Chapter 2
The Nature of Heat

Abstract When doing research on microwave-assisted chemistry and materials processing, what type of heat is used most often? This chapter discusses qualitatively issues such as heat, temperature, thermodynamics, and heat transfer without unnecessary use of equations. Understanding this chapter will provide a better understanding of later chapters. In addition, the coffee break talks about relationships between microwaves and foods, as well as the history of microwave cooking ovens.

Keywords Heat · Joule · Calorie · Maxwell · Chronological history
              Temperature · Thermal energy · Heat transfer · Conduction heating
              Convection heating · Radiation heating · Microwave cooking ovens

2.1 What is Heat?

The goal of this chapter is to describe various facets of heat and heat transfer. Research into microwave chemistry and materials processing through microwave heating can lead to some surprises and strange phenomena, not otherwise observed by conventional heating. The mechanisms of these phenomena have yet to be fully understood. First, however, we need to consider the nature of heat.

2.2 Historical Aspects of Heat

The nature of heat was clearly described in the mid-eighteenth century by the Scottish scientist Joseph Black who distinguished between the quantity of heat in a substrate and its temperature. He realized that thermometers could be used to determine the quantity of heat if temperatures were measured over a period of time, while the body was either heated or cooled. His experiments used two similar glass flasks, followed by pouring the same quantity of water into both and placing them in a freezing mixture. In one flask, he had added a small quantity of alcohol to
prevent freezing. Subsequent to the removal of the flasks from the bath, he noted that water was frozen in one flask, while in the other the contents remained in the liquid state, though both flasks were at the same temperature. The two flasks were then allowed to warm up gradually. The temperature of the flask containing water and alcohol warmed up several degrees, while ice in the other flask remained at its freezing point. As the flasks had absorbed heat at the same rate, Black argued that the heat absorbed by the ice after 10 h should have raised the temperature of the same quantity of water by 78 °C (140 °F), which he described as being the latent heat of fusion of water. Black then proceeded to extend the experiments to measuring the latent heat of vaporization of water [1]. Black’s theory of latent heat marked the beginnings of thermodynamics. He also showed that different substances have different specific heats. The theory proved important not only in the development of abstract science but also most importantly in the development of the steam engine. The latent heat of water is large compared with many other liquids, which led James Watt to attempt improving the efficiency of the steam engine invented by Thomas Newcomen [1].

By the late 1700s, the experiments of Fahrenheit, Black, and others had established a systematic, quantitative way of measuring temperatures, heat flows, and heat capacities. However, these experiments threw no new light on exactly what was flowing, i.e., was heat just another invisible fluid? In 1787, Lavoisier thought so, calling it a caloric fluid (from the Greek word for heat). The existence of such a fluid was thought plausible at the time as heat flowed from a hot body to a cold body. In addition, the quantitative calorimetric experiments of Black and others had established heat as a conserved quantity. Because of this heat flow, it was believed that its particles repelled each other [2].

The first serious enquiry on the soundness of the caloric theory of heat took place in a cannon factory in Bavaria under the direction of Benjamin Thompson (also known as Count Rumford of the Holy Roman Empire). Ever the skeptical thinker, though Thompson was studying cannon boring, he was really thinking about whether or not Lavoisier’s caloric fluid really had any validity. In the factory, the cannon cylinders were bored using an iron bit inside a brass cylinder which led to the generation of frictional heat, which, within the caloric theory, was accounted for by the pressure and movement squeezing out caloric fluid. Thompson subsequently measured how much heat was produced for an extended period by immersing the hot brass cylinder into water. To his astonishment, the water (2 gallons) began to boil without fire.

The relation between work and heat was clarified by the study of James Prescott Joule (England) who reported that when a motor was energized by a battery, the conducting wire was heated. This led Joule to write in his 1844 paper: the mechanical power exerted in turning a magneto-electric machine is converted into the heat evolved by the passage of the currents of induction through its coils, whereas the motive power of the electromagnetic engine is obtained at the expense of the heat due to the chemical reactions of the battery by which it is worked [3]. Joule further suggested that heat is the movement form of energy, equivalent to heat and dynamic work, and equivalent to heat and kinetic work. To establish the
equivalence between heat and work, he performed an experiment in which water was stirred by the power of two weights as illustrated in Fig. 2.1. At about the same time, the equivalence of dynamic work and heat was also inferred by Julius Robert von Mayer (Germany).

