Chapter 3

Thermodynamic Fundamentals

INTRODUCTION

Thermodynamics is the branch of science that deals with energy and its transformations. Thermodynamics is normally associated with heat, but the subject deals not only with heat but all forms of energy. The principles of thermodynamics are well established and have been applied to physical, chemical, and biological systems. Lehninger[1] has stated that the proper study of biology, for example, should start from thermodynamic principles as the central theme that can best systematize biological facts and theories. This same statement can be made about the study of composting systems. Application of thermodynamic principles is a fundamental way of analyzing composting systems just as it has been a fundamental method for analysis of other physical, chemical, and biological processes. Because the laws of thermodynamics appear to be inviolable, application of these laws will reveal much about the limitations and expectations of composting systems.

The subject of thermodynamics should be distinguished clearly from the related subject of kinetics. Thermodynamics deals with the energy changes that accompany a process. Kinetics deals with rates or velocities of reactions and cannot be inferred from thermodynamics. For example, organic molecules in a piece of paper contain a rather substantial amount of energy. If a match is struck to the paper the energy is released at a rapid kinetic rate. If the paper is decomposed by microbial action, as in a compost pile, the energy is released at a much slower kinetic rate. The same amount of energy is released in either case but the kinetics are quite different. The subject of this Chapter is energy changes as determined by thermodynamics. Kinetic principles of composting are discussed in Chapter 10.

For most organisms life is a constant struggle or search for energy supplies needed to power the cellular machinery. Certain higher organisms, such as man, have freed themselves from the constant search for energy. Nevertheless, the human body is constantly "burning" various stored substances for energy. If these stored reserves are not replaced at periodic intervals, death is inevitable. Microorganisms, however, spend nearly their entire life cycles in search of energy sources. Despite this difference, many of the fuels used by microbes are also used by man.

From a thermodynamic standpoint, all life forms can be viewed as chemical machines which must obey the laws of energy and heat as most all other nonliving processes. Thus, thermodynamics places limits on living systems just as it does on physical systems constructed by man to extract energy from his surroundings. This discussion of thermodynamics will necessarily be brief but of sufficient depth to serve the purposes of this book. The interested reader is referred to the numerous excellent texts available on chemical thermodynamics and bioenergetics for more in-depth discussion.

Although the need for an energy supply is common to all life forms, the actual source can be markedly different. The study of different energy sources available to microbes is probably the best approach to understanding the differences between life forms. It will also lead to a better understanding of reactions that organisms mediate and the useful tasks to which they can be directed in properly engineered systems. In this sense the designer of a composting plant differs little from the biochemical engineer designing an industrial fermentation, enzyme extraction, or antibiotic production plant or the sanitary engineer designing a biological waste treatment facility. All must understand the microbes involved, reactions they mediate to obtain energy, environmental conditions required for growth and metabolism, and, in certain cases, conditions required to kill organisms such as pathogens.

HEAT AND WORK, THE CONSERVATION OF ENERGY

To begin this discussion, the terms "heat" and "work" need to be defined. Heat is energy that flows because of a temperature difference between two bodies. The basic unit of heat is the calorie, which is the energy required to raise 1 g of water 1°C. The energy required actually varies somewhat with temperature, and it is common to specify the 15°C calorie as the heat flowing into 1 g of water when its temperature increases at atmospheric pressure from 14.5 to 15.5°C The equivalent English unit is the 60°F Btu (British thermal unit), which is the quantity of heat flowing into 1 lbm (pound mass) of water when its temperature increases at atmospheric pressure from 59.5 to 60.5°F. These exact definitions are seldom necessary for environmental engineering purposes, and it is sufficient to define the specific heat of water as 1.00 cal/g °C, which is equivalent to 1.00 Btu/lb °F. The specific heat of other materials varies significantly and is usually much lower than that of water. The specific heats of ethanol, acetone, aluminum, and copper are 0.65, 0.50, 0.22, and 0.093 cal/g °C, respectively.

Note that the previous definitions specified atmospheric pressure conditions. Specific heat can be measured under both constant volume and constant pressure conditions. c_v is the specific heat at constant volume and c_p the specific heat at constant pressure. There is little difference between the two for liquids and solids. With gases, however, c_p is greater than c_v because of the added heat energy required to expand a gas against a constant pressure. Most biological processes operate under conditions of constant pressure in aqueous solutions, and the distinction is not as significant to liquid phase systems. Dry gases and water vapor are important components in a composting system, however, and the distinction will be important in later studies.

The concept of work is essential to the study of thermodynamics. Work may be mechanical, electrical, magnetic, or of other origin. Consider the mechanical system shown in Figure 3.1. Work is the application of force through a distance. If the force on the piston is constant, the incremental work, dw, in moving the piston through the distance, dl, is given as
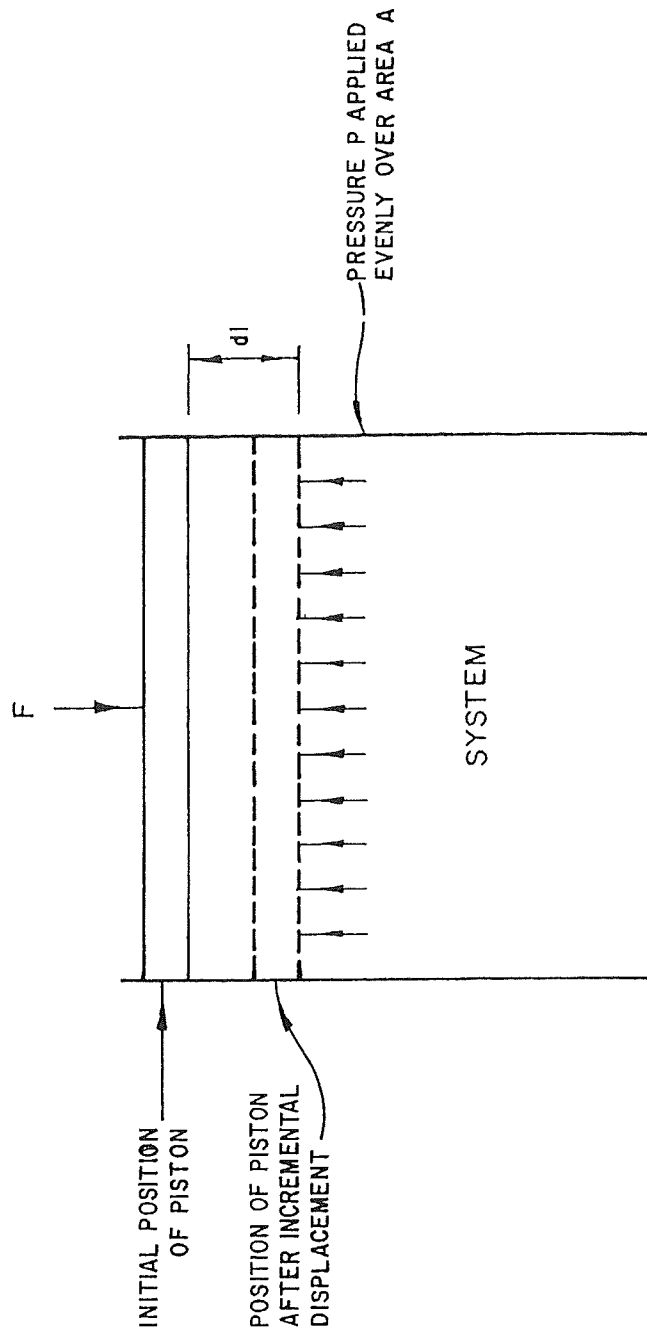
$$dw = Fdl \tag{3.1}$$

Figure 3.1.   Schematic illustration of mechanical work being performed on a system.

The force, F, is equal to the product of pressure, P, times area, A. Thus,

$$dw = PAdl = PdV \qquad (3.2)$$

Since dV is positive when the volume increases, work in an expansion process is positive. Work is measured in foot-pounds, joules, or ergs.

