

An Introduction to Chemical Thermodynamics

Part 1 — Matter, Energy and the First Law

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ABSTRACT

This is the first in a series of articles presenting an introductory outline of chemical thermodynamics and chemical kinetics, with emphasis on those aspects of particular relevance to pyrotechnics. A brief comment on the molecular theory of matter is followed by a discussion of basic mechanics to introduce the concepts of work and energy. The non-conservation of mechanical energy leads to the idea of heat as a form of energy, and to the Law of Conservation of Energy. The concepts of temperature and thermal equilibrium are then introduced. An introduction to thermodynamic systems, thermodynamic states and state functions is presented. The first Law of Thermodynamics is introduced as a statement of the Law of Conservation of Energy in terms of changes in internal energy, heat and work. The enthalpy is shown to be a useful thermodynamic state function; the enthalpy change in a process corresponds to the heat transferred between a system and its surroundings at constant pressure. Calculations of the heat transferred in chemical reactions are demonstrated. A Table of standard enthalpies of formation of a range of pyrotechnically interesting materials is included for use in such calculations.

Keywords: thermodynamics, thermochemistry, energy, heat, flash powder

Introduction

Pyrotechnic devices use the energy released by chemical reactions to produce a variety of effects including heat, light, sound and motion. The relationship between chemical change and energy is of central importance to a scientific approach to pyrotechnics. The branch of science

that deals with this relationship is *chemical thermodynamics*. Thermodynamics can predict whether or not a chemical reaction is possible, and how much energy would be released or absorbed by that reaction. It cannot, however, predict how fast a reaction will be. That is the concern of *chemical kinetics*. The energy involved in chemical reactions and the speed of those reactions are both of obvious interest to the pyrotechnist. This series of articles will give an introduction to chemical thermodynamics and chemical kinetics, with an emphasis on those aspects of relevance to pyrotechnics.

The following sections will often contain mathematics. To a newcomer to science, it can be rather intimidating to see lines of mathematical symbols appearing in the middle of a discussion about some aspect of the physical world. It is by no means obvious how these symbols can have anything to do with what happens in the world outside. Some writers add to the confusion by claiming that the behavior of the real world is in some mysterious way “governed” by mathematics. What really happens is this: Scientists take some aspect of the real world and treat it *as if* it were one of the abstract objects dealt with by mathematics. You do this, perhaps without realizing it, all the time. Suppose you were packing eggs, and you packed twelve eggs to a box, and twelve boxes per crate, and someone asked you how many eggs you had packed. You would count the crates and multiply 12 to get the number of boxes and multiply that number by 12 to get the number of eggs. You would treat the eggs, boxes and crates as if they were *numbers*, obeying the rules of arithmetic. This is a very simple example of a *mathematical model*, whereby a real situation is converted to a problem in mathematics. The reason for making mathematical models is that mathematics provides a very powerful set of procedures for reasoning in a

completely logical and consistent way. If the model is well chosen, the mathematical argument can reveal all sorts of relationships between aspects of the real world. If the results of the mathematical reasoning are consistent with what is observed, it is evidence that the mathematical model was indeed well chosen. Instead of saying that the behavior of the physical world is “governed” by mathematics, we should say that aspects of it are *described* or *modeled* by mathematics.

The mathematics in this article is set out in more detail than is usual, in an effort to avoid the frustration that arises when a reader cannot follow a step that might be obvious to the mathematically-minded.

Chemical Thermodynamics

Chemical thermodynamics can provide an understanding of what drives chemical change. It provides ways to calculate whether a particular reaction is possible and what energy changes would be associated with that reaction. Calculations, using tables of thermodynamic data, can reveal the maximum possible amount of energy that could be provided by a particular reaction, such as that between potassium nitrate, charcoal and sulfur in Black Powder. A calculated value for the energy released in a pyrotechnic reaction can then be used to estimate the maximum possible temperature that could be reached. Such information can be useful when designing compositions for producing colored flames, for example. Thermodynamic calculations can provide useful information about the composition of chemical systems at equilibrium that would be difficult, or impossible, to obtain by experimental measurement. Such information is useful in calculations for the design of efficient rocket motors.

Thermodynamics originated from efforts to understand the limitations of steam engines. Its application to chemistry happened at about the same time that the molecular theory of matter was being developed. Thermodynamics makes no assumptions whatsoever about the structure of matter. It is much easier, however, to understand the application of thermodynamics to

chemistry if the behavior of molecules is brought into the picture.

A Preamble about Matter

Since chemical thermodynamics is concerned with matter and energy, it is appropriate first to review some relevant ideas about matter. The most obvious characteristic of matter is its complexity. Stars, planets, plants, rocks, people, cities – all are aggregates of matter in varying degrees of complexity. The task of understanding such complexity might seem impossible. Chemistry approaches the understanding of matter by focusing attention on the forms with the least complexity. Over the past few centuries, chemists have subjected matter to various processes of chemical analysis, reducing structures and objects to materials, and then attempting to reduce each material to its simplest constituents. This led to the recognition of a relatively small number of **chemical elements**, materials that could not be decomposed into simpler substances by chemical analysis. The next level of complexity is the **chemical compound**. Chemical compounds are substances made up of chemical elements, in *constant proportions by mass*. Elements and compounds, because they are of constant chemical composition, are called **pure substances**. Compounds are formed from their elements (either directly or indirectly by way of intermediate compounds) by **chemical reactions**. During some chemical reactions, **energy** is released. In others, it is absorbed from the surroundings by the reacting materials.

The Molecular Structure of Matter

Probably the most important idea in physical science is the notion that matter is made up of very small particles, called **molecules**. Each pure substance consists of molecules of the same kind. Molecules can be broken down into smaller particles, called **atoms**. The molecules of each of the chemical elements are made up of atoms having the same, unique set of chemical properties. They may vary in mass (atoms of the same chemical type but having different masses are called **isotopes**) but their chemical properties are essentially identical. The mole-

cules of elements may consist of single atoms (helium, neon, argon and gaseous mercury are examples), or of two or more atoms bound together. Examples include oxygen (O_2 , a pair of oxygen atoms), white phosphorus (P_4 , a tetrahedron of phosphorus atoms) and sulfur (S_8 , a ring of eight sulfur atoms). The word “atom” means “indivisible”, and at one time it was thought that the atom represented the limit to the breaking down of matter. These days, it is known that atoms consist of an extremely small, but massive, central **nucleus** surrounded by a rather complex outer structure of **electrons**. Chemical reactions occur when the outer electrons of atoms rearrange themselves. These rearrangements can result in atoms of various sorts becoming linked together by new electronic structures, forming molecules. Only the outermost electrons are involved the rearrangements that take place in chemical reactions. An arrangement of electrons that links two atoms together is referred to as a **chemical bond**.

The simplest type of electronic rearrangement to imagine is the loss of a single electron from an atom. The electron-deficient atom left after this process is called a positive **ion**. Metals, such as sodium, iron and gold, are made up of positive ions, stacked in regular patterns, surrounded by a “sea” of loose electrons that can move around freely, provided they do not move too far from the ions. These mobile electrons are responsible for the high electrical conductivity of metals and for their characteristic metallic luster. Other atoms, such as those of non-metallic elements like oxygen and chlorine, can gain electrons and form negative ions. Compounds such as magnesium oxide (MgO) and sodium chloride ($NaCl$) consist of positive metal ions and negative non-metal ions stacked in regular patterns. These compounds are examples of **ionic compounds**. In substances such as elemental sulfur (S_8) and oxygen (O_2), and compounds such as water (H_2O) and alcohol (C_2H_5OH) and also in ions such as the ammonium ion (NH_4^+) and the nitrate ion (NO_3^-), the atoms are linked by pairs of electrons shared between the atoms. These shared pairs of electrons are called **covalent bonds**.

Molecular Structure of the States of Matter

Most pure substances can occur in three physical states: solid, liquid and gas. The three physical states differ in the way in which the molecules are arranged in space. Molecules in every state of matter are in constant motion. In a solid, molecules are close together and move mainly by vibrating about their rest positions. In a gas, molecules are relatively far apart and move at random through the entire volume available to be occupied by the gas. In a liquid the molecules can move freely, but tend to remain close to each other.

