" as something contained by a "hot" object, or lacking in a "cold" object. While perfectly intelligible in everyday language, this conception of heat is an error in the thermodynamic sense.

In the thermodynamic sense, heat is a *process* not an entity. It is the process by which energy is transferred from a system at high temperature to a system at low temperature. While acknowledging that heat is a process, chemists typically make use

of the phrase “energy as heat” in order to avoid a lot of awkward language. We will adopt this idiom from now on.

The transfer of energy as heat into or out of a thermodynamic system involves neither work done on or by the system, nor transfer of matter into or out of the system. There can be no transfer of energy as heat between systems at the same temperature, while transfer of energy as heat from a hotter to a cooler system is necessary, immediate, and spontaneous. (This is a consequence of the **Second Law of Thermodynamics**, discussed below.)

If two closed systems are in direct, physical contact, the two possible modes by which energy may be transferred as heat between them are **conduction**, if the systems are immobile relative to one another; or **friction**, if the systems are in relative motion. If the systems are not in contact, heat may be transferred between them by **radiation** from one to the other through space. We will consider the case of conduction.

The atoms or molecules that make up thermodynamic systems are in constant random motion involving translations, vibrations, and rotations. This random motion on the atomic scale (also known as the **microscopic scale**) is called **thermal motion**.

Conduction is the process by which thermal motion in the system at high temperature stimulates an increase in the thermal motion of the system at low temperature. Think of when the cue ball “breaks” the racked balls at the beginning of a game of pool. In this analogy, the cue ball represents atoms of high thermal motion in the hot system, while the stationary balls represent atoms of low thermal motion in the cold system. When the cue ball collides with the stationary balls, it imparts its kinetic energy to them and causes them to move in several directions and speeds. This is a good mental model for the mechanism of conduction. For an example of “breaking” pool, see: https://youtu.be/8p_NBIKb9Bg?t=99

Heat & Work: Similarities & Differences

Now that we have an understanding of both heat and work, it is useful for us to consider their essential similarities and differences. Both heat and work involve transfer of energy between *two* systems, or between system and surroundings; neither is a property of any *one* system alone. Work is distinguished from heat in that work involves *organized* motion in the surroundings while heat involves *random* motion in the surroundings. Moreover, if we confine our thinking to the motion of machines, work is *useful* whereas heat is not.

To make the latter distinction more clearly, consider the machine illustrated in Figure 3. In this set-up, the system is the gas. The surroundings are all of the components of the machine. When the gas contained within the cylinder expands, it pushes the piston outwards (rightwards), which turns the cog clockwise and lifts the weight against the force of gravity by winding a string onto a spindle. Work therefore involves transformation of energy stored on the microscopic scale within the system into organized motion in the surroundings on the **macroscopic scale**, that is, on a scale which can be directly observed. The gas does work (loses energy) equivalent to the potential energy gained by the weight. This directed motion against an opposing force demonstrates the usefulness of work.

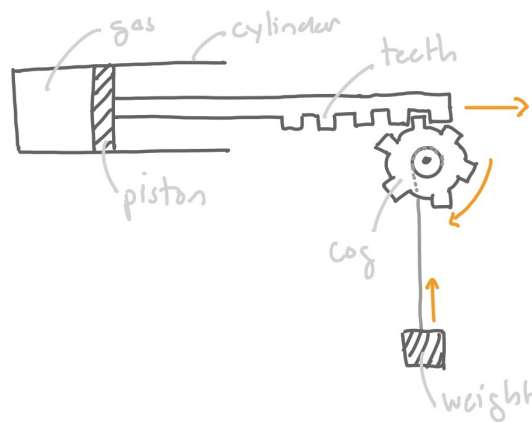


Figure 3. A system to lift a weight by expansion of a gas. The orange arrows indicate the directions of movement of the various components.

By contrast, frictional heating of the system's components brought about by their relative motion (for example, of the walls of the cylinder and the piston) diminishes the system's capacity to lift the weight. This happens because a fraction of the gas's available energy is "wasted" by increasing the thermal motion of the atoms in the components; this fraction cannot be expended in bringing about directed motion in the surroundings. This "loss to heat" is a general problem of all machines.