Because heat and work are both forms of energy one should be able to equate them. James Prescott Joule verified this in a number of experimental systems between about 1840 and 1850. In each case the amount of work yielded the same amount of heat, about 4.18×10^7 ergs of work per calorie of heat. In honor of Joule, 10^7 ergs were set equal to 1 J. Thus, today we say that 4.18 J = 1 cal. In English units, 778 ft·lb is equivalent to 1 Btu.

THE FIRST LAW OF THERMODYNAMICS

Consider the system shown in Figure 3.2. If energy can be neither created or destroyed, heat energy that flows into the system, +q, must either be stored within the system, flow out of the system or appear as work done by the system. In other words, energy that flows into a system must be fully accounted for in other forms of energy. This is a statement of the law of conservation of energy which is also referred to as the first law of thermodynamics. Stated yet another way, energy can be neither created nor destroyed. The German physicist Hermann Ludwig von Helmholtz is usually credited with the first formal statement of this principle in 1847, although it had been intuitively accepted as early as the 18th century. Notice that this concept is referred to as the First Law of Thermodynamics. There is no proof of this concept. It is accepted as a first principle, a fundamental concept that describes observed phenomena and which has never been shown to be violated. We will place considerable reliance on the concept of an "energy balance" in later discussions of composting systems.

Returning to Figure 3.2, the First Law for the system shown can be stated as

$$q = \Delta E + w \qquad (3.3)$$

where
- E = the change in internal energy of the system
- $+q$ = heat flow into the system
- $+w$ = work done by the system

If the system is maintained at constant volume (isovolumetric), Equation 3.3 becomes

$$q_v = \Delta E \quad (V = \text{constant}) \qquad (3.4)$$

No work of expansion or contraction can be performed in a constant volume system, and heat absorbed by the system is exactly balanced by increased internal energy within the system.

The heat per unit mass flowing into a substance can be defined as
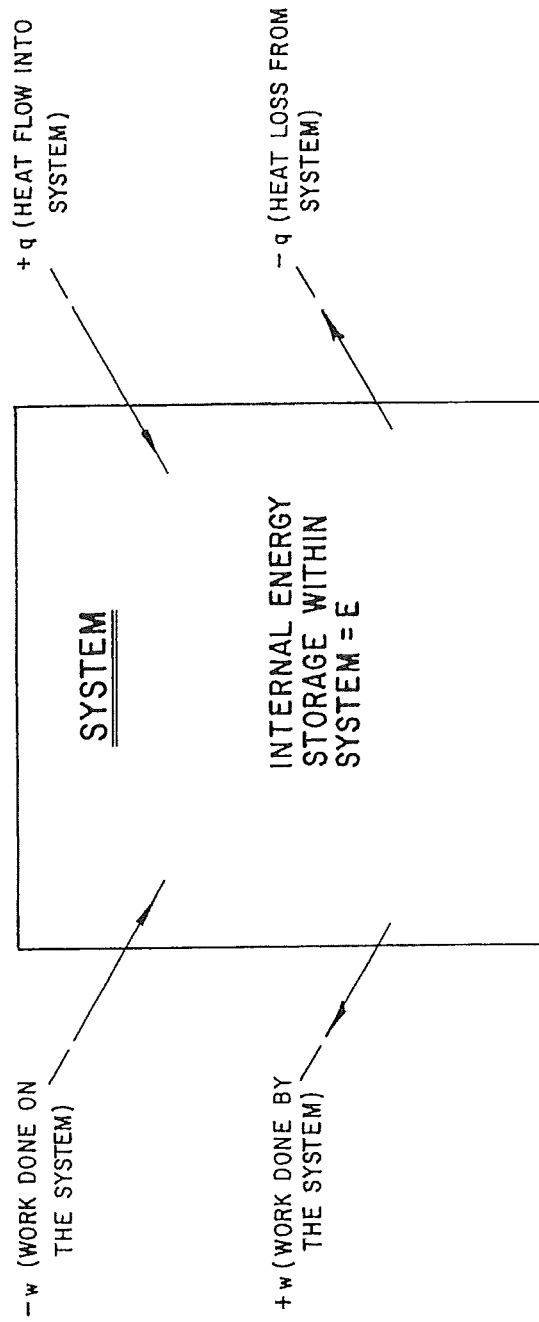
$$dq = mcdT \qquad (3.5)$$

where

SYSTEM

INTERNAL ENERGY
STORAGE WITHIN
SYSTEM = E

+ q (HEAT FLOW INTO
SYSTEM)

− q (HEAT LOSS FROM
SYSTEM)

− w (WORK DONE ON
THE SYSTEM)

+ w (WORK DONE BY
THE SYSTEM)

Figure 3.2.   Schematic illustration of the principle of conservation of energy, also known as the First Law of Thermodynamics. Note the sign convention on the terms for heat and work.

c = the specific heat capacity

m = the mass

T = the temperature.

Integrating this expression,

$$q = m \int_{T_1}^{T_2} c\,dT \qquad (3.6)$$

The specific heat must be known as a function of T to complete the integration. Fortunately, values of specific heat for most substances remain relatively constant over small temperature ranges. If the temperature range is large, the variation of specific heat with temperature can be approximated by a polynomial, which has the advantage of being integrated easily. Usually a second or third-degree polynomial is used with the form

$$c = a + bT + cT^2 + dT^3$$

where a, b, c, and d are constants that depend on the particular gas. This complication is not necessary to the present analysis, because the change in specific heat for composting gases is not significant over the temperature range in question.

Assuming a constant-volume process with constant specific heat, Equation 3.6 integrates to

$$q_v = mc_v \Delta T \qquad (\Delta T \text{ not large}) \qquad (3.7)$$

Heat flow into a substance under constant pressure can also be determined from the specific heat and temperature difference. Integrating Equation 3.6 under conditions of constant pressure gives

$$q_p = mc_p \Delta T \qquad (\Delta T \text{ not large}) \qquad (3.8)$$

Equation 3.8 will be extremely useful in conducting energy balances on composting processes, because they normally operate under conditions of constant pressure.

Many chemical and most biological processes operate under conditions of constant pressure. Applying Equation 3.3 to the system in Figure 3.1, assuming constant pressure and movement of the piston over the incremental small distance, dl, gives the following:

$$dq = dE + p\,dV \qquad (3.9)$$

Integrating and recalling that p is constant,

$$q_p = E_2 - E_1 + pV_2 - pV_1 \qquad (3.10)$$

Rearranging,

$$q_p = (E_2 + pV_2) - (E_1 + pV_1) \qquad (3.11)$$

Because constant pressure systems are so important in chemical and biochemical systems, the terms in parenthesis have been defined as the enthalpy, H, of the system. Thus,

$$q_p = H_2 - H_1 = \Delta H \tag{3.12}$$

When chemical changes result in the absorption of heat, i.e., heat flows into the system, the reaction is termed <u>endothermic</u> and both q and ΔH are taken as positive values. Reactions that result in the evolution of heat, i.e., heat flows from the system, are termed <u>exothermic,</u> and q and ΔH have negative values. The chemical reactions that result during composting usually occur under conditions of constant pressure. Thus, heat release can be determined from the enthalpy changes accompanying the reactions.

It is common to measure elevations against a reference point. Thus, the elevation of a mountain is referenced to sea level or some other datum, the height of a ceiling to the floor beneath it, and so on. Similarly, measurement of enthalpy is simplified by establishing a datum against which all other values can be measured. The datum is termed a standard state and is conveniently taken as the stable state of the compound at 25°C and 1 atm pressure. For example, the standard state of oxygen is a gas. By convention, enthalpy of an element in its standard state is set equal to zero. The enthalpy of a compound is determined from the heat of reaction necessary to form the compound from its elements. For reactions in solution, the standard state corresponds to a concentration at unit activity (approximately a 1 M solution). Enthalpy change calculated under standard state conditions is usually termed $\Delta H°$. Standard enthalpy values for a few compounds of interest are presented in Table 3.1.