At the 1847 annual meeting of the British Association for the Advancement of Science, Joule attempted to discredit the caloric theory of heat and the theory of the heat engine articulated by Sadi Carnot and Émile Clapeyron; he argued for the mutual convertibility of heat and mechanical work and for their mechanical equivalence. William Thomson (also known as Lord Kelvin; England) was skeptical of Joule’s viewpoints and though he felt that Joule’s results necessitated a theoretical explanation, he remained deeply committed to the Carnot–Clapeyron theory. Lord Kelvin predicted that the melting point of ice must fall with pressure; otherwise, its expansion on freezing could be exploited in a perpetuum mobile [5]. Dissatisfied with the gas thermometer that provided only an operational definition of temperature, he extended the Carnot–Clapeyron theory further and proposed an absolute temperature scale in which …a unit of heat descending from a body A at the temperature T of this scale, to a body B at the temperature (T−1), would give out the same mechanical effect [work], whatever be the number T…; Kelvin further noted that such a scale would be …quite independent of the physical properties of any specific substance… [6]. Kelvin also speculated that a point would be reached at which no further heat (caloric) could be transferred—this is now referred to as the point of absolute zero, which Guillaume Amontons had mentioned in 1702 and that Carnot had published in 1824 in Réflexions sur la Puissance Motrice du Feu (Reflections on the Motive Power of Heat). At the time, −267 °C (zero degrees Kelvin) was estimated as being the absolute zero temperature [7]. In addition, Kelvin described the internal energy of a system as being the sum of the kinetic
energy of an atom or molecule and the system’s potential energy. Specifically, he stated that the gap in the internal energy with the change of state of the system is equal to the sum of the work added from outside and the calorie. Later, heat was summarized as a physical point by James Clerk Maxwell (England) in his 1871 book “Theory of Heat” (Fig. 2.2).

Table 2.1 summarizes the chronological history into the nature of heat and the contributions of the many individuals involved.

Carnot also made significant contributions to the determination of what heat is all about, when he attempted to answer two questions about the operation of heat engines [9]: (i) Is the work available from a heat source potentially unbounded? and (ii) Can heat engines in principle be improved by replacing the steam with some other working fluid or gas? One important conclusion that Carnot came to was that the motive power of heat is independent of the agents employed to realize it; its quantity is fixed solely by the temperatures of the bodies between which is effected, finally, the transfer of caloric. [10]. In other words, the efficiency of a reversible heat engine is independent of the agents employed to achieve it, its quantity depending solely on the difference in the temperatures of the bodies and the reversible transfer of entropy, $\Delta S$.

### 2.3 Heat Versus Temperature

Clearly, heat is the form of energy transferred between two substances each of which is at a different temperature. At this stage, it is common knowledge that the direction of heat flow occurs from the substance at the higher temperature to the
### Table 2.1 Chronological history of the nature of heat