Temperature

We use the words "cold" and "hot" to describe objects. For example, we say that a cube of ice is "cold" and that the kettle on the stove is "hot." What we mean by this, in the thermodynamic sense, is that if we were to touch the cube of ice, energy as heat would flow out of our fingers and into the ice; and if we were to touch the kettle, energy

as heat would flow out of it and into our fingers. (Ouch!) These decreases and increases in the thermal energy of the molecules within our fingers give rise to the sensations of cold and hot in our brains. Therefore, in order to make determinations of the degree of coldness or hotness, we need a “probe,” like our fingers, out of which, or into which, energy as heat may flow.

Temperature (the physical quantity that expresses “hot” and “cold”) is measured (or, probed) using a **thermometer**, which itself may be considered as a thermodynamic system. When a thermometer is brought into contact with a system of interest, energy as heat will be transferred by conduction into it, if it is colder than the system; or out of it, if it is warmer than the system. This transfer will bring about an observable change in thermometer, such as a change in the level of liquid mercury in a glass capillary. As energy as heat flows into the thermometer from the system, this level will rise due to the thermal expansion of the mercury; as energy as heat flows out of the thermometer into the system, the level will fall as the volume of the mercury falls. When the thermometer and the system of interest have come to thermal equilibrium, the level of mercury in the capillary will stabilize and the temperature can be read by comparing the level to a scale etched into the glass. In this way, the flow of heat into, or out of, the thermometer can be measured.

Various scales of temperature are in common use, such as degrees Celsius and Fahrenheit. The scale of temperature relevant to thermodynamics is the kelvin scale, K. This is known as the **absolute temperature scale** because 0 K is the lowest possible temperature that a thermodynamic system can attain. Figure 4 shows the variation in volume with temperature in degrees Celsius of 1 mol of an ideal gas at 1 atm pressure. The temperature at which the volume of this gas is 0 L is $-273.15\text{ }^{\circ}\text{C}$, which is 0 K.

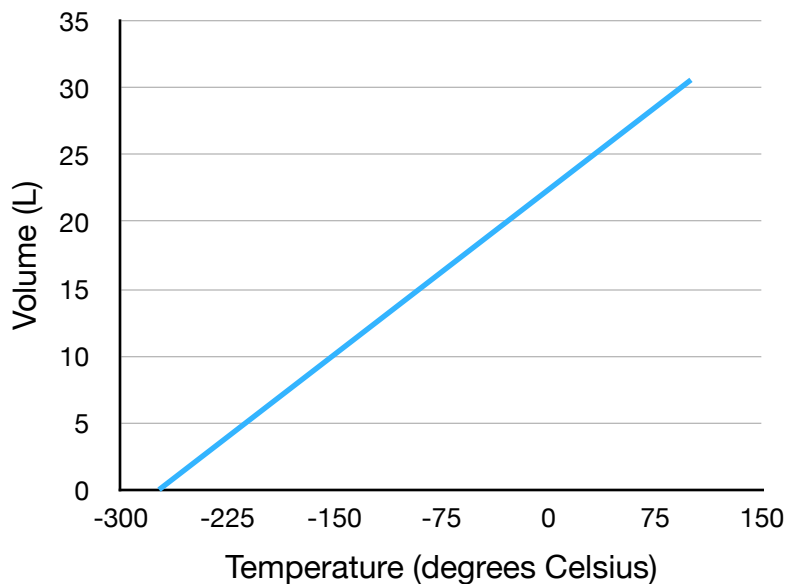


Figure 4. Volume of 1 mol of an ideal gas as a function of temperature in degrees Celsius.

Intensive and Extensive Properties

An **intensive property** is a physical quantity whose magnitude is independent of the size, amount, and shape of the substance for which it is measured. The temperature and pressure of a gas, for example, are intensive properties. Consider a vessel of volume V containing a gas whose temperature and pressure are T and P , respectively.

Now imagine dividing this container into two compartments of volume $\frac{V}{2}$ and

measuring the temperature and pressure of the gas in each compartment. You would find that the values of these properties were unchanged at T and P . Now imagine dividing each of the compartments in half once again so as to give four compartments of volume $\frac{V}{4}$. The temperature and pressure of the gas in each of these would still be T

and P . This subdivision could be done any number of times to give arbitrarily small compartments with no effect on the temperature and pressure.

An **extensive property**, on the other hand, is one whose magnitude depends upon amount of the substance for which it is measured. We can see clearly in the thought experiment outlined above that volume is an extensive property. Its value decreases by 50% each time we divide the container in half. Intensive properties can be constructed from ratios of extensive properties. For example density, which is intensive, is the ratio

of mass to volume (both extensive.) Table 1 lists intensive and extensive properties that are relevant to thermodynamics.