Both internal energy and enthalpy are properties of a system. This means that changes in enthalpy and internal energy between two equilibrium states of a system are the same for all paths followed between the two states. In other words, internal energy change and enthalpy change depend only on the beginning and end points of a process. For example, heat absorbed in an isobaric (constant pressure) process is equal to the enthalpy difference between beginning and end states regardless of path. Because enthalpy is a property of a system, its values can be tabulated. The reader is probably familiar with steam tables that contain tabulated values of enthalpy for water and water vapor as functions of temperature and pressure. Not all terms mentioned in this discussion are system properties. Work, for example, depends on the path followed between equilibrium states and is not a property of a system.

The distinction between a property of a system and other functions that depend on path may seem rather subtle. However, the distinction is quite important and has direct application to thermodynamic analysis of composting systems. The inlet and outlet conditions around a compost process often can be defined without knowledge of the path followed between end points. Fortunately, it is not necessary to know the path to determine the enthalpy change. The following example should help clarify the distinction and highlight its importance.

Example 3.1

Consider a compost process operated under constant pressure conditions in which water and vapor enter at temperature $T_1 = 15.5°C$ (60°F). The reactor is maintained at a temperature $T_2 = 71.1°C$ (160°F), and different proportions of water and vapor exit the reactor at T_2. Determine the heat required to accomplish the mass and temperature changes assuming two different thermodynamic paths as follows: (1) assume that water is vaporized at temperature T_1 and then water and vapor are heated to T_2 and (2) assume inlet water and vapor are first heated to temperature T_2 and then a portion is vaporized at temperature T_2.

Table 3.1.   Standard State Enthalpy and Free Energy of Formation at 25°C

Substance	State[a]	H°	G°
CH_4	g	−17.89	−12.14
CH_3COOH	aq	−116.74	−95.51
$C_6H_{12}O_6$	aq		−217.02
CO_2	g	−94.05	−94.26
CO_2	aq	−98.69	−92.31
H_2O	lq	−68.32	−56.69
H_2O	g	−57.80	−54.64
H_2S	aq	−9.4	−6.54
NH_4^+	aq	−31.74	−19.00
SO_4^{-2}	aq	−216.90	−177.34
H^+ (pH = 7)	aq		−9.67
NH_4Cl	c	−75.38	−48.73
Cl^-	aq	−40.02	−31.35

Source: Perry and Chilton,[2] *CRC Handbook of Chemistry and Physics,*[3] Lehninger,[4] and Sawyer and McCartey.[5]

[a] Aq = aqueous, g = gas, lq = liquid, c = crystal.

Inlet T = 15.5°C   Exit T = 71.7°C

0.1 g H_2O vapor → | Compost Process | → 0.6 g H_2O vapor

1.0 g H_2O liquid → | p = constant | → 0.5 g H_2O liquid

Solution

1. From steam tables the following table of enthalpy values can be constructed:

	Enthalpy (cal/g)	
Temperature (°C)	Water	Steam (Sat.)
15.5	15.59	604.28
71.1	71.09	627.89

2. For path 1 the enthalpy change can be determined as

$$\Delta H = 0.5(71.09 - 15.59) + 0.5(604.28 - 15.59) + (0.5 + 0.1)(627.89 - 604.28)$$

     liquid to T_2 vaporize at T_1 all vapor to T_2

$$\Delta H = 336.26 \text{ cal}$$

3. For path 2 the enthalpy change is determined as

$$\Delta H = 1.0(71.09 - 15.59) + 0.5(627.89 - 71.09) + 0.1(627.89 - 604.28)$$

     liquid to T_2 vaporize at T_2 input vapor to T_2

$$\Delta H = 336.26 \text{ cal}$$

4. The enthalpy change is the same regardless of path, and one need only select a convenient path and be consistent in any subsequent calculations. This result will have a direct bearing on energy balances conducted in later chapters.

The heat release accompanying any chemical reaction is determined as the sum of the enthalpy of products minus reactants. The equation for oxidation of glucose is

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$
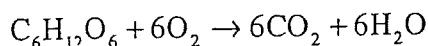
$$\Delta H_R^\circ = -673,000 \text{ cal / mole}$$

The heat of reaction ΔH°_R is negative, which means that 673 kcal of heat energy is released to the surroundings per mole (180 g) of glucose oxidized. If the reaction is conducted by microbes, some of the chemical bond energy will be captured for use by the microbes, reducing somewhat the amount that appears as heat.

For microbial reactions all reactants and products should be assumed to be in the aqueous state, since all energy yielding reactions are conducted within the cellular cytoplasm. For combustion reactions the O_2 and produced CO_2 are usually assumed to be gaseous. If the produced water remains as a vapor the enthalpy change is termed the lower heat value (LHV) of combustion. If produced water is condensed to a liquid, additional heat is released and the enthalpy change is termed the higher heat value (HHV) of combustion. Only the LHV is available for recovery from combustion reactions, whereas the HHV is available in microbial systems because the water remains as a liquid within the cell.

Every organic molecule has a characteristic heat of combustion of significant magnitude and, in each case, of negative sign. Organic molecules contain energy in the chemical bonds that form the molecule. This energy is released as the molecule is degraded into simpler compounds, such as CO_2 and H_2O, which have a lower energy content.

Heats of reaction for the aerobic oxidation of various organics are presented in Table 3.2. It is interesting to note that the heat of reaction, expressed per gram of organic, varies significantly between the three major foodstuffs: proteins, carbohydrates, and lipids (fats). Lipids contain over twice the energy per gram as proteins and carbohydrates, including both starch and cellulose. Because most organic wastes are composed of a mixture of these natural foodstuffs, the heat of combustion can be expected to vary from a low of about 2100 to about 9300 cal/g (3800 to 16,700 Btu/lb). Comparative heating values of various fuels and municipal waste products are presented in Table 3.3. The organic components in domestic sludge commonly contain about 5550 cal/g of organic matter (10,000 Btu/lb).

THE SECOND LAW OF THERMODYNAMICS

In the latter part of the 19th century there was considerable interest among the early founders of thermodynamics as to the direction in which spontaneous chemical reactions would proceed. The French chemist Pierre Berthelot proposed that reactions would proceed spontaneously in the direction of negative ΔH. In other words, only exothermic reactions were spontaneous. This seemed to make a great deal of common sense. Organic molecules would always burn to form CO_2 and H_2O, but the latter would not spontaneously combine to form organic molecules.

Table 3.2.   Heats of Combustion of Some Organic Fuels[a]

Feed	Formula	Molecular Weight	$\Delta H°_R$ (cal/mol)	gCOD[b] mol	gCOD/ g organic	kcal/g	kcal/g COD
Carbohydrate							
Glucose	$C_6H_{12}O_6$	180	−673,000	192	1.067	3.74	3.51
Lactic acid	$CH_3CH(OH)COOH$	90	−326,000	96	1.067	3.62	3.40
Polysaccharides, (e.g., starch and cellulose)	$(C_6H_{10}O_5)_x$				1.185		
Lipid							
Palmitic acid	$CH_3(CH_2)_{14}COOH$	256	−2,398,000	736	2.87	9.37	3.26
Tripalmitin	$(CH_3(CH_2)_{14}COO)_3(C_3H_5)$	809	−7,510,000	2,320	2.87	9.28	3.24
Protein							
Glycine (amino acid)	$CH_2(NH_2)COOH$	75	−163,800	48	0.64	2.18	3.41
Hydrocarbons							
n-Decane	$CH_3(CH_2)_8CH_3$	142	−1,610,000	496	3.49	11.34	3.25
Methane	CH_4	16	−210,800	64	4.00	13.18	3.29

[a] Heats of combustion were obtained from CRC Handbook of Chemistry and Physics, 50th ed. and corrected to products of combustion as $(CO_2)_g$, $(H_2O)_{aq}$, and $(NH_a^+)_{aq}$.
[b] Chemical oxygen demand.