A Digression into Mechanics

Already in this discussion several *mechanical* concepts have been mentioned without definition or explanation. These concepts included motion, mass and energy. While these ideas might already be quite familiar, it is useful to review them. This requires a brief look at the classical Laws of Motion. It will be assumed that the ideas of space, distance and time can be taken for granted. The aim is to review the rules that describe how objects move; that is, how their position in space changes with time.

Displacement, Speed and Velocity

If you see an object at one place, and some time later see it somewhere else, the object has undergone a **displacement**. Displacement is measured in units of length or distance, and in scientific work the unit of length is the **meter (m)**. By timing the object as it moves from one place to another, you can work out how far it travels in a unit of time, such as one second. That gives its **average speed** in **meters per second (ms^{-1})**. If the speed is the same from one instant to the next, and if the object is moving in a straight line, the object is travelling at constant **velocity**. Velocity has the same units as speed (meters per second), but speed is only one aspect of velocity. The other aspect is direction. Left to its self, an object will maintain its velocity. It will keep moving with the same speed, in the same direction, forever. This might

seem an absurd statement, because everyday observation shows that moving objects usually stop moving unless something is done to keep them in motion. The point is that the objects in everyday life are not left to themselves, but are always interacting with something else. Another way of looking at it is that a change in the velocity of an object requires an explanation, but a constant velocity does not.

Acceleration, Force, Newton's First Law

If the velocity of an object changes, either in speed or direction, the object has undergone **acceleration**. The units of acceleration are **meters per second per second (ms^{-2})**. In ordinary conversation, the term "acceleration" means an increase in speed. In physics, acceleration means any change in velocity. This can be an increase or decrease in the speed of an object, or a change in its direction of motion. Acceleration, being a change in velocity, requires an explanation. By definition, acceleration is the result of a **force**. In everyday language the word "force" is associated with pushing, shoving, compelling, making something happen. In physics, force is that which causes acceleration. All the discussion of motion so far can be summarized in a simple statement: "An object will remain at rest, or in uniform motion in a straight line, unless acted on by a force". This is **Galileo's Law of Inertia, or Newton's First Law of Motion**.

Mass, Newton's Second Law of Motion

It is obvious from everyday experience that a push or shove that produces a certain change in the motion of one object will not necessarily have the same effect on a different object. By definition, the ratio of the force on an object to the resulting acceleration is the **mass** of the object.

$$\begin{aligned} \text{force} \div \text{acceleration} &= \text{mass} && \text{or} \\ \text{force} &= \text{mass} \times \text{acceleration.} \end{aligned}$$

This relationship is **Newton's Second Law of Motion**.

It is known from experiment that in the absence of air, objects near the surface of the earth fall towards the ground at the same speed. That means that they all experience the same acceleration, known as the **gravitational acceleration**, g meters per second per second. The force that acts on bodies near the earth's surface is therefore $m \times g$, where m is the mass (units not yet defined). The mass of an object can most easily be described by comparing the gravitational force acting on it to that acting on some reference object. The comparison is readily carried out using a **balance**.

For historical reasons, the reference object for mass is a piece of platinum-iridium alloy called the standard **kilogram**.

In scientific work, mass is measured in **kilograms (kg)**. Force is measured in terms of the acceleration that it produces in an object of unit mass. A force that produces an acceleration of one meter per second per second when acting on an object having a mass of 1 kilogram is called a **newton (N)**.

Mass and Weight

It is worth recalling that mass is a fundamental property of an object and does not vary from place to place. In contrast, the **weight** of an object is the force exerted by the gravitational interaction between the object and the earth (or the moon, if the object happens to be on the moon). Because the gravitational acceleration near the earth's surface is constant, it is convenient to describe weight in units of mass, when really we should use units of force. If the day ever comes when people regularly travel between the earth and the moon, the distinction between mass and weight will be common knowledge. Spring balances and electronic balances would need to be re-calibrated for use on the moon. A beam balance, of course, would be accurate in either location.

Pressure

Having introduced the concept of force, it is appropriate to mention **pressure**, which is simply the force applied per unit area of a surface. Pressure is extremely important in discussing the behavior of gases. It is measured in **pascals (Pa)**. A pressure of one pascal corresponds to a force of one newton per square meter. Living as we do at the bottom of a vast ocean of air, we are subjected to a relatively constant pressure of around 100 kilopascals. A pressure of 101.33 kilopascals is *defined* as one **atmosphere**, and is often used as a unit of pressure in thermodynamics. To avoid confusion, however, the pascal will be used as the unit of pressure in this discussion. It should be mentioned, too, that pressure gauges, even though they might be calibrated in pascals, often take their zero point as 1 atmosphere. Such gauges actually read the difference between the measured pressure and one atmosphere, the so-called gauge pressure. In thermodynamic calculations, pressure must be measured from a true zero point of zero newtons per square meter.

Newton's Third Law of Motion

Much of the discussion so far has really been giving definitions. Now it is time to introduce some results of experiments and observations. One important result is that acceleration always involves the interaction of at least two objects. There is a general rule that summarizes the results of many experiments and observations. "If two isolated objects interact in a manner that results in their acceleration, the accelerations of the two objects will be in opposite directions". The objects are described as "isolated" to indicate that the only force acting on them is the one involved in the interaction. If the two interacting objects are identical, the accelerations will not only be in opposite directions but of the same magnitude. If the two interacting objects are different, their accelerations will be inversely proportional to their masses. In other words, when two objects interact, the force acting on one object will be of the same magnitude, but in the opposite direction, as the force acting on the other. This is **Newton's Third Law of Motion**. The traditional statement of

that Law is "For every action, there is an equal but opposite reaction".

Work

When a force acts on an object and accelerates it, the force is said to have done **work**. The amount of work is obtained by multiplying the force by the distance over which it acts. The units of work are **newton meters (Nm)**. A good example of work is the lifting of a weight. To raise a weight of mass m kilograms, you must apply a force of $(m \times g)$ newtons to overcome the gravitational force of mg newtons acting on the object. If you lift the object h meters, you will have exerted a force of mg newtons over a distance of h meters. You will have done mgh newton meters of work.

When you lift a weight,
work done
= force $\times$ distance
= mass $\times$ acceleration $\times$ distance
= m kilograms $\times g$ meters per second
per second $\times h$ meters
= mgh newton meters.

Energy

Energy is one of the most important concepts in physical science. Perhaps because of its central role in scientific explanation, it is also one of the most difficult concepts to define. Fortunately, the ultimate nature of energy is irrelevant for the purposes of this discussion. In mechanics, energy can be defined as the *capacity to do work*, and it is expressed in the same units as work; the amount of energy required to do one newton meter of work is the **joule (J)**. Conversely, the joule can be used as a unit of work, exactly equivalent to the newton meter.

This definition of energy as the capacity to do work is not entirely satisfactory, because in thermodynamics situations arise where energy is not available to do work. It could be argued that to speak of a "capacity to do work" that is not available to do work is not particularly meaningful. As will be seen, however, this idea

of “unavailable energy” is of fundamental importance in thermodynamics and is easy to understand from the molecular perspective.

For the moment, it is necessary only to review energy in simple mechanical systems.

Potential Energy

Imagine a small heavy object, of mass m_1 kilograms, at rest on the floor, attached to a string threaded through a pulley fixed to the ceiling. You will also need to imagine that the pulley is absolutely perfect, offering no resistance whatsoever to the motion of the string. If you pull downwards on the other end of the string, the string will eventually become tight and will exert a force on the object. If you increase the force until it exceeds the weight of the object (m_1g newtons, where g is the gravitational acceleration), the object will be accelerated and will rise toward the ceiling. If you keep pulling the string until the object is a distance of h meters above the ground, you will have exerted a force of m_1g newtons over a distance of h meters and you will have done m_1gh newton meters (i.e., joules) of work in lifting the object.