Table 1. Common intensive and extensive properties.

Intensive Properties	Extensive Properties
concentration	amount of substance
melting and boiling point	mass
density	volume
specific heat capacity	heat capacity
temperature	internal energy
pressure	Gibbs free energy
	enthalpy
	entropy

Heat and Temperature

We have learned that thermodynamic systems are distinguished by the permeability of their boundaries to energy and matter. Now that we have defined heat, work, and temperature, we are in a position to consider closed systems more carefully. (Recall that closed systems are those that may exchange energy with its surroundings, but not matter.)

The boundary of a closed system may be permeable or impermeable to energy as heat. Boundaries that are permeable to energy as heat are called **diathermic** while those that are impermeable are called **adiabatic**. If a closed system is contained by an adiabatic boundary, it will not exchange energy as heat with the surroundings even in the case of a difference in temperature between the two.

As chemists, we are often called to consider the energy as heat produced or absorbed by reacting atoms or molecules. The branch of thermodynamics that is concerned with relation between heat and reactions is **thermochemistry**. Chemical reactions that release energy as heat into their surroundings are called **exothermic** (“exo” = out of); those that absorb energy as heat from their surroundings are called **endothermic** (“endo” = into.)

We are now in a position to consider how temperature relates to chemical reactions occurring in solution. In our experimental set-up, the reaction may be either exothermic or endothermic; and the boundary containing the solution in which the reaction occurs may be either diathermic or adiabatic. We assume that (i) starting temperature of the solution is equal to the temperature of the laboratory; and (ii) the solution does not change volume during the course of the reaction. Our procedure is to measure the temperature of the solution as a function of time once the reaction has begun.

The four possible outcomes of this experiment are shown in the two-by-two matrix illustrated in Figure 5. In all cases, the early, flat portion of the temperature-time plot represents the steady initial temperature prior to the start of the reaction, which is the same as the temperature in the laboratory.

In Case (1), an exothermic reaction releases energy as heat into the solution. This causes an increase in the thermal motion of the molecules from which the solution is constituted, which is reflected in an increase in the temperature as the reaction progresses. The reaction begins quickly, so the initial increase in the temperature is steep. As the reaction progresses, however, it slows down and the rate of change of temperature slows, too. Because the boundary with the wider laboratory in this case is adiabatic, the energy as heat released by the reaction cannot escape from the solution and once the reaction is complete, the increased temperature is fixed at a higher level than it was before the reaction began. In Case (2), an endothermic reaction contained within an adiabatic boundary produces the mirror image result.

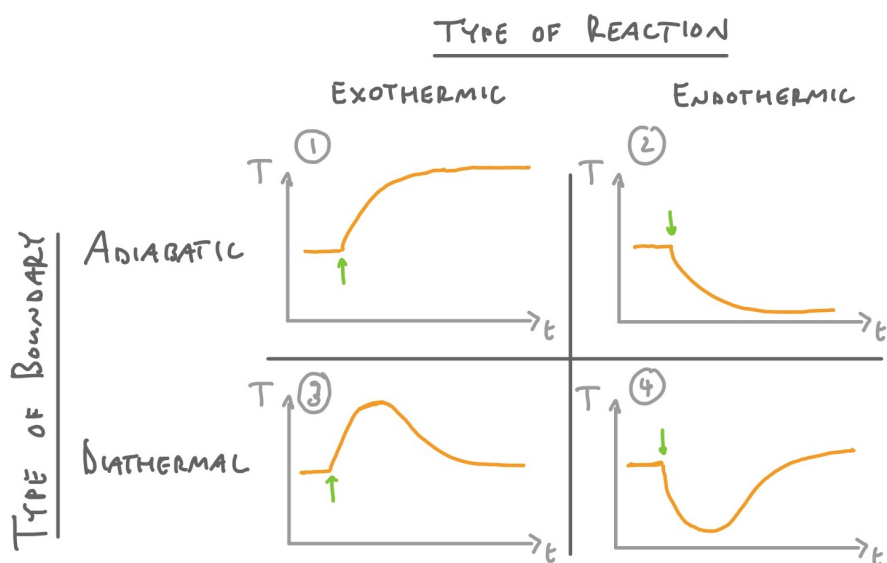


Figure 5. The four possible outcomes of temperature (T) as a function of time (t) resulting from exothermic and endothermic reactions occurring in solutions

contained within adiabatic and diathermic boundaries. The green arrows indicate the beginning of the reaction in each case.