Table 3.3.   Comparative Heating Values of Various Fuels

Fuel	Heat Value	
	cal/gm	Btu/lb
No. 2 oil	10,900	19,640
No. 6 oil	9,720	17,510
Natural gas	12,700	22,880
Bituminous coal	7,560	13,620
Wood (air dried)	3,060	5,510
Grease and scum	9,280	16,720
Sludge (dry, ash-free)	5,560	10,020
Digested sludge (dry solids)	2,950	5,315
Digester gas	8,560	15,420
Municipal refuse (@ 20% moisture)	2,720	4,900

Source: Burd[6] and Olexsey.[7]

Unfortunately for Berthelot, there were a few chemical reactions that did not follow this rule. For example, consider the dissolution of ammonium chloride crystals in water.

$$NH_4Cl_c \rightarrow NH^+_{4\,aq} + Cl^-_{\,aq}$$
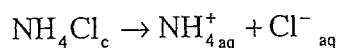
$$\Delta H°_R = (-31.74 - 40.02) - (-75.38) = +3.68 \text{ kcal / mole}$$

When added to water the crystals dissolve completely, provided the solubility limit is not exceeded. In other words, the reaction proceeds spontaneously to the right even though the reaction is endothermic. Something was missing from Berthelot's suggestion regarding the direction of spontaneous reactions.

The missing factor was the tendency of all systems to seek a state of maximum randomness or disorder. In the above example, the solution of ammonium and chloride ions in water is

more random than the highly organized structure of the original crystal. Thus, the crystal tends to dissolve even though the reaction is endothermic, driven by the tendency toward maximum randomness, entropy.

Development of mathematical formulations to describe the tendency toward randomness dominated much of theoretical thermodynamics in the 19th century. The concept of entropy was developed from a search for a function that would serve as a criterion for spontaneity of physical and chemical changes. The search led to the formulation of the Second Law of Thermodynamics, which states that all spontaneous changes in an isolated system occur with an increase in entropy or randomness. In 1876 and 1878 an American chemist, Josiah Willard Gibbs, published papers in which the two laws of thermodynamics were applied to chemical reactions. Gibbs showed that the change in enthalpy was composed of two parts: (1) a change in useful or available energy, termed free energy, ΔG (later named the Gibb's free energy) and (2) a change in entropy, ΔS. The relationship is

$$\Delta H = \Delta G + T\Delta S \quad (\text{T and p} = \text{constant}) \tag{3.13}$$

or

$$\Delta G = \Delta H - T\Delta S \tag{3.14}$$

In any spontaneous process the change in entropy, ΔS, must always be positive. Thus, in the case of ammonium chloride the product of T ΔS is greater than the enthalpy increase, H, giving a net decrease in free energy calculated as

$$NH_4Cl_c \rightarrow NH_{4\,aq}^+ + Cl_{\,aq}^-$$
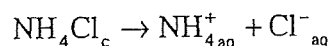
$$\Delta G_R^o = (-19.00 - 31.35) - (-48.73) = -1.62 \text{ kcal / mole}$$

In any spontaneous process, whether endothermic or exothermic, the entropy must increase and the free energy decrease. Final realization of this concept was one of the crowning achievements of 19th century thermodynamics.

It can be shown that ΔG gives the useful work that can be derived from a chemical reaction occurring under constant pressure and temperature conditions. Since these are exactly the conditions under which most biochemical reactions occur, the Gibb's free energy function can be used to determine the energy available to microbes from various chemical reactions. The original premise of this chapter can now be restated in a more sophisticated manner: "All life forms require a source of free energy to maintain life."

Standard states must again be established to measure changes in free energy. For convenience, standard states are defined in a manner similar to enthalpy changes. For reactions that occur in solution the standard state corresponds to a concentration at unit activity (approximately 1 M solution). In addition, hydrogen ion at unit activity (pH = 0) is assigned a standard free energy of zero. Standard free energy values for a number of compounds of interest are presented in Table 3.1.

FREE ENERGY AND EQUILIBRIUM

Consider a reaction in which "a" can proceed to "b", and vice versa:

$$a \Leftrightarrow b$$

Such a reaction is termed an equilibrium reaction. Most of the metabolic reactions mediated by microbes are composed of a series of such equilibrium reactions; thus, they are important to living systems. Let us assume that initially no "b" is present in solution. Then the reaction will proceed to the right, producing "b" and consuming "a". As soon as "b" becomes present in solution, some of it will begin to react back to the left producing "a". Eventually, a dynamic condition will be established when the rate of production of "b" is balanced by the production of "a". At that point the system is in equilibrium.

Now let us consider the free energy changes that occur in the above equilibrium. The initial movement of "a" to form "b" occurs because of a decrease in free energy for the reaction. It becomes apparent that the magnitude of the free energy change must be related to the concentration of the reactant and product. At equilibrium the rate of production of "b" is exactly balanced by production of "a". There is no tendency for the reaction to make a net movement in either direction. At this point the free energy change for the reaction must be zero. If it were negative, the reaction would move to produce more "b". If it were positive the reaction would move in the reverse direction to produce more "a."

Consider the reaction

$$aA + bB \Leftrightarrow cC + dD$$
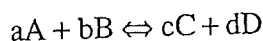
It can be shown that the effect of concentration of the different species can be described as

$$\Delta G_R = \Delta G_R^o + RT \ln\{[C]^c[D]^d / [A]^a[B]^b\} \qquad (3.15)$$

where

ΔG_R = reaction free energy change, cal/mol
ΔG_R^o = reaction free energy change under standard state conditions cal/mol
R = universal gas constant = 1.99 cal/deg-mol
T = absolute temperature, °K
$[A]$ = molar concentration of species A

Equation 3.15 can be used to adjust standard free energy values for the effect of concentration. The reaction free energy ΔG_R must be zero at equilibrium, thus

$$\Delta G_R^o = -RT \ln\{[C]^c[D]^d / [A]^a[B]^b\}_{eq} \qquad (3.16)$$

The term in brackets is actually the equilibrium constant for the reaction

$$K_{eq} = \text{equilibrium constant} = \{[C]^c[D]^d / [A]^a[B]^b\}_{eq} \qquad (3.17)$$

Thus,

$$\Delta G_R^o = -RT \ln K_{eq} \qquad (3.18)$$

This equation is one of the more important results of chemical thermodynamics because it allows prediction of equilibrium constants from standard free energy changes.

REACTION RATES AND TEMPERATURE

Rates of chemical reactions are usually a function of temperature. A convenient method of expressing the effect of temperature is to determine the rate of activity at one temperature to the rate at a temperature 10°C lower. This ratio is the temperature coefficient Q_{10}. As a general rule of thumb, most chemical reaction rates about double for each 10°C rise in temperature (i.e., $Q_{10} = 2$). For biologically mediated reactions such a relationship is also observed over the limited temperature ranges suitable for living organisms. Temperatures outside this range cause enzymes responsible for mediating the desired reactions to be inactive. Diffusion-controlled reactions usually exhibit a $Q_{10} < 2$ because diffusion coefficients vary less with temperature. On the other hand, temperature coefficients for enzyme coagulation and heat inactivation of microbes are characteristically greater than 2. Therefore, the effect of temperature on chemical and biochemical reaction rates is of considerable importance in the decomposition of waste materials and in thermal inactivation kinetics.

In 1889 the Swedish chemist Svant August Arrhenius developed a mathematical relationship between temperature and the rate of reaction. Based on experimental and theoretical considerations, Arrhenius proposed the following relationship:

$$\frac{d(\ln k)}{dT} = \frac{E_a}{RT^2} \tag{3.19}$$

where

k = reaction rate constant
E_a = activation energy for the reaction, cal/mol
T = absolute temperature, °K

Activation energy is interpreted as the amount of energy a molecule must have to undergo a successful chemical reaction. The integrated form of Equation 3.19 becomes

$$\ln \frac{k_2}{k_1} = \frac{E_a (T_2 - T_1)}{RT_1 T_2} \tag{3.20}$$

where k_2 and k_1 are the reaction rate constants at temperatures T_2 and T_1, respectively. Between 20 and 30°C, a Q_{10} value of 2 corresponds to an activation energy of about 12.25 kcal/mol.