Suppose now that you tie your end of the string to another object, and release it. The string will exert an upward force on the second object equal to the weight m_1g newtons of the first object. The earth’s gravity will exert a downward force m_2g newtons on the second object. If m_2 is less than m_1 , then the second object will be subjected to a net upward force of $(m_1g - m_2g)$ newtons. It will accelerate upwards. Meanwhile, the first object, experiencing a net downward force of $(m_1g - m_2g)$ newtons, will accelerate towards the floor. It will fall a distance of h meters before it crashes into the floor. The second object, having been accelerated to a certain upward velocity, will now experience only the downward force of gravity m_2g . If it has reached a sufficiently high upward velocity, it may hit the ceiling or reach the end of the string, but ultimately it will come to rest hanging h meters above the floor. The overall effect has been to lift a weight of mass m_2 kilograms to a distance h meters above the floor. The net work that has been done is m_2gh new-

ton meters (joules). Notice that the work done in lifting the second object (m_2gh newton meters) is *less* than the work done in raising the first object (m_1gh newton meters) because m_2 was less than m_1 .

Suppose now that the mass m_2 of the second object is only a few milligrams less than that of the first object. The second object will experience a very small upward force, and it will accelerate upwards very slowly. At the same time the first object will accelerate downwards very slowly until it lands gently on the floor. The second object, having reached only a very small velocity, will very quickly come to rest at a height h meters above the floor. The net work that has been done is again m_2gh newton meters. Notice that the work done in lifting the second object (m_2gh newton meters) is again less than the work done in raising the first object (m_1gh newton meters) because m_2 was less than m_1 .

Carrying this line of argument to its limit, as the mass of the second object approaches that of the first, the net force acting on each object will approach zero. When the second object is only a tiny amount less massive than the first, the second object will take an extremely long time to rise to its ultimate height of h meters above the floor and will overshoot its rest position by only a minute distance. The work done will be m_2gh newton meters, which in this case is very close to the work m_1gh newton meters that was done when the first object was lifted h meters above the ground.

Ultimately, a weight of mass m kilograms hanging h meters above the floor has the capacity to do mgh newton meters of work in falling to the floor. It therefore possesses a **potential energy** of mgh joules. In this example, the object possesses potential energy because of its *position* in the gravitational field of the earth. Potential energy is also possessed by objects such as compressed springs, to which a force has been applied over a distance to distort the shape of the object.

Equilibrium

When the masses of two objects hanging from a string on either side of a pulley are exactly equal, the upward and downward forces acting on each object are exactly balanced. The forces are said to be in **equilibrium**. Once a system is in equilibrium, there are no net forces available to do work. *A system in equilibrium can do no work. The available energy is zero.*

When the masses of the two objects are unequal, the system will come to rest with one weight on the floor and the other hanging in the air. Again, the forces acting on each weight are exactly balanced, the available energy is zero, and the system can do no work. The system has come to equilibrium, but the equilibrium is clearly very different from that achieved when the two weights were equal. In that case, a tiny change in the mass of either weight would upset the equilibrium. This leads to the idea of a *reversible* process. A process is **reversible** if its direction can be reversed by an infinitesimally small change.

Equilibrium and Reversibility

The thought experiment with the hanging weights provides a useful mechanical example of a reversible process.

Imagine that the two weights are of exactly equal mass, and that they are hanging at equilibrium on either side of a perfect pulley that offers absolutely no resistance to motion. Now, imagine that the mass of one object be increased by a very small amount. Perhaps a very tiny speck of dust falls on it. The forces on the two weights are no longer equal. The heavier weight will start to accelerate downward, with an extremely small acceleration. Now suppose that the speck of dust is blown off the weight with a gentle puff of air that imparts no vertical acceleration to either weight. The net forces acting on each object will again be zero, and acceleration will cease. According to Newton's First Law, each body will keep moving upward or downward at the very tiny velocity that it had acquired after its very small acceleration. After an extremely long time, the system will come to equilibrium with one object on the

floor and the other object h meters above the ground. At any instant, the addition of a tiny mass to the rising object would cause it to experience a net downward force so the direction of motion would reverse. Such a process, that can be set into reverse by an infinitesimally small change, is an example of a **reversible** process.

Notice that when this reversible process eventually comes to equilibrium, the system will have done the maximum possible amount of work.

In thermodynamics, a process carried out reversibly will always perform the maximum possible amount of work, but will take an infinitely long time to do so. All natural processes take place in a finite amount of time, and are thus irreversible. None the less, the concept of a reversible process is important in thermodynamics because of the link between reversibility and maximum work. This will be discussed further in the section dealing with the Second Law of Thermodynamics.

Kinetic Energy

Kinetic energy is the energy possessed by a body because of its *state of motion*.

A thought experiment can show how a moving body can do work in being brought to rest. Imagine a body of mass m_1 kilograms moving with a uniform velocity of v meters per second over the surface of an ideal, friction-free table. At the edge of the table is a perfect pulley, over which passes a string attached to a small object of mass m_2 kilograms sitting on the floor. The moving object is travelling away from the pulley. At a certain point the string is suddenly attached to the moving object. It pulls tight, and lifts the second object off the ground. The string exerts a force on the moving object, causing it to accelerate in the opposite direction to its direction of motion. Eventually the moving object comes momentarily to a stop after having moved through a distance of h meters. The small object has been raised a height of h meters above the ground, so the moving object has done m_2gh newton meters of work.

In bringing the moving object to a halt, the force m_2g newtons has been applied over a dis-

tance of h meters. This force was applied to an object of mass m_1 kilograms and accelerated it from an initial velocity of v meters per second to a final velocity of 0 meters per second.

The distance h over which the force acted is given by the average velocity v_{av} multiplied by the time t :

$$h = v_{av} t$$

The average velocity v_{av} is half the sum of the initial velocity (v) and the final velocity (0 meters per second), so

$$\begin{aligned} h &= \frac{1}{2} (v+0)t \\ &= \frac{1}{2} vt \end{aligned}$$

The final velocity (0 meters per second) is given by the initial velocity (v) plus the acceleration $-a$ multiplied by the time t . Notice that the acceleration is given a negative sign, because it is acting in the opposite direction to the initial velocity v .

$$0 = v - a t,$$

$$\text{so } t = v \div a$$

$$\begin{aligned} \text{and } h &= \frac{1}{2} v t \\ &= \frac{1}{2} v (v \div a) \\ &= \frac{1}{2} v^2 \div a \end{aligned}$$

But

$$\begin{aligned} \text{force} &= \text{mass} \times \text{acceleration} \\ &= m_1 a \end{aligned}$$

$$\begin{aligned} \text{and work} &= \text{force} \times \text{distance} \\ &= m_1 a h \\ &= m_1 a (\frac{1}{2} v^2 \div a) \\ &= \frac{1}{2} m_1 v^2 \text{ newton meters} \end{aligned}$$

The work done by a body of mass m_1 kg being to rest from an initial velocity of v meters per second is $\frac{1}{2} m_1 v^2$ newton meters. A body of mass m kg moving with a velocity v meters per second has a kinetic energy of $\frac{1}{2} m v^2$ joules.

Conservation of Energy

In the thought experiment just described, the moving body on the table top was brought momentarily to rest, while the small body sus-

pended from the pulley was raised a distance h meters above the floor. The potential energy of the suspended body became $m_2 g h$ joules, while the kinetic energy of the body on the table became 0 joules. Obviously this situation can only last for an instant. The stationary body, under the influence of the force $m_2 g$ in the string, will begin to accelerate in the opposite direction as the suspended object falls towards the floor. The falling object will end up on the floor, having fallen through a distance h meters, and its potential energy will again be zero. By reversing the arguments in the previous section, it is easy to show that the object on the table will end up with a velocity of v meters per second, in the opposite direction to that of its initial velocity. Its kinetic energy is again $\frac{1}{2} m_1 v^2$ joules. Energy has been converted from kinetic energy to potential energy and back again.

In some mechanical devices, conversion from potential to kinetic energy and back again can (at least in theory) proceed indefinitely. An example is the pendulum. At the top of its swing, the pendulum is momentarily at rest, so its kinetic energy is zero and its potential energy is at a maximum. At the bottom of its swing, the pendulum is moving at its maximum velocity, its kinetic energy is at a maximum and its potential energy is at a minimum. As the pendulum swings to the top at the other side, the kinetic energy decreases to zero and the potential energy rises back to the maximum value. In principle, if there were no losses of energy, this process could repeat indefinitely. Such a system is called a **conservative system**, because the total mechanical energy is conserved. A real pendulum does not keep swinging indefinitely but eventually comes to a halt. This indicates that the transformation of potential energy to kinetic energy and back again is not 100% efficient. What happens to the lost energy? Part of it goes to stir up the air through which the pendulum moves, and some is used in moving the parts of the suspension device past each other (fibers in a string, for example, move against each other as the pendulum swings). Ultimately, this energy is converted to **heat**. The air and the rope are a little bit warmer at the end of the process than they were at the beginning.

