

Chapter 1: The Basics

Physical chemistry is concerned with the gray area that lies between physics (the study of energy) and chemistry (the study of matter). As such, physical chemistry is all about how energy can be stored through, extracted from, and used to drive chemical reactions and chemical systems. A major topic that focuses on how energy and matter interact and affect one another is thermodynamics. But before diving into thermodynamics, it is important to set down a few definitions that make it possible to begin slicing up the topic.

The System and the Surroundings

The Zeroth Law of Thermodynamics deals with the temperature of a system. And while it may seem intuitive as to what terms like “temperature” and “system” mean, it is important to define these terms. The easiest terms to define are the ones used to describe the system of interest and the surroundings, both of which are subsets of the universe.

Universe – everything

System – subset of the universe that is being studied and/or measured

Surroundings – every part of the universe that is not the system itself.

As it turns out, there can be several types of systems, depending on the nature of the boundary that separates the system from the surroundings, and specifically whether or not it allows to the transmittance of matter or energy across it.

Open System – allows for both mass and energy transfer across its boundary

Closed System – allows for energy transfer across its boundary, but not mass transfer

Isolated System – allows neither mass nor energy transfer across its boundary

Further, systems can be **homogeneous** (consisting of only a single phase of matter, and with uniform concentration of all substances present throughout) or **heterogeneous** (containing multiple phases and/or varying concentrations of the constituents throughout.) A very important variable that describes a system is its composition, which can be specified by the number of moles of each component or the concentration of each component. The number of moles of a substance is given by the ratio of the number of particles to Avogadro’s number

$$n = \frac{N}{N_A}$$

where n is the number of moles, N is the number of particles (atoms, molecules, or formula units) and N_A is Avogadro’s number ($N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$).

Other important variables that are used to describe a system include the important variables of pressure, temperature, and volume. Other variables may also be important, but can

often be determined if these **state variables** are known. Oftentimes, knowing a small number of state variables is all that is required to determine all of the other properties of a system. The relationship that allows for the determination of these properties from the values of a couple of state variables is called an **equation of state**.

Variables that describe a system can be either **intensive** (independent of the amount of any given substance present in the system) or **extensive** (dependent on the amount of substance present in the system.) Temperature and color are examples of intensive variables, whereas volume and mass are examples of extensive variables. The value of intensive properties is that they can be conveniently tabulated for various substances, whereas extensive properties would be specific to individual systems.

Oftentimes it is the case that the ratio of two extensive variables results in an intensive variable (since the amount of substance cancels out.) An example of this is density, which is the ratio of mass and volume. Another example is molar volume (V_m) which is the ratio of volume and number of moles of substance. For a given substance, the molar volume is inversely proportional to the density of the substance.

In a homogeneous system, an intensive variable will describe not just the system as a whole, but also any subset of that system. However, this may not be the case in a heterogeneous system!

Pressure and Molar Volume



Figure 1. Evangelista Torricelli (1608 - 1647)

Italian physicist Evangelista Torricelli (1608 – 1647) (Evangelista Torricelli) was the inventor of an ingenious device that could be used to measure air **pressure**. Basically, he took a glass tube closed at one end, and filled it with mercury. He then inverted it, submerging the open

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end below the surface level in a pool of mercury. The mercury in the glass tube was then allowed to drain, leaving a vacuum (known as a “Torricellian vacuum”) in the open space at the closed end of the tube. Remarkably, the tube did not drain completely! Torricelli, was able to use the residual column height to measure the pressure of the air pushing down on the surface of the pool of mercury. The larger the pressure pushing down on the exposed surface, the larger the column height is observed to be. The ambient air pressure can be computed by equating the force generated by the mass of the mercury in the column to the force generated by ambient air pressure (after normalizing for surface area). The resulting relationship is

$$p = \rho g h$$

where ρ is the density of the mercury (13.1 g/cm^3), g is the acceleration due to gravity, and h is the height of the column. Torricelli found that at sea level, the height of the column was 76 cm.