There are several other commonly used forms of the Arrhenius expression based on Equation 3.20. Taking the antilog of both sides of Equation 3.20 and rearranging,

$$k_2 = [k_1 e^{(E_a/RT_1)}] e^{(-E_a/RT_2)} \tag{3.21}$$

Because k_1 corresponds to temperature T_1, the term in brackets can be considered a constant for a given reaction. Thus,

$$k_2 = C e^{(-E_a/RT_2)} \tag{3.22}$$

Most biological processes operate over a limited temperature range. This is true even in composting systems. A temperature range from 0 to 80°C, which seems fairly extreme,

corresponds to a range of only 273 to 353°K. Thus, the product of T_1 and T_2 changes only slightly over the biological temperature range. It is frequently assumed that E_a/RT_2T_1 is constant over this range so that Equation 3.20 becomes

$$\ln(k_2 / k_1) = \phi(T_2 - T_1) \qquad (3.23)$$

or

$$k_2 = k_1 e^{\phi(T_2 - T_1)} \qquad (3.24)$$

Although ϕ should be reasonably constant, it has sometimes been found to vary considerably, even over small temperature ranges. It is considered good practice to state the applicable temperature range whenever a value of ϕ is given. By way of comparison, a Q_{10} of 2.0 corresponds to a ϕ of 0.069.

LIFE AND ENERGY

Strictly speaking, the thermodynamic principles outlined above apply only to "closed" systems, defined as those that do not exchange matter with their surroundings or across the system boundary. Living systems are constantly exchanging matter with their surroundings and hence are termed "open" systems. Furthermore, they seldom attain true thermodynamic equilibrium. Instead there is a continual flux of metabolic materials that may result in a dynamic "steady-state". Under such steady-state conditions the rate of formation of a component is balanced by the rate of subsequent breakdown or conversion to another component. Nevertheless, principles of equilibrium thermodynamics have been applied to living systems with much success, and we need not be overly concerned with slight deviations from theoretical accuracy. The field of irreversible thermodynamics has been developed to deal with steady-state systems such as living microbes. One useful result of irreversible thermodynamics is the realization that steady-state is characterized by achievement of the minimum possible rate of entropy production for a given substrate use rate.[8]

Another attribute of living cells is that they are highly ordered systems composed of many sophisticated molecular structures. As such, there is a local decrease in entropy within the cell. It was observed before that any spontaneous process must occur with a net increase in entropy. Therefore, the local decrease in entropy within the cell is maintained at the expense of a larger increase in entropy in the surroundings. Consider, for example, an organism using the organic molecule glucose as a food source. The end products of aerobic metabolism are CO_2 and H_2O, which are more random than the original glucose molecule. Since the glucose is taken from the media surrounding the cell and CO_2 and H_2O are discharged back into it, an increase in entropy of the surroundings has occurred. Lehninger[1,4] stated that living organisms create and maintain their essential orderliness at the expense of their environment, which they cause to become more disordered and random.

Local decreases in entropy are not unique to living systems. Energy flow into a nonliving system can often cause a local decrease in entropy even though the net entropy must increase. What is unique to living systems is the use of enzyme-catalyzed chemical reactions to effect and maintain the decreased entropy within the cell. In recognition of these factors the late Isaac Asimov[9] distinguished life and living organisms as "characterized by the ability to effect a temporary and local decrease in entropy by means of enzyme-catalyzed chemical reactions."

One final attribute of microbial systems that should be considered is their remarkable ability to exploit available sources of chemical free energy. It is rare that an organic or inorganic reaction that yields free energy is *not* used by microbes. If it is assumed that all such reactions are capable of use by microbes, one will rarely be in error. Poindexter[10] has indicated that bacteria and fungi are particularly omnivorous and as a group can use for growth every known naturally occurring organic compound. No wonder these microbes are particularly important in composting systems.

ESTIMATING HEATS OF REACTION

It is often difficult to estimate heats of reaction for organic wastes from standard enthalpy values. Usually such wastes comprise a mixture of organics of unknown composition. In such a case, standard enthalpy values are of little use except in defining the probable range of heats of reaction. However, several experimental and empirical approaches are available for determining heats of reaction.

The heating value of an organic waste can be determined by calorimetric measurements. The quantity of heat released, however, is a function of the path followed during oxidation of the sample material. One method of determining the heat of reaction for a given chemical reaction is by means of an "open calorimeter", in which pressure is maintained constant at 1 atm. Under constant pressure conditions, heat released is equal to the enthalpy change for the reaction. Another type of calorimeter is the "bomb calorimeter", in which reactions are conducted under conditions of constant volume. Thus, heat released in a bomb calorimeter would differ somewhat from that in a constant-pressure calorimeter. Fortunately, these differences are usually small for organic materials, which release considerable energy on oxidation. Methods are also available to correct bomb calorimeter results to conditions of constant pressure.[11]

The calorimeter approach is undoubtedly the most accurate way to determine heats of reaction for unknown mixtures of organics. However, calorimetric tests are not routine for most water quality laboratories, and analysis by specialty labs equipped for this purpose is usually required. As a result, a number of approximate formulas based on both theoretical and experimental approaches have been developed.

Fair et al.[12] determined fuel values of different types of vacuum-filtered sewage sludges. A bomb calorimeter was used in these experiments, but actual heat release under constant pressure conditions would probably not differ significantly. The empirical formula describing their results is

$$Q = a[P_v (100) / (100 - P_c) - b][(100 - P_c) / 100] \qquad (3.25)$$

where

Q = fuel value, Btu/lb ds

a = coefficient equal to 131 for raw and digested primary sludge, 107 for raw waste activated sludge

b = coefficient equal to 10 for raw and digested primary sludge, 5 for raw waste activated sludge

P_v = percent volatile solids in sludge

P_c = percent of inorganic conditioning chemical in sludge

Table 3.4.   Representative Chemical Analysis and Heat Content of Dry Refuse and Sewage Sludges

Constituent	Refuse (wt %)	Raw Sludge (wt %)	Digested Sludge (wt %)
Carbon	33.11	37.51	24.04
Hydrogen	4.47	5.54	3.98
Oxygen	25.36	22.56	12.03
Nitrogen	0.60	1.97	2.65
Chlorine	0.41	0.33	0.17
Sulfur	0.14	0.37	0.75
Metal	11.64		
Glass, ceramics, stone	16.23		
Volatiles @ 110°C		3.66	3.01
Ash	8.04	28.06	53.37
Total	100.00	100.00	100.00
HHV, cal/gm	3280	3910	2570

Source: Loran.[15]

A formula presented by Spoehr and Milner[13] relates the heat of combustion to the degree of reduction of the organic matter. This is a rational approach because the heat of combustion has already been shown to be significantly lower for carbohydrates than for the more reduced lipids and hydrocarbons. Products of combustion are assumed to be gaseous carbon dioxide, liquid water, and nitrogen gas. The degree of reduction for any type of organic matter is

$$R = 100[2.66(C) + 7.94(H) - (O)] / 398.9 \qquad (3.26)$$

where C, H, and O are the weight percentages of carbon, hydrogen and oxygen, respectively, on an ash-free basis. The heat of combustion is

$$Q = 127R + 400 \qquad (3.27)$$

where Q is the heat of combustion, cal/g ash-free ds. Representative ultimate analyses for domestic sludge and refuse are presented in Table 3.4.

Another formula, similar to that presented by Spoehr and Milner, is called the Dulong formula and is also useful in estimating gross heating values from the feed composition:[14]

$$Q = 145.4(C) + 620[H - (O / 8)] + 41(S) \qquad (3.28)$$

where

Q = heat of combustion, Btu/lb ash-free ds

S = sulfur content on an ash-free basis, weight %

Equations 3.27 and 3.28 both require an ultimate analysis of the waste to determine the percentages of carbon, hydrogen, oxygen, and sulfur. This may not be a routine test in many water quality laboratories. Equation 3.25 requires analysis only of the volatile solids (VS) content, which is easily handled. However, Equation 3.25 was developed only for municipal sludge and should not be extended to other organic wastes.

A rule of thumb that is reasonably accurate for most organics is that about 3.4 ± 0.2 kcal are released per gram COD of the waste. Because the COD test is routinely practiced by many laboratories, it allows a relatively easy approximation of the heat of combustion. Heats of reaction were calculated for the foodstuffs presented in Table 3.2. When expressed in terms of kcal/g COD, the caloric values are reasonably constant even though they vary considerably when expressed per unit weight of organic.