In the last century the British scientist James P. Joule carried out careful experiments that showed that mechanical work could be converted entirely into heat. Before then, heat and work were measured in different units. Now, (at least in scientific work), the same units are used for both.

The conversion of mechanical work into heat is important in pyrotechnics. Devices such as the friction match, the party popper, the pull-wire igniter and the percussion cap all rely on the conversion of mechanical work into heat that subsequently ignites a pyrotechnic composition. Unintended initiation of pyrotechnic mixtures during manufacturing and processing can result from the mechanical work associated with friction, shock or impact being transformed into heat. The heat produced in such processes is highly localized and can be very effective in initiating certain sensitive mixtures.

It is a fundamental postulate of thermodynamics that when heat is taken into account, the total amount of energy in the universe is constant. This is the **Law of Conservation of Energy**.

Heat as a Form of Energy

As outlined in the preceding sections, energy is transferred between mechanical systems as work. The Law of Conservation of Energy is based on the recognition that energy can also be transferred as heat. There are several other processes that can transfer energy. Electric currents and various types of radiation are two examples. In this discussion of chemical thermodynamics, however, it will be sufficient to consider only heat and work.

Classical chemical thermodynamics made no reference to the molecular structure of matter. It is, however, very useful to interpret thermodynamic properties by relating them to the behavior of molecules. Heat can be thought of as the energy associated with the random motion of molecules. This makes the connection between mechanical work and heat much easier to understand. In Joule's experiments, water stirred by mechanically driven paddles became hotter. From a molecular perspective one can imagine the uniform motion of the molecules in the paddles moving nearby water molecules, ini-

tially in a rather uniform way. The motion of the water molecules would quickly become randomized as one molecule collided with another, so ultimately the effect of the stirring paddles would be to increase the random motion of the molecules—in other words, to heat the water. Each molecule has a certain mass m , and at any instant of time has a certain velocity v . At that instant the molecule has a kinetic energy $\frac{1}{2}mv^2$. The average kinetic energy of the molecules is directly related to the **temperature** of the material.

As well as energy being transferred between molecules by direct mechanical impact, it can also be transferred by **electromagnetic radiation**. A proper discussion of this would take up considerable space. It is sufficient to note that this radiation is familiar to us as **light** and **radiant heat** (or **infra-red** radiation), the only fundamental difference between these being the energy with which the radiation is associated. The energy of electromagnetic radiation can be thought of as being packaged into little particles called **photons**. The energy of a photon is related to the wave properties of the radiation through **Planck's relationship**:

$$E = h\nu = hc \div \lambda,$$

where ν is the **frequency** in cycles per second (units: **inverse seconds**, s^{-1} , often called **Hertz**, **Hz**), c the velocity of light (2.9979×10^8 meter per second in vacuum) and λ the wavelength in meters. The constant of proportionality h is **Planck's Constant** (6.6262×10^{-34} joule seconds). Radiation emitted by a molecule travels through space and can be absorbed by another, resulting in a transfer of energy from one molecule to another without any direct contact between them.

Temperature

The idea of temperature is familiar from everyday life, as an indicator of ‘hotness’ or ‘coldness’. Historically, people have chosen some property of matter that varies with ‘hotness’ or ‘coldness’ and used it as the basis of a system for measuring temperature. Such a property is the volume of a fixed mass of gas or liquid. A fixed mass of gas or liquid, arranged in such a way that changes in volume can be readily measured, can be used as a temperature measuring instrument or **thermometer**. The thermometer is calibrated by placing it in environments where the temperature is reproducible. One such environment is a mixture of pure water and ice. The temperature of this mixture has been assigned the value of 0 degrees Celsius (°C). The temperature of pure water boiling at atmospheric pressure has been assigned the value of 100 degrees Celsius. The liquid or gas in the thermometer has a certain volume in the melting ice, and another, larger volume in the boiling water. This range of volumes is divided into 100 equal parts, and a change of one of these units of volume is defined to correspond to a change in temperature of 1 degree Celsius. It is found experimentally for gases that one degree Celsius corresponds to a change of $1/273$ of the volume at 0 degrees Celsius. This suggests that if the temperature were reduced to -273 degrees Celsius, the volume of the gas would shrink to zero. While this is only a “thought experiment”, because all real gases turn into liquids before the temperature reaches -273 degrees Celsius, it suggests the very important idea of an absolute zero of temperature at -273 degrees Celsius. More accurate estimates give the value as -273.15 degrees Celsius. The temperature scale used in scientific work, the kelvin (or absolute) scale, uses the same degrees as the Celsius scale but starts at absolute zero. The kelvin temperature is obtained by adding 273.15 to the Celsius temperature. The unit of temperature on the absolute scale is the **kelvin (K)**.

The Zeroth Law of Thermodynamics

Temperature could be defined as the property that is measured by thermometers. This is expressed in a formal way as follows:

Two bodies that are in thermal equilibrium with a third body are in thermal equilibrium with each other. They share a common property called “*temperature*”.

This statement is the **Zeroth Law of Thermodynamics**.

The ‘third body’ referred to in the Zeroth Law is the thermometer. Being in thermal equilibrium means that the transfer of heat from the body to the thermometer is exactly balanced by the transfer of heat from the thermometer to the body. This situation is easily recognized, because the reading of the thermometer is then constant.

Molecular Interpretation of Temperature

As will be shown later, temperature is a measure of the **average kinetic energy** associated with **random motion of the molecules**.

Heat Capacity

It is found experimentally that different amounts of energy are required to change the temperature of the same mass of different substances by the same amount. The **heat capacity** of a substance is the quantity of energy required to raise the temperature of a specified amount of the substance by 1 kelvin. In thermodynamics, particularly when dealing with gases, it is necessary to distinguish between C_v , the heat capacity at constant volume, and C_p , the heat capacity at constant pressure.

Amount of a Substance

In chemical thermodynamics the **amount of a substance** is specified in **moles (mol)**. One mole of any substance is the molecular weight of that substance expressed in grams. The molecular weight is simply the sum of the atomic

weights of all the atoms in one molecule of the substance. The atomic weight is the ratio of the mass of that atom to the mass of an atom of the most common type of carbon atom, which has been assigned a mass of exactly 12 **atomic mass units** or **daltons**. One mole of a substance contains 6.022×10^{23} molecules. This enormous number

602,200,000,000,000,000,000,000
molecules per mole is called **Avogadro's Number**.

Thermodynamic Systems

Like all sciences, thermodynamics attempts to gain some understanding of the incredibly complex world by focusing attention on small, simple aspects of it. In any thermodynamics experiment, whether done in the laboratory or in the imagination, the objects that are being studied are very carefully defined and are called the **system**. Everything else in the world is called the **surroundings**. The system may interact with the surroundings, or it may be kept separate from the surroundings so that there is no interchange of matter or energy between it and the surroundings. The system is then said to be **isolated**. A system that cannot exchange matter with its surroundings, but may exchange energy, is called a **closed** system. A system that can exchange both matter and energy with its surroundings is called an **open** system. The combination of system and surroundings is called the **universe**.

Thermodynamic States and State Functions

Having decided what the system of interest is, the next step is to describe it as completely, yet as concisely, as possible. The aim is that anyone given the description should be able to reproduce the system in all its relevant aspects. Thermodynamics does not concern itself with the molecular structure of matter, so the position and energy of all the individual molecules in the system is not relevant. That is just as well. On the molecular level, the world is in a state of constant change. If the position and energy of all the molecules in the system (the **mi-**

croscopic state of the system) could ever be described, the description would be correct only for an instant. It could be reproduced only by pure chance, and then only for an instant.