$$p = \left(13.69 \frac{\text{g}}{\text{cm}^3}\right) \left(9.8 \frac{\text{m}}{\text{s}^2}\right) (76 \text{ cm}) \left(\frac{100^2 \text{ cm}^2}{\text{m}^2}\right) \left(\frac{\text{kg}}{1000 \text{ g}}\right) \left(\frac{\text{N}}{\frac{\text{kg m}}{\text{s}^2}}\right)$$

$$100\,000 \frac{\text{N}}{\text{m}^2} = 100\,000 \text{ Pa}$$

A force of 1 N acting on an area of 1 m^2 is a Pascal (Pa). A standard atmosphere is 101,325 Pa (101.325 kPa), or 76.0 cm Hg (760 mm Hg.) Another commonly used unit of pressure is the bar.

$$1 \text{ bar} = 100,000 \text{ Pa}$$

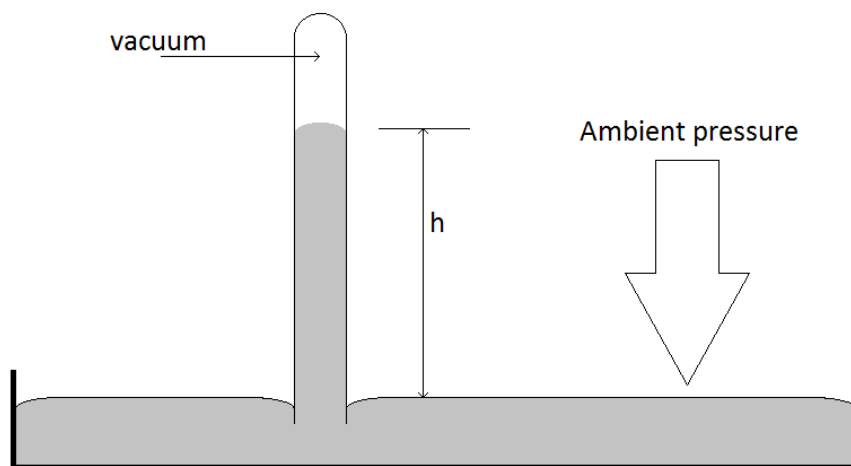


Figure 2. Set up for the Torricelli barometer.

Temperature

Another important variable that describes the state of a system is the system's **temperature**. Like pressure, temperature scales experienced an important process of development over time. Three of the most important temperature scales in US culture are the Fahrenheit, Celsius, and Kelvin scales.

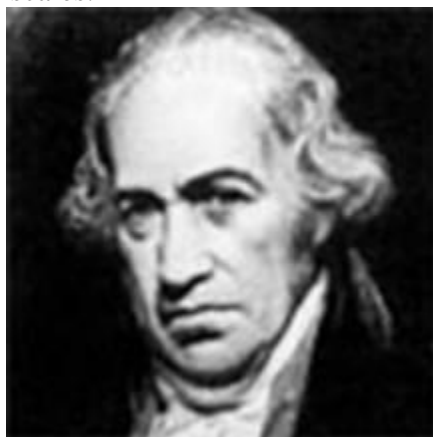


Figure 3. G. Daniel Fahrenheit (1686 – 1736)

G. Daniel Fahrenheit (Gabriel Fahrenheit Biography, 2016) wanted to develop a temperature scale that would be convenient to use in his laboratory. He wanted it to be of convenient magnitude and wanted to avoid having to use any negative values for temperature. So he defined the zero of his temperature scale to be the lowest temperature he could create in his laboratory, which was in a saturated brine/water/ice slurry. He then defined 100 °F as his own body temperature. As a result, using his temperature scale, water has a normal melting point (the temperature at 1.00 atm pressure at which water ice melts) of 32 °F. Similarly, water boils (again at 1 atm pressure) at a temperature of 212 °F. The difference between these values is 180 °F.