<table>
<thead>
<tr>
<th>Year</th>
<th>People (country)</th>
<th>Research</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000 BC</td>
<td>Egypt</td>
<td>The ancients viewed heat as that related to fire. Ancient Egyptians in 3000 BC viewed heat as having Mythological origins</td>
</tr>
<tr>
<td>500 BC</td>
<td>Philosopher, Heraclitus (Greece)</td>
<td>The universe was postulated as a continuous state of flux or permanent condition of change as a result of transformations of fire. Heraclitus summarized his philosophy as “All things are an exchange for fire”</td>
</tr>
<tr>
<td>460 BC</td>
<td>Hippocrates (Greece)</td>
<td>Father of medicine. He postulated that Heat is a quantity that functions to animate and derives from an internal fire located in the left ventricle</td>
</tr>
<tr>
<td>1200s</td>
<td>A. A. Baydawi (Islamic philosophy)</td>
<td>Natural heat would be the heat of a fiery atom that is broken, and heat may occur through motion change, the proof of this being through experiment</td>
</tr>
<tr>
<td>1600s</td>
<td>F. Bacon (England)</td>
<td>Heat itself, its inherent nature and essence is motion and nothing else</td>
</tr>
<tr>
<td>1600s</td>
<td>E. Torricelli (Italy)</td>
<td>Torricellian vacuum was made with a mercurial column and existence of the atmospheric pressure was found</td>
</tr>
<tr>
<td>1660</td>
<td>R. Boyle (England)</td>
<td>The pressure and volume of a gas are in inverse proportion to each other at a fixed temperature (Boyle’s law)</td>
</tr>
<tr>
<td>1669</td>
<td>J.J. Becher (Germany)</td>
<td>The basis of the caloric theory is proposed</td>
</tr>
<tr>
<td>1701</td>
<td>S.I. Newton (England)</td>
<td>A law of Newtonian cooling in heat transfer was announced</td>
</tr>
<tr>
<td>1724</td>
<td>D.G. Fahrenheit (Germany)</td>
<td>Supercooling phenomenon of water was found. The boiling point of water changes with pressure</td>
</tr>
<tr>
<td>1742</td>
<td>A. Celsius (Sweden)</td>
<td>The centigrade scale was proposed in which the temperature between the freezing point of water and its boiling point is divided into 100 equal parts</td>
</tr>
<tr>
<td>1763</td>
<td>J. Black (England)</td>
<td>Specific heat and the concept of latent heat were defined.</td>
</tr>
<tr>
<td>1774</td>
<td>A.-L. Lavoisier (France)</td>
<td>Burning is explained as a “combination with oxygen”</td>
</tr>
<tr>
<td>1798</td>
<td>C. Rumford (England)</td>
<td>It was shown that heat occurs by work, and the caloric theory was overturned</td>
</tr>
<tr>
<td>1800s</td>
<td></td>
<td>Practical use of a heat engine was developed at this time. It was suggested that heat is one form of energy</td>
</tr>
<tr>
<td>1822</td>
<td>J.B.J. Fourier (France)</td>
<td>The heat conduction phenomenon was studied by the “analytic theory of heat” and Fourier’s law was announced</td>
</tr>
<tr>
<td>1824</td>
<td>N.L.S. Carnot (France)</td>
<td>Integrity of the reversible cycle was indicated from “consideration about the power of the heat” (Carnot cycle)</td>
</tr>
</tbody>
</table>
substance at the lower temperature. The units used to describe heat are *calories* or *Joules*. Heat transfer through conduction can occur by contact between the source and the destination body; it can also occur by radiation between remote bodies, conduction and radiation through a thick solid wall, way of an intermediate fluid body (as in convective circulation), or a combination of these [11]. Because heat refers to a quantity of energy transferred between two bodies, it is not a function of the state of either of the bodies, in contrast to temperature and internal energy. Instead, according to the first law of thermodynamics, heat exchanged during some process contributes to the change in the internal energy, and the amount of heat can be quantified by the equivalent amount of work that would bring about the same change [12].

Too often people erroneously use the word heat and temperature interchangeably to mean the same thing. Specifically, the word temperature refers to a measure of how hot or how cold a substance is. In other words, temperature refers to the average kinetic energy per molecule of a substance; it is measured in degrees Celsius (C), degrees Fahrenheit (F) or, in scientific articles, temperature is given in degrees Kelvin (K). Hence, simply stated, temperature is how hot or cold an object is, while heat is the energy that flows from the hotter substrate to the cooler substrate [13].