Thermodynamics deals only with those aspects of a system that can be measured by large-scale devices such as thermometers, measuring rods and pressure gauges. Such properties are called **macroscopic** properties, and it is those properties that are used to describe thermodynamic systems. A complete description of the macroscopic properties of a system is called the **thermodynamic state** of the system. The thermodynamic state can be described by a relatively small number of properties, called **state functions**. State functions are *chosen* so that their values depend only on the thermodynamic state of the system, and not on the path that was taken to reach that state. There are two sorts of state functions: **intensive functions**, such as temperature and pressure, do not depend on the amount of matter in the system. **Extensive functions**, such as mass and volume, depend on the amount of matter (number of moles) present. It is obvious that mass must be an extensive function. One can, however, imagine a system of fixed volume, into which any quantity of gas might be compressed. In such a system volume would not be an extensive function, but a constant. For volume to be an extensive function, the *volume of the system must be variable*. Such systems are often modeled as a cylinder closed with a perfectly sealed, massless piston that offers no resistance to motion.

State functions are always indicated by capital letters, but not all quantities indicated by capital letters are state functions. A quantity indicated by a lower-case letter will not be a state function, and its value may depend on the path that was taken by the system to arrive at its present state.

The algebraic relationship between the state functions is called the **equation of state** of the system. An example is the **equation of state for a perfect (or ideal) gas**. A perfect gas is simply one in which the physical volume of the molecules is negligible in comparison to the volume of the gas, and in which forces between the molecules are negligible. The system to which the equation of state for a perfect gas applies is

a fixed amount of perfect gas in a container of variable volume, such as a cylinder sealed with a perfect, frictionless, massless piston. The container is equipped with a thermometer and a pressure gauge. The volume can be calculated from the position of the piston. The equation of state is

$$PV = nRT$$

P is the pressure in pascals, V is the volume in cubic meters, n is the number of moles of the gas, R is the **universal gas constant** (8.3143 joules per mole per kelvin) and T is the temperature in kelvins.

Each side of this equation can be expressed in units of energy:

The left-hand side is the energy associated with the *mechanical* properties of the system:

$$\begin{aligned} PV &= \text{newtons per meter}^2 \times \text{meter}^3 \\ &= \text{newton meters} = \text{joules} \end{aligned}$$

The right hand side is the energy associated with the *thermal* properties:

$$\begin{aligned} nRT &= \text{number of moles} \times \text{joules per mole} \\ &\quad \text{per kelvin} \times \text{kelvins} \\ &= \text{joules} \end{aligned}$$

The equation of state is simply the Law of Conservation of Energy applied to a perfect gas.

The equation indicates that for a fixed amount (n moles) of gas, there are only *two* properties that need to be specified. For example, if the pressure and the temperature are specified, the volume of the gas is fixed. This is a consequence of the Law of Conservation of Energy, as expressed in the equation of state.

The equation of state can be re-arranged to indicate how the volume varies with the other parameters.

$V = nRT \div P$ indicates that the volume (V) of a fixed amount (n moles) of gas at a constant temperature T is inversely proportional to the pressure P . This relationship was established experimentally in the 17th century and is known as **Boyle's Law**. $V = nRT \div P$ also shows that the volume of a fixed amount (n moles) of gas

at a fixed pressure P is proportional to the absolute temperature T . This relationship, also first established experimentally, is known as **Charles' Law**. Finally, $V = nRT \div P$ shows that a fixed volume of any perfect gas under the same conditions of temperature and pressure contains the same number of moles, and hence the same number of molecules. This was first proposed by Avogadro, and is called **Avogadro's hypothesis**.

A great deal of information about the behavior of gases is thus summarized in the simple equation $PV = nRT$.

Changes in State Functions

If a system undergoes a change from one thermodynamic state to another, the new state will, by definition, be described by a new set of values of the state functions. The values of the state function after the change will depend only on the properties of the new state. They will not be influenced in any way by any properties that the system might have had while it was in the process of undergoing the change. Many thermodynamic calculations deal with changes in state functions. Such changes are always calculated by subtracting the value of the initial state function from that of the final one. For example, for a temperature change from a starting temperature T_1 to a final temperature T_2 the change of temperature ΔT is given by

$$\Delta T = T_2 - T_1.$$

The symbol Δ that indicates "change of" is the capital form of the Greek letter delta. The symbol " ΔT " is read "delta tee".

State Functions and Equilibrium

A system is in equilibrium when the values of the state functions are constant in all parts of the system. In other words, for a system at equilibrium

$$\Delta X = 0$$

where X is *any* state function. This is one definition of thermodynamic equilibrium.

Internal Energy and the First Law of Thermodynamics

So far, three state functions have been introduced. These are the temperature, T , the volume, V , and the pressure, P . All of these can be measured easily. There are other state functions that are not measured directly. Such a state function is the **internal energy** of a system, denoted by the symbol U . This is the sum total of the energy, in whatever form, stored in a system. The total energy will obviously vary according to the amount of substance in the system, so internal energy is an extensive function. The absolute value of the internal energy of a system is not of concern to thermodynamics, but changes in internal energy are of central importance. Suppose a system undergoes a change in internal energy from an initial (unknown) value of U_1 joules to a final value (unknown) value of U_2 joules. Then the change in internal energy, ΔU , is

$$\Delta U = U_2 - U_1$$

This might not seem very useful, since U_2 and U_1 are both unknown. The equation is nothing more than another statement of the law of conservation of energy. The change in internal energy, ΔU , represents the net energy that has come into the system from the surroundings or that the system has lost to the surroundings. For the purposes of this discussion, only two ways of a system exchanging energy with the surroundings are relevant. Energy can be transferred *mechanically*, as **work**, denoted by w . For example, if a gas expands against an external pressure, the gas does work. Energy can also be transferred as **heat**, denoted by q . The change in internal energy can now be written:

$$\Delta U = q - w.$$

This states that the change in internal energy, ΔU , of a system is given by the heat, q , *absorbed by the system* minus the work, w , *done by the system* on its surroundings.

This statement, which is again a statement of the Law of Conservation of Energy, is the **First Law of Thermodynamics**.

Heat or work going *into* the system from the surroundings increases the internal energy of

the system, and heat or work leaving the system *decreases* the internal energy.

The Enthalpy

The four state functions introduced so far are the intensive functions temperature, T , and pressure, P , and the extensive functions volume, V , and internal energy U .

It is convenient to define another state function, called the **enthalpy**, H . This is given by

$$H = U + PV$$

Notice that H has units of energy. Since U , P and V are all state functions, H is necessarily one as well. Notice, too, that U and V are extensive functions, and consequently H is also an extensive function. Since the purpose of state functions is to give the most concise description of a system, it might seem counterproductive to introduce another function that combines three others. Why use five when four would be enough?

The reason will emerge from the following discussion. The change in enthalpy when a system with an original enthalpy H_1 changes to a final enthalpy H_2 is given by

$$\begin{aligned}\Delta H &= H_2 - H_1 \\ &= U_2 + P_2V_2 - (U_1 + P_1V_1) \\ &= U_2 - U_1 + P_2V_2 - P_1V_1 \\ &= \Delta U + \Delta(PV) \\ &= q - w + \Delta(PV)\end{aligned}$$

Chemical reactions are often carried out in systems open to the atmosphere, that is, under conditions of constant pressure. Then,

$$\Delta(PV) = P\Delta V, \text{ and}$$

$$\Delta H = q - w + P\Delta V$$

At constant pressure the work w done by the system on the surroundings is simply the pressure P multiplied by the change in volume, ΔV .

$$w = P\Delta V.$$

Therefore, at constant pressure,

$$\begin{aligned}\Delta H &= q - w + P\Delta V \\ &= q - P\Delta V + P\Delta V \\ &= q\end{aligned}$$

The change in enthalpy is thus a measure of the heat transferred between the system and the surroundings at conditions of constant pressure. This is what makes the enthalpy such a useful function in chemical thermodynamics. If the enthalpy change is positive, the system will absorb heat from the surroundings. An example is ammonium nitrate dissolving in water. Such a process is **endothermic** (heat taken in). If the enthalpy change is negative, the system will release heat into the surroundings. Such a process is **exothermic** (heat given out). An example is sodium hydroxide dissolving in water.

Thermochemistry

To find the heat emitted or absorbed in a chemical reaction at constant pressure, all that is required is the enthalpy change associated with that reaction. Enthalpy changes are very easily calculated from tables of **the standard enthalpy of formation**, ΔH_f° , of various substances (see Table 1 at end of article). The superscript ($^\circ$) indicates that the change in state function is calculated for reactants and products at some standard set of conditions, usually 298.15 K (25 $^\circ$ C) and 1 atmosphere pressure.