Figure 4. Anders Celsius (1700 - 1780)

Anders Celsius (Biography.com) also thought a 100 degree temperature scale made sense, and was given the name “the centigrade scale”. He defined 0 °C on his scale as the normal boiling point of water, and 100 °C as the normal freezing point. By today's standards, this

inverted temperature scale makes little sense. The modern Celsius temperature scale defines 0 °C as the normal freezing point of water and 100 °C as the normal boiling point. The difference is 100 °C. Comparing this to the Fahrenheit scale, one can easily construct a simple equation to convert between the two scales.

$$\begin{aligned}212\text{ }^{\circ}\text{F} &= 100\text{ }^{\circ}\text{C}(m) + b \\32\text{ }^{\circ}\text{F} &= 0\text{ }^{\circ}\text{C}(m) + b\end{aligned}$$

Solving these equations for m and b yields

$$\begin{aligned}m &= \left(\frac{9\text{ }^{\circ}\text{F}}{5\text{ }^{\circ}\text{C}}\right) \\b &= 32\text{ }^{\circ}\text{F}\end{aligned}$$

And so conversion between the two scales is fairly simple.

$$\begin{aligned}y\text{ }^{\circ}\text{F} &= x\text{ }^{\circ}\text{C}\left(\frac{9\text{ }^{\circ}\text{F}}{5\text{ }^{\circ}\text{C}}\right) + 32\text{ }^{\circ}\text{F} \\x\text{ }^{\circ}\text{C} &= (y\text{ }^{\circ}\text{F} - 32\text{ }^{\circ}\text{F})\left(\frac{5\text{ }^{\circ}\text{C}}{9\text{ }^{\circ}\text{F}}\right)\end{aligned}$$

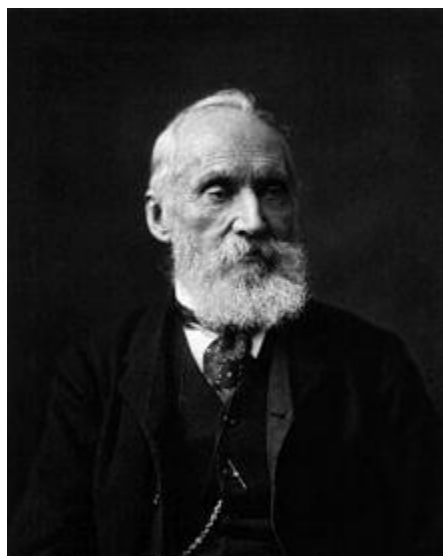


Figure 5. William Lord Kelvin (1824 - 1907)

Many physical properties of matter suggest that there is an absolute minimum temperature that can be attained by any sample. This minimum temperature can be shown by several types or experiments to be -273.15 °C. An absolute temperature scale is one that assigns the minimum temperature a value of 0. One particularly useful scale is named after William Lord Kelvin (Kelvin, Lord William Thomson (1824-1907) , 2007). The Kelvin scale fixes the normal melting

temperature of water at 273.15 K and the boiling point at 373.15 K. As such, temperatures can be converted using the following expression:

$$z\text{ K} = x\text{ }^{\circ}\text{C} \left(\frac{1\text{ K}}{1\text{ }^{\circ}\text{C}} \right) + 273.15\text{ K}$$

The Zeroth Law of Thermodynamics

Temperature is an important property when it comes to measuring energy flow through a system. But how does one use or measure temperature? Fortunately, there is a simple and intuitive relationship which can be used to design a thermometer – a device to be used to measure temperature and temperature changes. The zeroth law of thermodynamics can be stated as follows:

If a system A is in thermal equilibrium with a system B, which is also in thermal equilibrium with system C, then systems A and C share a property called temperature.

This basic principle has been used to define standard temperature scales by the International Committee on Weights and Measures (BIPM) to guide the adoption of the International Practical Temperature Scale of 1990 (Mangum & Furukawa, 1990).

IPT-90 is defined by using various physical properties of substances (such as the triple point of water) which occur at very specific temperatures and pressures, and then assigning the measurable values such as the resistance on a standard **platinum resistance thermometer** (Strouse, 2008).