### Table 2.1 (continued)

<table>
<thead>
<tr>
<th>Year</th>
<th>People (country)</th>
<th>Research</th>
</tr>
</thead>
<tbody>
<tr>
<td>1843</td>
<td>J.P. Joule (England)</td>
<td>That the energy of 10 J is needed to lift a 1 kg of a substance by 1 m was clarified</td>
</tr>
<tr>
<td>1843</td>
<td>B.P.E. Clapeyron (France)</td>
<td>Thermal equilibrium and the leading role of thermodynamic theory were investigated</td>
</tr>
<tr>
<td>1850</td>
<td>R.J.E. Clausius (Germany)</td>
<td>The basis for the second law of thermodynamics was established</td>
</tr>
<tr>
<td>1859</td>
<td>G.R. Kirchhoff (Germany)</td>
<td>Kirchhoff’s principle on heat radiation of a black body was reported</td>
</tr>
<tr>
<td>1859</td>
<td>J.C. Maxwell (England)</td>
<td>The basis for the Kinetic theory of gases was defined</td>
</tr>
<tr>
<td>1865</td>
<td>R.J.E. Clausius (Germany)</td>
<td>Entropy was defined</td>
</tr>
<tr>
<td>1875</td>
<td>J.W. Gibbs (USA)</td>
<td>The groundwork for chemical thermodynamics was laid from Gibbs’ free energy</td>
</tr>
<tr>
<td>1875</td>
<td>J.C. Maxwell (England)</td>
<td>“Maxwell’s devil” was imagined from a study of molecular theory of the specific heat, and irreversible progress of thermal phenomenon was defined</td>
</tr>
<tr>
<td>1877</td>
<td>L. Boltzmann (Austria)</td>
<td>A law of thermodynamics was dealt with statistically, and a relation between the entropy and state probability was found</td>
</tr>
<tr>
<td>1884</td>
<td>L. Boltzmann (Austria)</td>
<td>Stefan–Boltzmann’s law of radiation about heat radiation was advocated</td>
</tr>
</tbody>
</table>
When energy is added to a substance by heat and/or by doing work on it, then the added energy is saved in the substance such that elements and atomic motions become active and the internal energy increases. The internal energy decreases when the energy goes out of a substance through heat loss and/or by doing work, whereas temperature is regarded as the index of changes in the quantity of energy of a substance. Therefore, the temperature of a substance reflects the linear measure that shows macroscopically the state of the thermal balance and microscopically shows the movement inside the substance and the quantity of state of the oscillation energy. In classical mechanics, the temperature at which material (atomic) motion stops completely is the absolute zero point (−273 °C), i.e., 0 K or absolute zero.

Temperature increases typically originate by applying heat to a substance. On the other hand, it is also possible to do work on a system and increase its temperature (e.g., through friction). In this sense, heat and work are often confused but can be distinguished by examining an example. When energy is added to a system to cause movement (work) of all the system’s components, it suggests movement of the energy (Fig. 2.3a) so that it is possible to regard kinetic energy as the uniform motion of the internal energy. Also, when heat energy is added to a system, the constituents move randomly while undergoing vibrations and rotations. Thus, the energy will move from the high temperature side to the cold side (Fig. 2.3b). As such, heat can be regarded as movement of this random energy. In the case of microwave heating, heat occurs via a kinetic energy-like action—even though no heat energy, but microwave energy is added to the system. In the latter case, heat is created that spreads throughout the system.

Heat can be generated from various energy sources. The various interconnections amongst these sources are illustrated in Fig. 2.4 with the principal focus on heat energy (thermal energy). The most common heating method used in pre-historic times was fire generated by a sudden chemical reaction with oxygen, which results in a display of a flame and the generation of heat and light. However, the burning of important natural resources to generate heat energy and exhaust gases (e.g., the greenhouse gas CO₂) does not seem an economic source of heat. On the other hand, friction, which is a form of mechanical energy that generates heat, has been used for centuries.

To express quantitatively the amount of heat produced or applied to a system, the unit calorie was introduced to represent bringing 1.0 g of water from 14.5 to 15.5 °C; one calorie is equivalent to 4.186 J, thanks in part to James Prescott Joule (England) who had determined the amount of mechanical work needed to produce

![Fig. 2.3 Images of energy transfer to a substance by (a) doing work on the system and (b) applying heat to the system](image-url)
an equivalent amount of heat, now referred to as the mechanical equivalent of heat.
However, friction is not a suitable source of heat either because the absolute amount
of energy is small. Even electrical energy generates heat. Heat by impedance, i.e.,
electric current (Joule heat), was also proposed by Joule; this heat source is used in
many daily activities. Heat can also be used to produce chemical energy. Finally,
heat can be classified in different ways: as heat of vaporization, aggregation, fusion,
solidification, and sublimation in various chemical reactions. These various forms
of heat are often indicated in thermochemical reactions.