In Case (3), the exothermic reaction produces an initial increase in the temperature of the solution in the same manner as described for Case (1). However, in this case, because the diathermic boundary is permeable to the transfer of energy as heat, there is an opposition to the increase in temperature – a loss of energy as heat to the laboratory, which in this case is now cooler than the solution. As the reaction slows, the rate of production of energy as heat will be overtaken by the rate of loss of energy as heat to the wider environment and the temperature will begin to fall. Finally, when the reaction is complete and no more energy as heat is being produced internally, the entire solution will come to thermal equilibrium with the laboratory and the temperature of the solution will be equal to the temperature before the reaction began. In Case (4), an endothermic reaction contained within a diathermic boundary produces the mirror image result.

Heat Capacity

The increase in temperature of the solution in Case (1) of Figure 5, that is, $\Delta T = T_{\text{final}} - T_{\text{initial}}$, is directly proportional to the energy as heat released by the exothermic reaction, q ; the proportionality constant between these two quantities is the **heat capacity** of the solution, C . That is,

$$q = C\Delta T \quad (6)$$

Equation (6) may be rewritten to give C in terms of q and ΔT :

$$C = \frac{q}{\Delta T} \quad (7)$$

Equation (7) demonstrates that the heat capacity of a system is the energy as heat that must be transferred to it in order to increase its temperature by 1 K. The units of heat capacity are J K^{-1} . Heat capacity is an extensive property that depends upon the size of the system. The larger the system, the more energy as heat must be transferred to it to raise its temperature by 1 K. For example, the heat capacity of 1 kg of water is one thousand times larger than the heat capacity of 1 g of water. It is therefore useful to specify an intensive form of heat capacity called **specific heat capacity**.

Specific heat capacity, c , is the energy as heat that is required to raise the temperature of 1 kg of a substance by 1 K. Specific heat capacity is therefore the ratio of heat capacity to mass. The specific heat capacity of a substance of mass m is given by:

$$c = \frac{C}{m} = \frac{q}{m\Delta T} \quad (8)$$

The units of specific heat capacity are $\text{J K}^{-1} \text{kg}^{-1}$. Both heat capacity and specific heat capacity depend on the temperature and pressure of the system, so they are properly considered as functions of those variables rather than as constants, that is $C(P, T)$ and $c(P, T)$. However, for problems in introductory thermodynamics, they are often assumed to be constants. This assumption is usually justified on the grounds that within the narrow ranges of temperature and pressure under consideration, the variation in heat capacity is small enough to ignore.

Work and Temperature

The principal distinction between work and heat is made *in the surroundings*. If the thermal motion *of the system* were increased, or decreased, this would not by itself tell us whether work, or heat, was responsible for that change. Recall that energy transferred as work involves organized motion of atoms in the surroundings, while energy transferred as heat involves random motion of atoms in the surroundings. So, we need to look for changes in the surroundings to determine the origin of a change in the thermal motion of the system.

If, for example, the weight in Figure 3 were to fall, the cog would be turned counter-clockwise and the piston would be pushed inwards (leftwards). This would result in compression of the gas. In other words, the surroundings (as we have defined them) would do work *on* the system (the gas contained within the cylinder) to the extent of $w = -P\Delta V$. (In this case ΔV would be negative because $V_{\text{final}} < V_{\text{initial}}$, and w would be positive.)

At the microscopic scale, collisions of the atoms or molecules (particles) making up the gas with the head of the moving piston would result in their acceleration as the kinetic energy of the piston was transferred to them. (This happens in the same way that a ball accelerates away from the swinging bat that strikes it.) The organized motion of the piston would quickly be translated into random motion of the particles as they collided with one another, and the increased kinetic energy of the particles in the proximity of the piston head would likewise be distributed throughout the gas by these collisions.

Therefore, the inward motion of the piston would effect an increase in the thermal motion of the gas (the system).

What would be the effect of this increased thermal motion on the temperature of the gas? This would depend, as we have seen previously, on the permeability of the walls of the cylinder to heat. If this boundary were *adiabatic*, the temperature of the gas would increase sharply as the gas was being compressed and then remain at a fixed, elevated level, so long as its volume were held constant. If, on the other hand, the boundary were diathermic, there would be a gradual reduction in temperature following the initial increase as energy as heat was lost to the surroundings. These behaviours are analogous to Cases 1 and 3 in Figure 5.