Work and Energy

Temperature, pressure and volume are important variables in the description of physical systems. They will also be important to describe how energy flows from one system to another. Generally, energy can flow in two important forms: 1) work and 2) heat. The bookkeeping needed to track the flow of energy is what the subject of Thermodynamics is all about, so these topics will be discussed at length in subsequent chapters. However, a little bit of review is in order, just to set the foundation for the discussions that are forthcoming.

Energy

Energy is an important entity in the modern world. We use energy to light our homes, drive our cars, and power our electronic devices. According to Richard Smalley, co-winner of the 1996 Nobel Prize in Chemistry, energy is one of the (if not the biggest) challenge we face moving into the 21st century (energy.senate.gov, 2004):

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Energy is at the core of virtually every problem facing humanity. We cannot afford to get this wrong. ... Somehow we must find the basis for energy prosperity for ourselves and the rest of humanity for the 21st century. By the middle of this century we should assume we will need to at least double world energy production from its current level, with most of this coming from some clean, sustainable, CO₂-free source. For worldwide peace and prosperity it needs to be cheap.

- *Richard Smalley, Testimony to the Senate Committee on Energy and Natural Resources, April 26, 2004*

Energy can be measured in a multitude of different units, including joules (J), kilojoules (kJ), calories (cal), kilocalories (kcal), as well as several other set of units such as kJ/mol or kcal/mol.

A **calorie (cal)** was once defined as the amount of energy needed to raise the temperature of 1 g of water by 1 °C. This definition suggests a convenient property of water called the **specific heat**:

$$C = \frac{1 \text{ cal}}{g \text{ } ^\circ\text{C}}$$

The modern definition of a calorie is 4.184 **joule**,

$$C = \frac{4.184 \text{ J}}{g \text{ } ^\circ\text{C}}$$

where a joule is the energy necessary to move a mass a distance of 1 m against a resisting force of 1 N.

$$1 \text{ J} = 1 \text{ N m} = \frac{1 \text{ kg m}^2}{\text{s}^2}$$

A dietary **Calorie (Cal)** is equal to 1000 cal, or 1 kcal, and is often listed on the labels of food containers to indicate the energy content of the food inside.

Energy can take the form of **potential energy** (stored energy) and **kinetic energy** (realized energy) forms. Kinetic energy is the energy of motion. On the other hand, potential energy can be defined as the energy stored in a system that can be converted to kinetic energy someplace in the universe. Kinetic energy of a particle can be expressed as

$$E_{kin} = \frac{1}{2}mv^2$$

where m is the mass of the particle, and v is the magnitude of its velocity (or speed).

An example of a system in which energy is converted between kinetic energy and potential energy is a Hooke's Law oscillator. According to Hooke's Law, the force acting on an object is proportional in magnitude to the displacement of the object from an equilibrium position, and opposite in sign.

$$F = -kx$$

In this equation, F is the force, x is the displacement from equilibrium, and k is the constant of proportionality. The negative sign is necessary to insure that the force acting on the object is one that will tend to restore it to an equilibrium position ($x = 0$) irrespective of whether x is positive or negative.

As the object that follows Hooke's Law moves from its equilibrium position, the kinetic energy of its motion is converted into potential energy until there is no more kinetic energy left. At this point, the change in displacement will change direction, returning the object to the equilibrium position by converting potential energy back into kinetic energy.