2.4 Thermodynamics

Thermodynamics is the branch of science that is concerned with heat and tem-
perature and their relation to energy and work. The behavior of these four quantities
is governed by the laws of thermodynamics (see Table 2.2) irrespective of the
composition or specific properties of the system [14]. Thermodynamics applies to a
wide variety of topics in science and engineering, especially in physical chemistry,
chemical engineering, and mechanical engineering. Historically, thermodynamics
developed out of a desire to increase the efficiency of the early steam engines

Table 2.2 The physical quantities and the contribution of heat to the laws of thermodynamics

<table>
<thead>
<tr>
<th>Thermodynamic equilibrium</th>
<th>Physical quantity</th>
<th>Contribution to the heat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeroth law</td>
<td>Temperature ((T))</td>
<td>Refers to two objects in thermal equilibrium</td>
</tr>
<tr>
<td>First law</td>
<td>Internal energy ((U))</td>
<td>Explains the relationship between heat and work</td>
</tr>
<tr>
<td>Second law</td>
<td>Entropy ((S))</td>
<td>This parameter could decide the direction of movement of a change of state</td>
</tr>
</tbody>
</table>
particularly) through the work of the French physicist Nicolas Léonard Sadi Carnot (1824) who believed that engine efficiency was the key that could help France win the Napoleonic Wars [15]. Lord Kelvin was the first to formulate a concise definition of thermodynamics in 1854 when he stated that thermodynamics is the subject of the relation of heat to forces acting between contiguous parts of bodies, and the relation of heat to electrical agency [16].

A temperature gradient between two locations causes the flow of heat along a (thermally) conducting path between those two locations as long as the temperature difference is maintained. This flow of heat continues until the two objects reach the same temperature, i.e., the two objects are in thermal equilibrium at which point the flow of heat appears to no longer take place macroscopically. This principle is sometimes referred to as the Zeroth Law of thermodynamics because the First and Second Laws of thermodynamics had already been articulated. This Zeroth Law governs all objects—this is the tendency toward thermal equilibrium.

The First Law of thermodynamics relates the various forms of kinetic and potential energy in a system to the work that a system can perform and to the transfer of heat. This law is sometimes taken as the definition of internal energy and introduces an additional state variable: Enthalpy, a measure of the total energy in a thermodynamic system. The First Law of thermodynamics allows for many possible states of a system to exist.

The Second Law of thermodynamics states that the total entropy (also taken a measure of the disorder in a macroscopic system) of an isolated system always increases over time or remains constant in ideal cases where the system is in a steady state or undergoing a reversible process. The increase in entropy accounts for the irreversibility of natural processes and the asymmetry between the future and the past. Historically, the Second Law was an empirical finding that was accepted as an axiom of thermodynamic theory and has been expressed in many ways. As noted above, its first formulation is credited to Sadi Carnot (France 1824) who showed that there is an upper limit to the efficiency of conversion of heat to work in a heat engine.

2.5 Heat Transfer

The rate of heat transfer is dependent on the temperatures of the systems and the properties of the intervening medium through which the heat is transferred. The three fundamental modes of heat transfer are (i) heat transfer via conduction, (ii) heat transfer via convection, and (iii) heat transfer via radiation (Fig. 2.5).

Heat transfer via conduction: Conduction is the transfer of heat between substances that are in direct contact with each other. The better the heat conductor is, the more rapidly heat will be transferred. Metals are good conductors of heat. Conduction occurs when a substance is heated, following which the atoms or molecules gain more energy and vibrate more. These atoms or molecules bump into nearby atoms or molecules and transfer some of their vibration energy to them. This continues and passes the energy from the hot end (or hot
object) down to the cold end of the substance (or colder object). The temperatures of the two sides (or the two objects) become the same and soon reach thermal equilibrium.

**Heat transfer via convection:** Thermal energy is transferred from hot places to cold places by convection. Convection occurs when warmer areas of a liquid or gas rise to cooler areas in the liquid or gas. The cooler liquid or gas then takes the place of the warmer areas. This results in a continuous circulation pattern. Water boiling in a pan is a good example of this heat convection. Another good example of convection is in the atmosphere. The Sun warms the Earth’s surface, following which the warm air moves upward and the cool air moves in. Convective heat transfer is typically taken as free or natural convection heat transfer that happens naturally, while forced convection heat transfer makes water flow by force.