We're now in the position to illustrate the effects on temperature of work done on and by a gaseous system enclosed within both adiabatic and diathermal boundaries. These effects are captured in the two-by-two matrix shown in Figure 6.

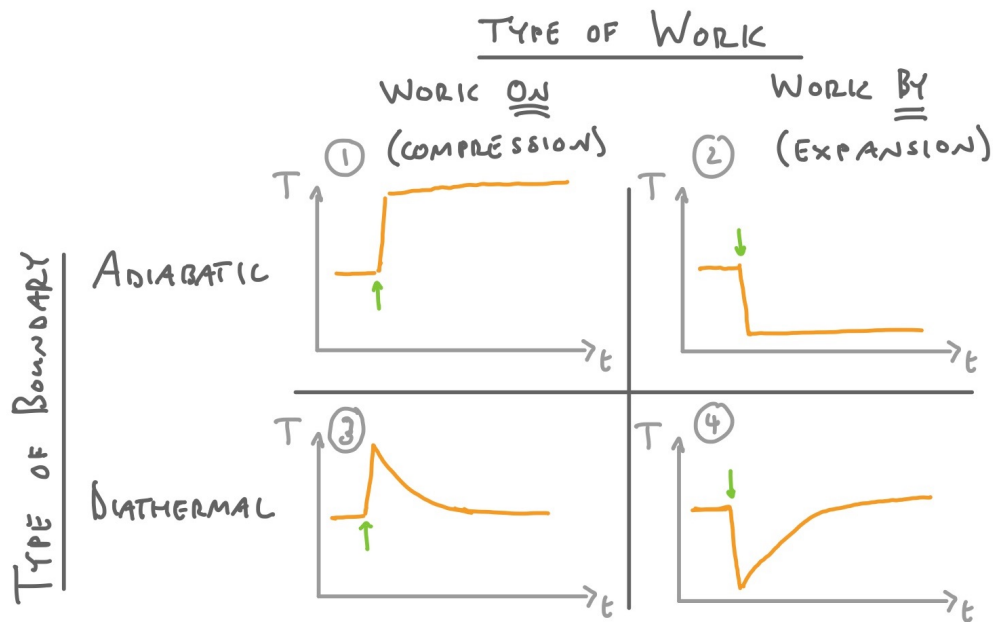


Figure 6. The four possible outcomes of temperature (T) as a function of time (t) resulting from work done on (compression) and by a gas (expansion) given adiabatic and diathermic boundaries. The green arrows indicate the instant of abrupt change in volume.

Energy

Now that we have an understanding of heat and work, we can see that these are different forms of energy. But what is energy? We have mentioned it several times without pausing to define it.

Energy is the physical property that must be transferred to a thermodynamic system either to perform work on it, or to heat it (or both.) Conversely, energy is the property transferred out of a system when it does work on, or heats, another system (or both.)

Energy is both quantifiable and conserved. That is, it is transferred in definite, measurable amounts, and cannot be created, or destroyed. For example, if System **A** does work on System **B**, then the energy lost by **A** is equal to the energy gained by **B**. It is often the case in thermodynamic studies that the two “systems” involved in this transfer are the system of interest and the surroundings.

The two fundamental forms of energy are *kinetic energy*, which is the energy associated with a moving object, and *potential energy*, which is the energy stored by an object owing to its position in a gravitational, electric, or magnetic field. The kinetic energy of an object of mass m moving at a velocity of v is given by:

$$KE = \frac{mv^2}{2} \quad (6)$$

The potential energy stored by an object of mass m lifted to a height h above the surface of the Earth is given by:

$$PE = mgh \quad (7)$$

where g is the gravitational acceleration of the Earth (approximately 9.81 ms^{-2} .)

The forms of energy that we are familiar with from everyday experience, such as, light, electricity, sound, and heat, can be described in terms of combinations of the kinetic and potential energies of the particles that are involved in carrying those forms of energy.

The SI unit of energy is the joule, which we have already defined in the context of work. One joule is the work done by the system to move a force of 1 N through a distance of 1 m. This makes it clear that energy can also be defined as the capacity to do work.

Internal Energy

Let us now define another thermodynamic quantity called **internal energy**. Internal energy (U) is the total energy contained within a system. It keeps account of the gains and losses of energy that are brought about by changes to the internal state of the system.

Thermodynamics is primarily concerned with *changes* in internal energy rather than its absolute value, which is impossible to determine with thermodynamics alone.