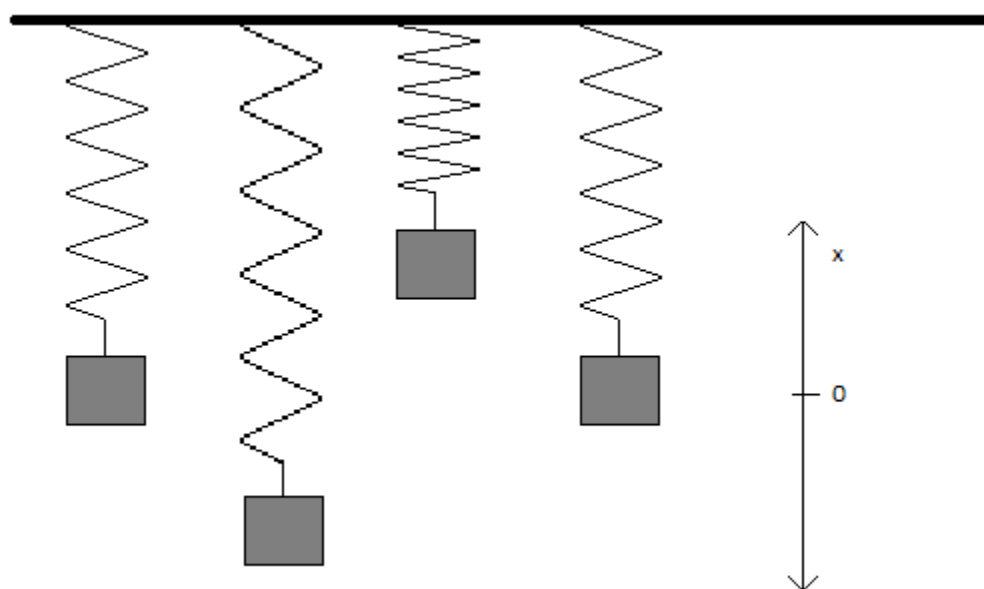


Figure 6. An example of a harmonic oscillator.

As the object is displaced along the x -axis (in the case shown in figure 6, this would be accomplished by stretching or compressing the spring), the potential energy increases. The force acting on the object will also increase as the object is displaced and will be directed opposite of the direction of displacement.

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$$F = -k x$$

According to Newtonian physics, the potential energy is given by the negative integral of the force with respect to position:

$$U(x) = - \int F(x) dx$$

Substitution yields

$$\begin{aligned} U(x) &= - \int (-k x) dx \\ &= \frac{1}{2} k x^2 + \text{const.} \end{aligned}$$

With the proper choice of coordinate system and other definitions, the constant of integration can be arbitrarily made to be zero (for example, by choosing it to offset any other forces acting on the object, such as the force due to gravity.) The kinetic energy is then given by the total energy minus the potential energy (since the total energy must be constant due to the conservation of energy in the system!)

$$E_{kin}(x) = E_{tot} - U(x)$$

Work

Work is defined as the amount of energy expended to move a mass against a resisting force. For a mass being moved along a surface, the amount of energy expended must be sufficient to overcome the resisting force (perhaps due to friction) and also sufficient to cause motion along the entire path.

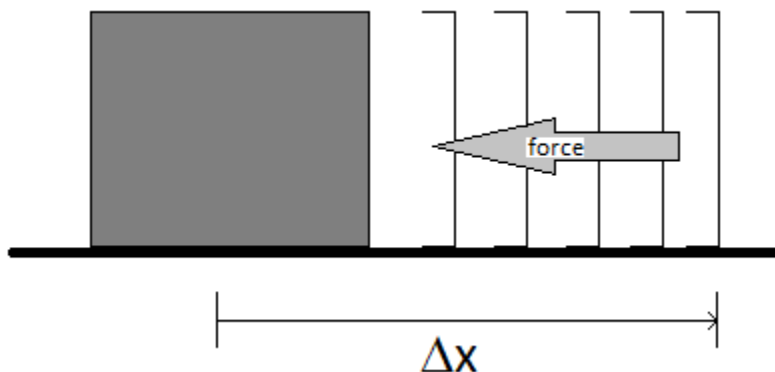


Figure 7. The work of displacement.

The energy expended as work in this case (if the force is independent of the position of the object being moved) is given by

$$w = -F \Delta x$$

where F is the magnitude of the resisting force, and Δx is the displacement of the object. The negative sign is necessary since the force is acting in the opposite direction of the motion. A more general expression, and one that can be used if the force is not constant over the entire motion is

$$dw = -F dx$$

This expression can then be integrated, including any dependence F might have on x as needed for a given system.

Another important way that work can be defined includes that for the expansion of a gas sample against an external pressure. In this case, the displacement is defined by a change in volume for the sample:

$$dw = -p_{ext} dV$$

This is a very convenient expression and will be used quite often when discussing the work expended in the expansion of a gas.