**Radiative heat transfer:** Radiation is a method of heat transfer that does not rely upon any contact between the heat source and the heated object, as is the case with conduction and convection. Heat can be transmitted through empty space by thermal radiation, often called Infrared radiation, and is a type of electromagnetic radiation. No mass is exchanged and no medium is required for the radiative process. Examples of radiation are the heat transmitted from the sun through the vacuum of space, or the heat released from the filament of a light bulb. Some of the radiative energy that reaches a cold object is absorbed, some of it is reflected, and some is transmitted through the object. Such a phenomenon is analogous to microwave heating: the incident microwave energy absorbed by the substance is partially reflected and through penetration is partially transmitted (see Sect. 4.1).

### 2.6 Coffee Break 2: Background on the Relationship Between Microwaves and Foods

It was well known that radio waves could heat dielectric materials. The use of dielectric heating in industrial and medical contexts was common. The idea of heating food with radio waves was not new, however. Bell Laboratories, General Electric (GE), and Radio Corporation of America (RCA) had all been working on variations of the technology for some time. Indeed, at the 1933 World’s Fair in...
Chicago, Westinghouse demonstrated a 10-kilowatt shortwave radio transmitter that cooked steaks and potatoes between two metal plates [17]. But nothing came of these culinary adventures. Raytheon engineer Percy Spencer took it further. A 1958 article in Reader’s Digest described Spencer’s accidental discovery that microwaves could heat food quickly. He sent out for a package of corn grains. When he held it near a magnetron, popcorn exploded all over the lab. Next morning, he brought in a kettle, cut a hole on the side, and put an uncooked egg (in its shell) into the pot. Then, he moved a magnetron against the hole and turned on the power. A skeptical engineer peeked over the top of the pot just in time to catch a face full of cooked egg. The reason? The yolk cooked faster than the outside, causing the

Fig. 2.6 Illustration in the use of microwaves for heating foods, including popcorn. Reproduced with permission from Ref. [18]. Copyright 1947 by the US Patent Office
egg to burst. In 1946, Spencer filed for patents on the use of microwaves for cooking food (e.g., Fig. 2.6). One of his patents even illustrated the popping of popcorn, cob, and all [18].

Fig. 2.7 Pictures of the first commercial Raytheon microwave oven (Radarange): 340 kg, 1.5 m tall, cost approximately $5000. (a) Oven front, (b) inside the oven, (c) use at a restaurant. Reproduced with permission from Ref. [19] for (a) and Ref. [20] for (b) and (c). Copyright 2013 and 2008 by the International Microwave Power Institute and Wicked Local
Legends exist about a serendipitous discovery of microwave cooking by Percy Spencer but all remember the discovery as a gradual process involving both chance and the deliberate efforts by many individuals, e.g., feelings of warmth near radiating tubes, experimenting with popcorn, etc. all of which led to the development of Raytheon’s first microwave ovens. Still, it was Percy Spencer’s discovery and participation that were key in convincing the company into exploiting this new cooking technology.

Despite the potential for near-instant snack foods, the first commercial Radarange microwave ovens unveiled by Raytheon in 1946 were intended for use in restaurants and for reheating meals on trains. Figure 2.7 shows the first Radarange models. They were massive and expensive appliances built around two 800-Watt magnetron tubes that had to be continuously water cooled. By 1955, Raytheon had begun licensing its microwave technology, and the first microwave oven designed for consumers went on sale at Tappan (USA). The Tappan RL-1 was wall mounted; it combined gas cooking with microwave assistance and cost US $1295 (almost $11,000 today), which put it outside the reach of most people. As microwave ovens became more common throughout the 1970s, concerns arose about the effects of microwave radiation on humans. As the New York Times described in 1974 [21]: If Marianne Leonard had to surrender just one of the appliances in her stainless steel and butcher block kitchen, which would it be? Her microwave oven? That’s the one thing I could do without, the Westport, Conn., woman said. Everything cooks so darn fast. You open the door and it’s not done. You leave it in another 30 s and it’s hard as a rock. I love it Phyllis Brodsky said of the microwave oven in her sleek, all-white kitchen in Croton-on-Hudson, N. Y. It’s wonderful for heating funny things like a second cup of coffee. It’s great for cooking a hot dog in 30 s.

References
The Nature of Heat

Microwave Chemical and Materials Processing
A Tutorial
Horikoshi, S.; Schiffmann, R.F.; Fukushima, J.; Serpone, N.
2018, XVII, 393 p. 240 illus., 118 illus. in color., Hardcover
ISBN: 978-981-10-6465-4