The reason that the heat released per unit of COD is relatively constant lies in the fact that COD is a measure of electrons transferred. During aerobic oxidation, 4 mol of electrons must be transferred for each mole of substrate oxygen demand:

$$\frac{1}{4} O_2 + 1e^- = \frac{1}{2} O^{-2}$$
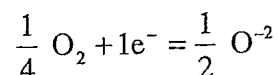
Thus, substrate COD is proportional to the number of electrons transferred during aerobic oxidation. Furthermore, heat of combustion per electron transferred to a methane-type bond is relatively constant at about 26.05 kcal per electron equivalent[8] or, since O_2 has four such electrons, 104.2 kcal/mol O_2. This in turn is equal to 3.26 kcal/g COD. For aerobic oxidation, therefore, the COD unit turns out to be a measure of energy release, and it is not surprising that energy release per electron transferred is relatively constant for a wide variety of substrates.

The correlation of calorific value with COD was experimentally verified by Zanoni and Mueller[16] for a number of primary, biological, and digested sewage sludges. They developed the following correlation:

$$Q = 3.81(COD) + 28.6 \tag{3.29}$$

where

$$
\begin{aligned}
Q &= \text{heat of combustion, cal/g ds} \\
COD &= \text{sample COD, mg COD/g ds}
\end{aligned}
$$

The constant 3.81 in Equation 3.29 is somewhat higher than the 3.26 factor discussed above. This may be related to formation of nitric and sulfuric acids which release heat in the bomb calorimeter but are not included in the above analysis of electron transfers.

A general rule of thumb for sewage sludges presented by Vesilind[17] and others is to expect about 5550 cal/g (10,000 Btu/lb) of dry volatile solids. This same range was verified by Zanoni and Mueller.[16] Caution should be exercised when using this rule of thumb because it is based on having a "typical" composition of proteins, carbohydrates, and fats in the sludge. This may not always be the case, particularly if there are large inputs of industrial wastes. For example, pulp and paper wastes can contain large amounts of cellulosic material which will lower the calorific content of the sludge.

Example 3.2

Given the raw sludge composition in Table 3.4, compute the heat of combustion by the techniques described above.

Solution

1. Calculate Q by Equation 3.25. The VS content is $100 - 28.06 = 71.94\%$. Assume that inorganic chemicals, such as lime and ferric chloride, are not used for conditioning so that $P_c = 0$. Using coefficients for raw primary sludge

$$Q = 131[71.94(100) / (100 - 0) - 10][(100 - 0) / 100] = 8114 \text{ Btu} / \text{lb ds}$$

$$Q = 4503 \text{ cal} / \text{g ds}$$

2. Calculate Q by Equation 3.27. The percentages of C, H, and O on an ash-free basis are

	% from Table 3.4	Adjusted to Ash-Free
C	37.51	57.17
H	5.54	8.44
O	22.56	34.39
	65.61	100.00

From Equation 3.26:

$$R = 100[2.66(57.17) + 7.94(8.44) - 34.39] / 398.9 = 46.3$$

Therefore, from Equation 3.27:

$$Q = 127(46.3) + 400 = 628 \text{ cal/g ash-free ds}$$

Because the sludge is 71.94% VS:

$$Q = 6280(0.7194) = 4518 \text{ cal} / \text{g ds}$$

3. Calculate Q by Equation 3.28. The percentages of C, H, O, and S on an ash-free basis are

	% from Table 3.4	Adjusted to Ash-Free
C	37.51	56.85
H	5.54	8.40
O	22.56	34.19
S	0.37	0.56
	65.98	100.00

$$Q = 145.4(56.85) + 620(8.4 - 34.19 / 8) + 41(0.56) =$$

$$10,847 \text{ Btu} / \text{lb ash-free ds}$$

$$Q = 10,847(0.7194) = 7803 \text{ Btu} / \text{lb ds}$$

$$Q = 4331 \text{ cal} / \text{g ds}$$

Note that sulfur can be oxidized by certain autotrophic organisms during composting. However, the contribution to the overall energy balance is small for the sulfur contents found in most sludges and other organic wastes.

4. Calculate Q based on sample COD. Average organic composition can be determined from the weight percentages and molecular weights of the components. Consider only the C, H, and O fractions:

$$C \quad 57.17/12 = 4.8$$

$$H \quad 8.44/1 = 8.4$$

$$O \quad 34.39/16 = 2.2$$

which gives an average composition of $C_{4.8}H_{8.4}O_{2.2}$. COD can be determined by balancing the chemical equation for oxidation to carbon dioxide and water.

$$\underset{101.2}{\overset{1g}{C_{4.8}H_{8.4}O_{2.2}}} + \underset{5.8(32)}{\overset{x}{5.8O_2}} = 4.8CO_2 + 4.2H_2O$$
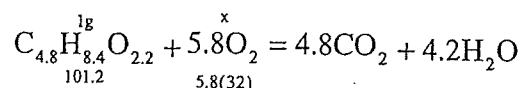
$$x = 5.8(32)(1\ g)/101.2 = 1.83\ g\ COD/g\ organic$$

Assuming an average of 3.26 kcal/g COD:

$$Q = 3260(1.83) = 6292\ cal\ /\ g\ ash\text{–}free\ ds$$

$$Q = 6292(0.7194) = 4526\ cal\ /\ g\ ds$$

Alternatively, Q can be estimated from Equation 3.29 as

$$COD = 1.83(0.7194) = 1.32\ g\ COD\ /\ g\ ds$$

$$Q = 3.81(1320) + 28.6 = 5058\ cal\ /\ g\ ds$$

5. Calculate Q from the rule of thumb for VS. Consider the organic fraction to contain 5550 cal/g VS.

$$Q = 5550(0.7194) = 3993\ cal\ /\ g\ ds$$

6. Note that the range of values calculated by these techniques is 3993 to 5058 cal/g ds or about ±12% of the average value. If the value estimated from Equation 3.29 is excluded, the range is about ±6%, which should be sufficiently accurate for most analyses of sludge composting systems.

One final point should be made concerning heats of reaction for mixtures of organics characteristic of most natural waste products. Actual heat release during composting is determined by those organics that actually degrade during composting. Thus, in the example above, heat release will be as calculated provided all organic components are equally degrad-

able. If all components of the mixture are not equally degradable the energy release could vary significantly. For example, if the lipid fraction were more degradable than either the protein or carbohydrate fractions, the heat release per gram of organic actually decomposed would be greater because of the higher caloric value of the lipids. The subject of degradability is discussed further in Chapter 9.

MECHANISMS OF HEAT TRANSFER

Three distinct mechanisms of heat or energy transfer can be described: conduction, convection, and radiation. Conductive transfer is defined as the transfer of heat between two points caused by a temperature difference but without any mass movement between the points. Conduction of heat into a compost particle or from one particle in contact with another are examples. The quantitative law of heat conduction was formulated in 1822 by Fourier as a generalization of his experimental investigations. Fourier's law states

$$dQ / dt = -kdAdT / dx \qquad (3.30)$$

Fourier's equation describes the amount of heat, dQ, that passes through a plane of area, dA, in time, dt, in response to a temperature gradient, dT/dx. The proportionality constant, k, is termed the thermal conductivity and usually is expressed in units of $cal/(h\text{-}cm^2\text{-}°C/cm)$ or $Btu/(h\text{-}ft^2\text{-}°F/ft)$. Thermal conductivity of a substance depends on the state of the substance (solid, liquid, or gas), and for a given state it will vary somewhat with temperature. Typical values of thermal conductivity in $cal/(h\text{-}cm^2\text{-}°C/cm)$ for a number of substances are: aluminum, 1800; stainless steel, 150; concrete, 15; water, ~5.6; water-saturated wood, 3; and corkboard, 0.40. Values between 2 and 4 have been measured for compost material.