The conversion of potential energy into kinetic energy generally is accomplished through work which is done someplace in the universe. As such, the concepts of energy and work are inexorably intertwined. They will be central to the study of thermodynamics.

The work of a “reversible” expansion

An important case of **limiting ideal behavior**¹ is that of the **reversible expansion**. For a change to be reversible there can be no net force pushing the change in one direction or the other. In order for this to be the case, the internal pressure (that of the system) and external pressure (that of the surroundings) must be the same.

$$p_{int} = p_{ext} = p$$

In this case, the work of expansion can be calculated by integrating the expression for dw .

¹ There are many cases of “limiting ideal behavior” which we use to derive and/or explore the nature of chemical systems. The most obvious case, perhaps, is that of the **Ideal Gas Law**. Thermochemistry and Chemical Kinetics: The Basics © 2021 Patrick E. Fleming – Available under Creative Commons Attribution-Noncommercial-Share Alike license 4.0 ([CC BY-NC-SA 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/))

$$w = \int dw = - \int p dV$$

Making a simple substitution from the ideal gas law

$$p = \frac{nRT}{V}$$

allows for the expression in terms of volume and temperature. If the temperature is constant (so that it can be placed before the integral) the expression becomes

$$w = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

where V_1 and V_2 are the initial and final volumes of the expansion respectively.

Example: Consider 1.00 mol of an ideal gas, expanding isothermally at 273 K, from an initial volume of 11.2 L to a final volume of 22.4 L. What is the final pressure of the gas? Calculate the work of the expansion if it occurs

- a) against a constant external pressure equal to the final pressure you have calculated.
- b) reversibly.

Solution: First, let's calculate the final pressure.

$$p = \frac{nRT}{V} = \frac{(1.00 \text{ mol})(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(273 \text{ K})}{(22.4 \text{ L})} = 1.00 \text{ atm}$$

(This may be a relationship you remember from General Chemistry – that 1 mole of an idea gas occupies 22.4 L at 0 °C!)

Okay – now for the irreversible expansion against a constant external pressure:

$$dw = -p_{\text{ext}} dV$$

So

$$w = -p_{\text{ext}} \int_{V_1}^{V_2} dV = -p_{\text{ext}} \Delta V$$

$$w = -(1.00 \text{ atm})(22.4 \text{ L} - 11.2 \text{ L}) = -11.2 \text{ atm L}$$

But what the heck is an *atm L*? It is actually a fairly simply thing to convert from units of *atm L*

to J by using the **ideal gas law constant**.

$$w = -(11.2 \text{ atm L}) \left(\frac{8.314 \frac{\text{J}}{\text{mol K}}}{0.08206 \frac{\text{atm L}}{\text{mol K}}} \right) = -1130 \text{ J}$$

Note that the negative sign indicated that the system is expending energy by doing work on the surroundings. (This concept will be vital in the Chapter 3!)

Now for the reversible pathway. The work done by the system can be calculated for this change using

$$w = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

$$w = -(1.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{mol K}} \right) (273 \text{ K}) \ln \left(\frac{22.4 \text{ L}}{11.2 \text{ L}} \right) = -1570 \text{ J}$$

Notes: First off, *notice how the value for the gas law constant, R, was chosen in order to match the units required in the problem.* (Read and recite that previous sentence to yourself a few times. The incorrect choice of the value of R is one of the most common errors made by students in physical chemistry! By learning how the units will dictate your choice of R, you will save yourself a considerable number of headaches as you learn physical chemistry!) Second, You may note that the magnitude of work done by the system in the reversible expansion is larger than that of the irreversible expansion. This will always be the case!