Recall that enthalpy is an extensive property, that is, it is proportional to the amount of substance present. Recall, too, that only *changes* in enthalpy are relevant. For convenience, the standard enthalpy of formation of the most stable form of any chemical element at 298.15 K and one atmosphere pressure (101.33 kilopascals) is given the value of 0 joules per mole. The standard enthalpy of formation of any compound that can be formed by direct reaction of the elements is then very easily obtained, at least in principle. Experimental details may well be quite difficult. All that is required is to measure the heat emitted or absorbed when a known amount of the compound is formed from the elements at 1 atmosphere pressure and 298.15 K. Since enthalpy is a state function, the intermediate values of temperature and pressure

during the reaction are irrelevant. As long as the reactants and products end up at 1 atmosphere and 298.15 K, the heat emitted or absorbed will correspond to the change in enthalpy.

Hess's Law of Heat Summation

The fact that the enthalpy change in a chemical reaction does not depend on the path was first stated by Germain H. Hess in 1840, and is often referred to as **Hess's Law**. Its usefulness can be illustrated by the classic example of how it can be used to calculate a quantity that would be impossible to measure experimentally: the standard enthalpy of formation of carbon monoxide.



The **standard enthalpy of formation** of carbon dioxide is easily calculated from the **molar heat of combustion**, the heat released when one mole of carbon is burned in an excess of oxygen:



The same approach is not possible for carbon monoxide, because it is impossible to burn carbon in oxygen to produce only carbon monoxide.

Carbon monoxide can, however, be burned in excess oxygen to produce carbon dioxide:



The combustion of carbon to carbon dioxide can now be *imagined* to take place in two steps:

Step 1:



Step 2:



By addition:



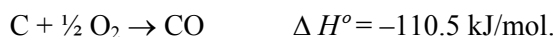
For this reaction $\Delta H^\circ = -393.5 \text{ kJ/mol}$, so

$$(x - 283.0) \text{ kJ/mol} = -393.5 \text{ kJ/mol}$$

$$x = -393.5 \text{ kJ/mol} + 283.0 \text{ kJ/mol}$$

$$= -110.5 \text{ kJ/mol}$$

Thus, for the reaction to form carbon monoxide



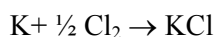
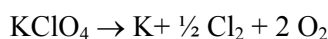
Application to Pyrotechnics

As an example, consider the thermochemistry involved in a *flash powder* consisting of a mixture of powdered aluminium and potassium perchlorate.

Potassium perchlorate decomposes on heating to form potassium chloride and oxygen:



This reaction can be *imagined* to take part in two stages:

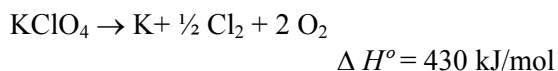


Of course the reaction certainly does not take place by these two steps. The enthalpy of the reaction must, however, equal the sum of the enthalpy changes of these two reactions. The enthalpy changes of these reactions can be obtained from tables of thermochemical data, such as Table 1.

The first reaction is the decomposition of 1 mole of potassium perchlorate into its elements. The enthalpy change is, therefore, *minus* the standard enthalpy of formation of potassium perchlorate, $-(-430 \text{ kJ/mol}) = 430 \text{ kJ/mol}$.

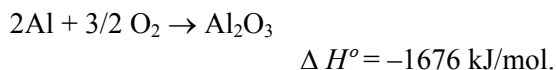
The second reaction is the formation of 1 mole of potassium chloride from its elements, and the enthalpy change is the standard enthalpy of formation of potassium chloride, -437 kJ/mol .

The total enthalpy change for the decomposition of 1 mole of potassium perchlorate is the sum of these two enthalpy changes:



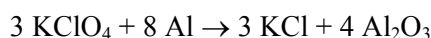
The decomposition of 1 mole of potassium perchlorate releases 7 kJ of heat.

Now consider the combustion of aluminium in oxygen to form 1 mole of aluminium oxide:



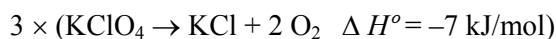
The enthalpy change for this reaction is, of course, the standard enthalpy of formation of aluminium oxide.

The reaction of aluminium with potassium perchlorate in flash powder is

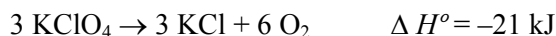


This can be imagined as taking place in two steps:

Step 1: decomposition of 3 moles of potassium perchlorate:

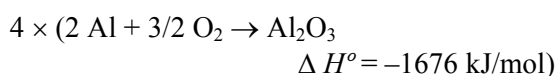


i.e.,

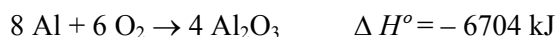


and

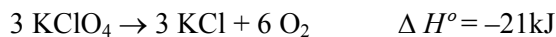
Step 2: Combustion of aluminium in oxygen to form 4 moles of aluminium oxide:



i.e.,



The total enthalpy change for the reaction is the sum of the enthalpy changes for the two steps:



The reaction of 3 moles of potassium perchlorate with 8 moles of aluminium releases 6725 kilojoules of heat.

It is useful to convert the units of measure of the amounts of the chemicals from moles to grams, because pyrotechnic mixtures are not usually specified in moles.

One mole of aluminium weighs 26.98 grams, and one mole of potassium perchlorate weighs 138.55 grams. These values are obtained from

the formula weights of these materials, listed in Table 1.

Three moles of potassium perchlorate weigh

$$3 \times 138.55 \text{ grams} = 415.65 \text{ grams.}$$

Eight moles of aluminium weigh

$$8 \times 26.98 \text{ grams} = 215.84 \text{ grams.}$$

Three moles of potassium perchlorate plus eight moles of aluminium weigh

$$(415.65 + 215.84) \text{ grams} = 631.49 \text{ grams.}$$

This quantity of mixture releases 6725 kilojoules, so the heat released per gram is:

$$6725 \text{ kJ} \div 631.49 \text{ g} = 10.64 \text{ kJ/g}$$

The percentage composition of this mixture is:

Potassium perchlorate:

$$415.65 \text{ grams} \div 631.49 \text{ grams} \times 100\% = 65.8\%$$

Aluminium:

$$215.84 \text{ grams} \div 631.49 \text{ grams} \times 100\% = 34.2\%$$

Lancaster^[1] quotes two mixtures for European style flash composition. One of these (66% potassium perchlorate and 34% aluminium) is almost identical to the mixture just discussed.

Such a mixture, in which the ratio of the components is exactly as required for the balanced chemical reaction, is called a **stoichiometric** mixture.

Lancaster^[1] also lists some flash mixtures that contain sulfur. One of the mixtures he quotes is 67% potassium perchlorate, 17% aluminium and 16% sulfur. It is instructive to calculate the heat output of this composition.

First, the percentage by weight is converted to moles per 100 grams, by dividing the percentage of each component by its formula weight:

Potassium perchlorate:

$$67.00 \div 138.55 = 0.4836 \text{ moles per 100 grams}$$

Aluminium:

$$17.00 \div 26.98 = 0.6301 \text{ moles per 100 grams}$$

Sulfur:

$$16.00 \div 32.06 = 0.4991 \text{ moles per 100 grams.}$$

From the previous discussion, every 8 moles of aluminium require 3 moles of potassium perchlorate. To find the amount of potassium perchlorate needed to burn the aluminium, divide the number of moles of aluminium by 8 and multiply by 3:

Amount of potassium perchlorate required to burn the aluminium:

$$0.6301 \div 8 \times 3 = 0.2363 \text{ moles.}$$

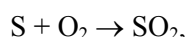
Amount left to burn the sulfur:

$$0.4836 - 0.2363 = 0.2473 \text{ moles.}$$

From the reaction

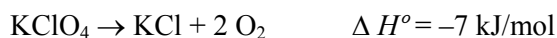


each mole of potassium perchlorate releases 2 moles of oxygen. The 0.2473 moles of potassium perchlorate left after burning the aluminium therefore release $2 \times 0.2473 = 0.4946$ moles of oxygen. This is available to burn the 0.499 moles of sulfur. The ratio of oxygen to sulfur is $0.4946 \div 0.4991 = 0.991$, very close to 1. The chemical equation for the burning of sulfur in oxygen is

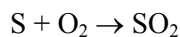


with a ratio of 1 mole of oxygen 1 mole of sulfur. This composition is therefore very close indeed to having exactly enough potassium perchlorate to burn the aluminium and sulfur to their oxides. It is another example of a stoichiometric mixture.