Thermal diffusivity is related to thermal conductivity by

$$a = k / \rho\, c_p \qquad (3.31)$$

where

a = thermal diffusivity, cm^2/h
ρ = mass density, g/cm^3
c_p = specific heat, $cal/g\text{-}°C$

Like thermal conductivity, thermal diffusivity is a property of the substance. The term $k/\rho c_p$ appears in many heat conduction problems and is related to the diffusion coefficient used in mass transfer problems.

Solutions to Equation 3.30 are beyond the scope of this book and the interested reader is referred to specialized books devoted to heat transfer. However, many useful estimates can be made for the case of one-dimensional steady-state conditions. Integrating Equation 3.30

$$q = kA\Delta T / \Delta x \qquad (3.32)$$

where

q = the rate of heat transfer
k = average thermal conductivity (assumed constant)
Δx = the length of the flow path

Convective heat transfer results from movement of mass between a high temperature zone, where heat is accepted, to a zone of lower temperature, where heat is released. Convective heat transfer occurs as a result of fluid motion in contrast to conductive heat transfer which occurs entirely by means of intermolecular energy transfers. Movement of air within a bed of composting particles is an example of convective heat transfer. Another is the evaporation of water, its transport and condensation in another part of the compost bed.

In many cases both conduction and convection operate to transfer heat. A case in point is heat transfer from the surface of a compost pile or from the walls of a compost reactor. Mass movement of ambient air across the pile will result in convective heat loss. In response to the resulting temperature difference, heat will be conducted from the interior of the pile or across the walls of the reactor. Steady-state heat transfer in such cases is often modeled by an equation of the form

$$q = UA(T_1 - T_2)\qquad(3.33)$$

where

U = overall heat transfer coefficient which includes effects of both conductive and convective heat transfer, cal/h-cm^2-°C

A = area perpendicular to direction of heat transfer, cm^2

T_1,T_2 = temperatures at points 1 and 2, °C

Estimates of overall heat transfer coefficients cannot be made entirely on the basis of theoretical arguments. Empirical relationships based on experimental data are usually required. For example, the value of U for heat loss from the surface of a compost pile would likely be a function of wind speed, relative humidity, and perhaps other factors. Even so, once the surface has cooled, further heat loss is probably limited by transport of heat (either by conduction or convection) from the interior of the pile.

A final form of heat transfer can occur as a result of radiant or electromagnetic energy exchange between two bodies of unequal temperature. Radiant energy can be transmitted in a vacuum and does not depend on direct physical contact or the movement of any fluid between the bodies. Radiant energy is always being exchanged, but a net exchange in one direction results only if there is a temperature difference between the two bodies. At temperatures below 300°C practically all radiant energy is in the infrared region of the spectrum. The reader is probably familiar with infrared satellite photographs which highlight temperature differences between objects. If composting is successful, its temperature should be greater than that of the surroundings, and some radiative losses can be expected from the surface.

Radiant energy transfer between two bodies, A and B, is described by the Stefan-Boltzmann Law:

$$q = \sigma A(T_a^4 - T_b^4)F_a F_e\qquad(3.34)$$

where

σ = Stefan-Boltzmann constant, 4.87×10^{-8} kcal/(h-m^2-°K^4)

F_a = configurational factor to account for the relative position and geometry of the bodies

F_e = emissivity factor to account for non-black body radiation

T_a,T_b = absolute temperature of bodies A and B, °K

Ideal radiators emit radiant energy at a rate proportional to the fourth power of the absolute temperature. As a result radiant energy losses become much more significant at higher temperatures.

Example 3.3

Determine the heat transfer rate from 1 m² of surface at a temperature of 60°C radiating to the ambient environment at 20°C. Assume an emissivity factor of 0.9 and configurational factor of 1.0. Compare this to the conductive transport of heat through a 30 cm layer of compost with a uniform temperature gradient from 60 to 20°C. Assume a k of 4.0 cal/(cm²-h-°C/cm).

Solution

1. Estimate the radiant energy transfer using Equation 3.24:

$$q = 4.87 \times 10^{-8}(1)[273+60)^4 - (273+20)^4](0.9)(1.0)$$

$$q = 216 \text{ kcal} / \text{h}$$

2. Using Equation 3.32 the conductive heat rate per m² of surface area can be estimated as

$$q = 4.0(10^4 \text{ cm})(60-20)/30\text{cm} = 5.3 \times 10^4 \text{ cal} / \text{h}$$

$$q = 53 \text{ kcal} / \text{h}$$

3. Using Equation 3.33, estimate a U value corresponding to the conductive heat loss rate in part 2.

$$q = UA(T_1 - T_2)$$

$$53 = U(1\text{m}^2)(60-20)$$

$$U = 1.3 \text{ kcal} / (\text{m}^2 - \text{h} - ^\circ\text{C})$$

4. The estimated value of U is consistent with values used for calculating losses from insulated, concrete anaerobic digesters. The latter typically range from about 0.5 to 1.5 kcal/m²-h-°C.

When a warm compost surface is exposed to cooler ambient air, such as after turning a windrow or pile, a rapid surface temperature drop should result from radiative and convective losses with the outside ambient air. Once the outer surface is cooled, further heat loss should be limited by conductive transport from the pile interior. Convective transport from air moving through the pile also occurs, but it can be accounted for from the temperature and quantity of output gases.

THERMAL PROPERTIES OF COMPOST

Before leaving this discussion of thermodynamics, the thermal properties of compost will be examined. Unfortunately, few if any tests have been reported on sludge, refuse, or yard

waste composts. However, Mears et al.[18] conducted some excellent work on compost produced from swine wastes. Their results should be reasonably applicable to other composts as well. Based on the previous discussions, the thermal properties of importance include the specific heat at constant pressure and thermal conductivity.

Mears et al. used a calorimetric technique to determine specific heat values. A wide-mouth Thermos® was used as a calorimeter. To account for heat lost to the thermos body during the experiment, the Thermos® was tested with a fluid of known specific heat to determine the fluid equivalent of the Thermos® as a function of depth. Water was the fluid of choice in these studies. Material to be tested was then placed in the calorimeter and a known quantity of hot water was added. The slurry was mixed for 5 min before taking final temperature measurements. Mixing of compost and water at the same temperature did not result in any measurable rise in temperature, indicating that any heat released in the wetting of compost was insignificant. This was not true for oven-dried samples, however, which did exhibit a significant heat of wetting. Therefore, if one were to measure the specific heat of very dry materials by the method of mixtures, the heat of wetting would have to be considered.

Thermal conductivity was measured by placing the sample in a long, thin-walled cylinder constructed of material with a high thermal conductivity, in this case aluminum. Insulating plugs were placed in the ends of the cylinder to restrict heat transfer in the axial direction. The cylinder, with its sample, was then placed in a hot water bath. Subsequent heat transfer was described as occurring in the radial direction into a cylinder of infinite length. Analytical solutions to this problem have been developed. By measuring temperature differences between the center of the cylinder of compost and the hot water bath vs time, thermal conductivity can be calculated. One problem with this technique is the fact that convective currents can arise from differential temperatures, and hence densities, of gases in the void spaces between particles. This is a problem encountered in measuring thermal conductivity of any fluid, and the effects of convective heat transfer cannot be entirely avoided. Apparently, these effects were minimized to a sufficient degree in the test equipment. Measurements of thermal conductivity of known materials containing void spaces, such as sand, in the same device were within 4% of accepted values.

Using these techniques, Mears et al. determined the thermal properties of composting material composed of swine waste amended with 5% by weight straw (10% by volume). The swine waste consisted of feces, uneaten feed, bones, plastics, paper, and glass. Large pieces of bone, plastic, etc. were excluded from the analysis, but usually totaled only 2 to 10% of the sample weight. A windrow composting technique was used and representative samples collected at weekly intervals. Results are presented in Figure 3.3 and Table 3.5.

In all cases the specific heat and thermal conductivity varied linearly with moisture content. Extrapolation of the curves to 100% moisture content gave results very close to the actual specific heat of water, 1.0 cal/g-°C, and thermal conductivity, 5.62 cal/(cm²-h-°C/cm). This means that in a thermodynamic analysis the water and solid fractions can be treated separately. The water portion of compost material can be assumed to have the thermal properties of water. The solid fraction can be assumed to have thermal properties equal to the extrapolated value at zero moisture. It also means that a compost sample can be tested at a single moisture content and the entire relationship established by using this point and the value for 100% water.