References

- Biography.com. (n.d.). *Anders Celcius*. (A&E Television Networks) Retrieved March 10, 2016, from Biography.com: <http://www.biography.com/people/anders-celsius-9242754>
- BIPM. (n.d.). *International Committee for Weights and Measures (CIPM)*. Retrieved March 10, 2016, from BIPM: Bureau International des Poids et Mesures: <http://www.bipm.org/en/committees/cipm/>
- energy.senate.gov. (2004, April 26). *Testimony of R. E. Smalley to the Senate Committee on Energy and Natural Resources; Hearing on sustainable , low emission, elect.* Retrieved March 10, 2016, from Energy Bulletin: <http://www2.energybulletin.net/node/249>
- Evangelista Torricelli*. (n.d.). Retrieved March 3, 2016, from Famous Scientists: <http://www.famousscientists.org/evangelista-torricelli/>
- Gabriel Fahrenheit Biography*. (2016). Retrieved March 10, 2016, from Encyclopedia of World Biography: <http://www.notablebiographies.com/Du-Fi/Fahrenheit-Gabriel.html>

Kelvin, Lord William Thomson (1824-1907) . (2007). (Wolfram Research) Retrieved March 10, 2016, from scienceworld.wolfram.com:

<http://scienceworld.wolfram.com/biography/Kelvin.html>

Mangum, B. W., & Furukawa, G. T. (1990). *Guidelines for Realizing the International Practical Temperature Scale of 1990 (ITS-90), NIST Technical Note 1265*. Gaithersberg, MD: National Institutes of Standards and Technology.

Strouse, G. F. (2008, January). Standard Platinum Resistance Thermometer Calibrations from the Ar TP to the Ag FP. *National Institute of Standards and Technology Special Publication 250-81*.

Vocabulary and Concepts

calorie (cal)	7	limiting ideal behavior	11
Calorie (Cal).....	7	open system.....	1
closed system	1	platinum resistance thermometer	6
energy.....	7	potential energy.....	7
equation of state	2	pressure	3
extensive	2	reversible expansion.....	11
heterogeneous	1	specific heat	7
homogeneous	1	state variables.....	2
Ideal Gas Law	11	surroundings.....	1
ideal gas law constant	12	system	1
intensive	2	temperature	4, 6
isolated system.....	1	universe	1
joule.....	7	work	9
kinetic energy.....	7		

Learning Objectives

Upon mastering the material covered in this chapter, one should be able to do the following:

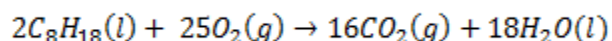
1. Write down expressions from which work of motion and of expansion can be calculated.
2. Express the “Zeroth Law of Thermodynamics.
3. Convert between temperatures on several scales that are commonly used.
4. Define boundaries that differentiate between a system and its surroundings.
5. Perform calculations involving Specific Heat and understand how the specific heat governs temperature changes for the flow of a given amount of energy.

Problems

1. Convert the temperatures indicated to complete the following table

°F	°C	K
	25	
98.6		
		373.15
	-40	
32		

2. Make a graph representing the potential energy of a harmonic oscillator as a function of displacement from equilibrium. On the same graph, include a function describing the kinetic energy as a function of displacement from equilibrium as well as the total energy of the system.
3. Calculate the work required to move a 3.2 kg mass 10.0 m against a resistive force of 9.80 N.
4. Calculate the work needed for a 22.4 L sample of gas to expand to 44.8 L against a constant external pressure of 0.500 atm.
5. If the internal and external pressure of an expanding gas are equal at all points along the entire expansion pathway, the expansion is called “reversible.” Calculate the work of a reversible expansion for 1.00 mol of an ideal gas expanding from 22.4 L at 273 K to a final volume of 44.8 L.
6. The reaction of combustion of the gasoline (assuming it is composed of n-octane only) is given by the following chemical equation:



From the following table, calculate the total amount of energy available to drive a 1500 kg car by burning 40.0 L of gasoline, assuming 25% efficiency of converting the chemical energy in the fuel into mechanical (kinetic) energy of the car. The density of n-octane is 703 kg/m³.

Compound	ΔH_f (kJ/mol)	MW (g/mol)
C ₈ H ₁₈ (l)	-208.27	114.2285
O ₂ (g)	0	31.9988
CO ₂ (g)	-393.475	44.0095
H ₂ O(l)	-285.828	18.01528