The heat released when aluminium burns with a stoichiometric quantity of potassium perchlorate has already been shown to be 10.69 kJ/g. It now remains to calculate the heat released when sulfur burns with a stoichiometric quantity of potassium perchlorate. The reaction for the decomposition of potassium perchlorate has already been discussed:



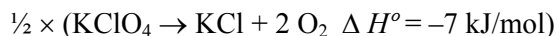
The burning of sulfur to sulfur dioxide



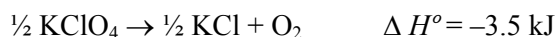
is the formation of one mole of sulfur dioxide from its elements, so the enthalpy change is the standard enthalpy of formation of sulfur dioxide, which from Table 1 is -297 kJ/mol .

The total reaction can be thought of as proceeding as follows:

Step 1: Decomposition of half a mole of potassium perchlorate to release a mole of oxygen:



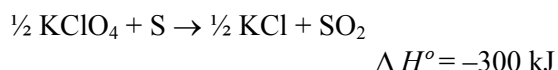
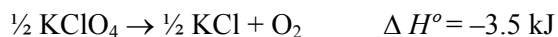
i.e.,



Step 2: Combustion of one mole of sulfur in one mole of oxygen to form one mole of sulfur dioxide:



The total enthalpy change for the reaction is the sum of the enthalpy changes for the two steps:



The next step is to convert the units from moles to grams. Half a mole of potassium perchlorate weighs

$$\frac{1}{2} \times 138.55 \text{ grams} = 69.275 \text{ grams.}$$

One mole of sulfur weighs 32.06 grams. Half a mole of potassium perchlorate plus a mole of sulfur weighs

$$(69.275 + 32.06) \text{ grams} = 101.34 \text{ grams.}$$

This quantity of mixture releases 300.5 kilojoules, so the heat released per gram is:

$$300.5 \div 101.34 = 2.965 \text{ kJ/g.}$$

One hundred grams of the original mixture can be thought of as being made up of two stoichiometric mixtures:

Mixture A: A mixture of 17.00 grams (0.6301 moles) of aluminium with the stoichiometric amount of potassium perchlorate (0.2363 moles or 32.74 grams). Total amount of mixture A:

$$17.00 + 32.74 = 49.74 \text{ grams} \div 100 \text{ grams.}$$

Mixture B: A mixture of 16.00 grams (0.499 moles) of sulfur with the stoichiometric amount of potassium perchlorate (0.2495 moles or 34.57 grams). Total amount of mixture B:

$$16.00 + 34.57 = 50.57 \text{ grams} \div 100 \text{ grams.}$$

Total (Mixture A + Mixture B) = (49.74 + 50.57) grams = 100.31 grams per 100 grams. The mixture is clearly very close to a 50:50 mix of mixtures A and B. The heat output per gram is therefore:

$$\begin{aligned} &\frac{1}{2} \times \text{heat output per gram Mixture A} + \\ &\frac{1}{2} \times \text{heat output per gram Mixture B} = \\ &\frac{1}{2} \times (10.69 \text{ kJ/g}) + \frac{1}{2} \times (2.965 \text{ kJ/g}) = \\ &(5.345 + 1.483) \text{ kJ/g} = 6.828 \text{ kJ/g} \end{aligned}$$

The heat output per gram of the flash mix containing sulfur is 6.828 kJ/g, while that of the mix containing no sulfur is 10.69 kJ/g.

This shows that the heat output is only one aspect of a pyrotechnic mixture. Another very important factor is the speed or rate of the reaction. While adding sulfur to the flash mix reduces the heat output, it might (and the evidence is that it does) increase the rate of the reaction. A discussion of how this might be so is outside the scope of this article, as it relates to chemical kinetics, not thermodynamics.

Another relevant difference between the two mixtures is that the one with no sulfur generates products that are solids at room temperature. The conversion of these to liquids and/or gases at the temperature of the reaction absorbs large amounts of heat. The only way in which the reaction can do mechanical work is by the heat of the reaction causing the expansion of a gas. This gas can include vaporized products (if there is sufficient heat to vaporize them) and the surrounding air that gets raised to high temperatures by the heat released in the reaction.

Suppose 1 gram of each mixture is ignited in a closed container of fixed volume V . An estimate of the maximum pressure reached in the container can be obtained from the equation $PV = nRT$. This gives the pressure as

$$P = nRT \div V$$

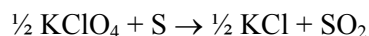
For a fixed volume (V) this equation predicts that the pressure will be proportional to the temperature (T) and to the number of moles of gas (n).

For the mixture of aluminium and potassium perchlorate, the chemical equation



shows that 3 moles of potassium perchlorate react with 8 moles of aluminium to produce 3 moles of potassium chloride plus 4 moles of aluminium oxide. Potassium chloride boils at 1437 K at atmospheric pressure, while aluminium oxide does not boil until 2950 K.^[3] The procedure for calculating the maximum temperature in a reaction will be explained in a later section. For the moment, it can be assumed that the temperature of the reaction is sufficient to vaporize the potassium chloride but not the aluminium oxide. From the equation, 3 moles of potassium perchlorate react with 8 moles of aluminium to produce 3 moles of potassium chloride vapor. As shown previously, 3 moles of potassium perchlorate and 8 moles of aluminium correspond to 631.49 grams of mixture. The amount of potassium chloride vapor produced by 1 gram of mixture is therefore $3 \div 631.49$ moles per gram = 4.75×10^{-3} moles per gram.

Now, for the reaction of sulfur and potassium perchlorate



it has been shown previously that $\frac{1}{2}$ mole potassium perchlorate and 1 mole of sulfur corresponds to 101.34 grams of mixture. The amount of potassium chloride produced is therefore $\frac{1}{2} \div 101.34$ moles per gram = 4.93×10^{-3} moles per gram. The amount of sulfur dioxide produced is $1 \div 101.34 = 9.86 \times 10^{-3}$ moles per gram.

As shown previously, the aluminium/sulfur/potassium perchlorate flash mixture was close to 1 part by weight of the aluminium/potassium perchlorate mixture and 1 part by weight of the sulfur/potassium perchlorate mixture.

The aluminium/potassium perchlorate mixture produces 4.75×10^{-3} moles of potassium chloride per gram. Half a gram of this mixture will contribute 2.445×10^{-3} moles of potassium chloride to the reaction products.

The sulfur/potassium perchlorate mixture produces 4.93×10^{-3} moles of potassium chloride per gram. Half a gram of this mixture will contribute 2.465×10^{-3} moles of potassium chloride to the reaction products. The total amount of potassium chloride produced per gram of mixture is therefore $(2.445 + 2.465)$

$\times 10^{-3}$ moles = 4.91×10^{-3} moles. This is very similar to the amount of potassium chloride (4.75×10^{-3} moles) produced by 1 gram of the aluminium/potassium perchlorate mix. However, the sulfur/potassium perchlorate mix also generates 9.86×10^{-3} moles of sulfur dioxide per gram of mixture. Half a gram of mixture will therefore contribute 4.93×10^{-3} moles of sulfur dioxide to the reaction products. The total number of moles of gas at the temperature of reaction is thus 4.91×10^{-3} moles (KCl) plus 4.93×10^{-3} moles (SO_2) = 9.84×10^{-3} moles of gas per gram of mixture. This is close to twice the number of moles of gaseous products formed by the aluminium/potassium perchlorate mixture. So, while the mixture that contains sulfur produces less heat per gram, it produces much more gas per gram. An estimation of the total pressure produced by the same mass of each mixture in a fixed volume requires an estimation of the maximum temperature. This calculation will be done in a subsequent article in this series.

It is worth emphasizing that the enthalpy of a reaction depends only on the reactants and products, and not on the path taken to go from one to the other. Consequently the possible formation of aluminium sulfide by reaction of the sulfur and aluminium can contribute nothing to the enthalpy of the reaction. While the reaction of aluminium and sulfur is indeed highly exothermic:



the heat released in this reaction would be exactly balanced by the heat absorbed when the aluminium sulfide was (conceptually, if not in reality) broken down into its elements before they were oxidized to form aluminium oxide and sulfur dioxide.