From the data of Table 3.5, it appears that both specific heat and thermal conductivity of the solid fraction increase with compost age. Mears et al.[18] speculated that this may be related to an increase in the proportion of inorganic material (ash) as a result of organic decomposition. Specific heat and thermal conductivity of inorganic components are generally greater than values for the organic fraction.
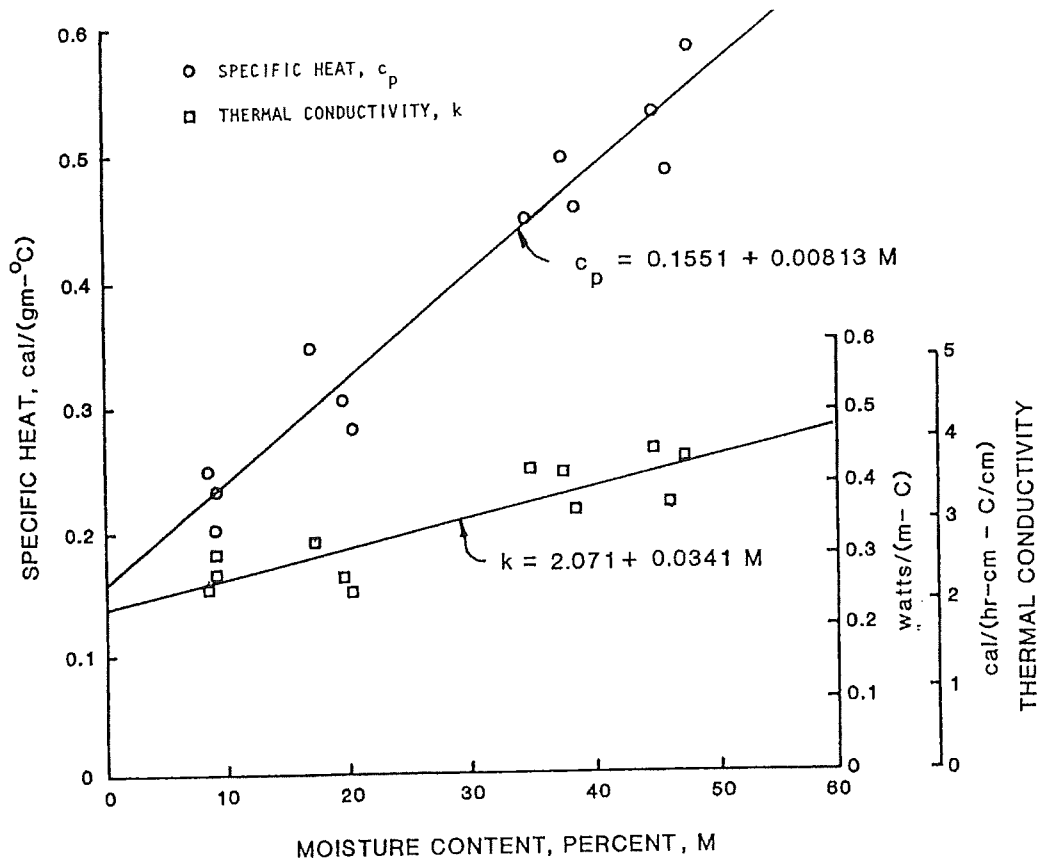
Figure 3.3. Specific heat, c_p, and thermal conductivity, k, of compost as a function of moisture content. Compost was produced from swine waste blended with about 5% straw by weight. Data shown correspond to Sample No. 6 from Table 3.5. From Mears et al.[18]

Table 3.5.   Specific Heat and Thermal Conductivity of Swine Compost

Sample No.	Age of Windrow (days)	Zero Moisture Intercept, I	Slope of Curve, S	100% Moisture Intercept, I + 100 S
Specific Heat, cal/g-°C[a]				
1	0	0.0550	0.00940	0.9951
2	7	0.0699	0.00921	0.9909
3	14	0.0771	0.00922	0.9991
4	20	0.0834	0.00906	0.9894
5	30	0.1289	0.00834	0.9629
6	35	0.1551	0.00813	0.9831
Thermal Conductivity, cal/(h-cm²-°C/cm)[b]				
1	0	0.875	0.0498	5.854
2	7	1.086	0.0473	5.816
3	14	1.323	0.0440	5.726
4	20	1.341	0.0403	5.374
5	30	1.854	0.0383	5.682
6	35	2.071	0.0341	5.476

Source: Mears et al.[18]

a Specific heat of water = 1.00 cal/g-°C.
b Thermal conductivity of water = 5.62 cal/(h-cm²-°C/cm).

As a result of these studies it can be concluded that compost will have a low specific heat that increases with increasing moisture content. Although a function of moisture, thermal conductivity is relatively low over the entire range of moisture contents. Therefore, a large compost pile will tend to be self-insulating, and heat losses by conduction should generally be small. In the case of wet substrates, values of specific heat and thermal conductivity for the mixture will likely decrease during composting since the loss of moisture should overshadow effects of increased ash content. Finally, thermal properties are likely a function of the particular compost material in question. Given the basic organic nature of composts, however, values should not be significantly different from those reported here. The laboratory techniques used by Mears et al. to measure thermal properties are very straightforward and it is hoped that the approach will be applied to other composts in the future.

SUMMARY

Thermodynamics is the study of energy and its transformations. It provides an underlying current for the understanding of physical, chemical, and biological systems. It places distinct limits on the energy transformations within systems as small as a single microbe or as large as the universe. One of the central themes of this book is the application of thermodynamic principles to composting systems, which by their nature are composed of physical, chemical, and biological processes. No single science unifies the diverse aspects of composting as does thermodynamics.

The First and Second Laws of Thermodynamics form the foundation upon which the science is based. Both are accepted as first principles that have been repeatedly upheld by human observations. The First Law states that energy can be neither created nor destroyed. In engineering terms it is commonly referred to as the Law of Conservation of Energy. The concepts of heat, work, internal energy, and enthalpy are related to the First Law. The Second Law resulted from a search to explain the direction in which spontaneous processes would occur. This led to the realization that all spontaneous changes in an isolated system occur with an increase in entropy or randomness.

The concept of free energy was developed from the First and Second Laws. Free energy gives the useful work which can be derived from a chemical reaction that occurs under constant pressure and temperature conditions. This is extremely useful because most microbial processes occur under such conditions. Therefore, a measure exists of the useful energy available from the feed substrate being used by a microbial population.

All chemical reactions have a standard free energy change, measured with all reactants and products at unit activity (approximately a 1 M concentration). Spontaneous chemical reactions proceed in the direction of decreasing free energy. If the free energy change is zero the reaction is at equilibrium. The standard free energy change can be related to the equilibrium constant for the reaction and can be adjusted for the effect of product and reactant concentrations which differ from the standard concentration.

The effect of temperature on the rate constant for chemical reactions can be estimated from the Arrhenius equation. Various simplified forms of the Arrhenius relationship are currently used in engineering practice.

Heats of combustion vary from about 2100 to 9300 cal/g for the three major foodstuffs: proteins, carbohydrates, and lipids (fats). Lipids generally contain about twice the energy per gram as proteins or carbohydrates. Expressed on a COD basis, however, most organics have a heat of combustion of about 3.26 kcal/g COD of the organic. It is often difficult to estimate heats of reaction for organic wastes from standard thermodynamic tables because the wastes

are likely to be composed of a mixture of compounds of unknown composition. Open and bomb calorimetric techniques can be used experimentally to determine the heats of combustion for such unknown materials. A number of empirical equations are also available which yield reasonably consistent results and require only routine laboratory analysis.

The water and solid fractions of a composting material can be treated as separate components from a thermodynamic standpoint. The water fraction exhibits the thermal properties of water, while the solid fraction has the properties of the dry solid. This result is significant to the development of energy balances presented in later chapters.

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