Effect of Temperature on the Enthalpy

Tables of standard enthalpies of formation usually list values at 298.15 K (25 °C).^[2,3] Barin's tables^[4] list enthalpies of formation at intervals of 100 K, so it is easy to calculate enthalpy changes at any desired temperature in the range listed.

It is useful to understand how enthalpy changes for reactions at other temperatures can be calculated from the standard enthalpies of formation of the reactants and products at 298.15 K.

Suppose you wanted to calculate the enthalpy change for some reaction at 500 K:

Reactants at 500 K → Products at 500 K

From tables, you have the enthalpy change for the reaction at 298.15 K.

Step 1. Imagine the reactants at 500 K are brought to 298.15 K, and calculate the enthalpy change for this process. For the simplest cases, this will be the heat capacity at constant pressure of the reactants multiplied by the temperature change. This is complicated by the fact that the heat capacity varies with temperature; formulae are available for some materials that give the heat capacity as a function of temperature. If one or more of the reactants undergoes a phase change (melts, for example) over the temperature range of interest, the enthalpy change for that process must also be included.

Step 2. Imagine that the reaction takes place at 298.15 K, forming products at that temperature. You can calculate the enthalpy change from tables.

Step 3. Imagine that the products at 298.15 K are heated to 500 K. The enthalpy change for this process is at least the heat capacities at constant pressure of the products multiplied by the temperature change. Again, it is necessary to account for the variation of heat capacity of each substance with temperature. The enthalpy changes associated with any melting or vaporization of the products must also be included.

The enthalpy change for the reaction at 500 K is simply the sum of the enthalpy changes for steps 1, 2 and 3.

For reactions with large enthalpy changes, the contributions of steps 1 and 3 can be small compared with that of step 2. In such cases, and for relatively small temperature changes, the enthalpy change of the reaction will vary to only a small extent with temperature.

Table 1. Some Formula Weights and Enthalpies of Formation for Some Substances Relevant to Pyrotechnics.

Chemical Name	Chemical Formula [a]	Formula Weight	ΔH_f° [b]
Aluminium	Al	26.98	0
carbide	Al_4C_3	143.96	-209
oxide	Al_2O_3	101.96	-1676
sulfide	Al_2S_3	150.16	-724
Ammonium			
chloride	NH_4Cl	53.49	-315
nitrate	NH_4NO_3	80.04	-366
perchlorate	NH_4ClO_4	117.49	-296
Antimony	Sb	121.75	0
oxide	Sb_2O_3	291.50	-720
sulfide	Sb_2S_3	339.69	-142
Arsenic	As	74.92	0
oxide	As_2O_3	197.84	-657
sulfide	As_2S_3	246.04	-167
Barium	Ba	137.34	0
carbonate	BaCO_3	197.35	-1216
chlorate	$\text{Ba}(\text{ClO}_3)_2$	304.24	-772
chloride	BaCl_2	208.25	-859
nitrate	$\text{Ba}(\text{NO}_3)_2$	261.35	-992
oxide	BaO	153.34	-554
peroxide	BaO_2	169.34	-634
sulfate	BaSO_4	233.40	-1473
sulfide	BaS	169.40	-460

Chemical Name	Chemical Formula [a]	Formula Weight	ΔH_f° [b]
Boron	B	10.81	0
oxide	B ₂ O ₃	69.62	-1272
Calcium	Ca	40.08	0
carbonate	CaCO ₃	100.09	-1207
oxide	CaO	56.08	-635
sulfate	CaSO ₄	136.14	-1434
Carbon	C (graphite)	12.01	0
monoxide	CO(g)	28.01	-111
dioxide	CO ₂ (g)	44.01	-394
Chlorine	Cl ₂ (g)	70.91	0
atomic chlorine	Cl(g)	35.45	121
Copper	Cu	63.54	0
(I) chloride	CuCl	98.99	-156
(II) chloride	CuCl ₂	134.45	-218
(I) oxide	Cu ₂ O	143.09	-171
(II) oxide	CuO	79.55	-155
carbonate, basic	CuCO ₃ ·Cu(OH) ₂ ·H ₂ O	221.10	-1051
Hydrogen	H ₂ (g)	2.02	0
chloride	HCl(g)	36.46	-92
sulfide	H ₂ S(g)	34.08	-21
(water)	H ₂ O(l)	18.02	-286
Iron	Fe	55.85	0
(III) oxide	Fe ₂ O ₃	159.69	-824
(II,III) oxide	Fe ₃ O ₄	231.54	-1118
Lead	Pb	207.20	0
(IV) oxide	PbO ₂	239.20	-274
(II,IV) oxide	Pb ₃ O ₄	685.60	-719
Magnesium	Mg	24.31	0
carbonate	MgCO ₃	84.31	-1096
chloride	MgCl ₂	95.22	-642
oxide	MgO	40.30	-601
Manganese	Mn	54.94	0
dioxide	MnO ₂	86.94	-520
Nitrogen	N ₂ (g)	28.01	0
(nitrous oxide)	N ₂ O(g)	44.01	82
(ammonia)	NH ₃ (g)	17.03	-46
Oxygen	O ₂ (g)	32.00	0
atomic oxygen	O(g)	16.00	249
Phosphorus	P(red amorph.)	30.97	-17
(V) oxide	P ₄ O ₁₀	283.89	-3010
Potassium	K	39.10	0
chlorate	KClO ₃	122.55	-398
chloride	KCl	74.55	-437
dichromate	K ₂ Cr ₂ O ₇	294.19	-2062
nitrate	KNO ₃	101.10	-495
oxide	K ₂ O	94.20	-361
perchlorate	KClO ₄	138.55	-430
permanganate	KMnO ₄	158.04	-837
sulfide	K ₂ S	110.26	-377

Chemical Name	Chemical Formula [a]	Formula Weight	ΔH_f° [b]
Silicon	Si	28.09	0
dioxide	SiO ₂ (quartz)	60.08	-911
Sodium	Na	22.99	0
bicarbonate	NaHCO ₃	85.00	-951
carbonate	Na ₂ CO ₃	105.99	-1131
chlorate	NaClO ₃	106.44	-366
chloride	NaCl	58.44	-411
nitrate	NaNO ₃	84.99	-468
oxalate	Na ₂ C ₂ O ₄	134.00	-1318
oxide	Na ₂ O	61.98	-418
perchlorate	NaClO ₄	122.40	-383
Strontium	Sr	87.62	0
carbonate	SrCO ₃	147.63	-1220
chloride	SrCl ₂	158.53	-829
nitrate	Sr(NO ₃) ₂	211.63	-978
oxalate	SrC ₂ O ₄	175.64	-1371
oxide	SrO	103.62	-592
Sulfur	S (rhombic)	32.06	0
dioxide	SO ₂ (g)	64.06	-297
trioxide	SO ₃ (g)	80.06	-396
Titanium	Ti	47.88	0
dioxide	TiO ₂	79.88	-396
Zinc	Zn	65.39	0
oxide	ZnO	81.39	-350
sulfide	ZnS	97.46	-192

[a] Unless otherwise indicated, these are crystalline solids. Gases are indicated as (g) and liquids as (l).

[b] Values are for 298.15 K, with units of kJ/mol.

Data are from References 2, 3, and 4. If data were inconsistent in the references, the most recent value is quoted. Data were rounded to the number of significant figures presented in the Table.

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Specific to Text

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General References and Suggestions for Further Reading

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For further reading, there are many books that deal with this subject. The simplest treatments are to be found in the general chemistry texts, followed by the physical chemistry texts and then the specialized texts on chemical thermodynamics. There are also many texts on engineering thermodynamics that contain little of direct relevance to chemical thermodynamics. Of the books listed, that by E. B. Smith and the two books by B. H. Mahan are particularly recommended. The work by P. W. Atkins is a comprehensive physical chemistry textbook with an excellent treatment of chemical thermodynamics. The first volume of I. Barin's superb 2-volume collection of thermochemical data contains a concise overview of chemical thermodynamics and some useful worked examples.