Chapter 2
General Concepts

2.1 Introduction

This book is about energy, and various mechanisms by which it can be stored for use at a later time, for a different purpose, or at a different place.

Energy is a key component of what is called *thermodynamics*. Thermodynamic principles are involved in considerations of the different types of energy and their relation to macroscopic variables such as temperature, pressure, volume, and chemical and electrical potentials. It is also centrally involved in the transformation of energy between different forms, such as heat and mechanical, electrical, chemical, magnetic, electrostatic, and thermal energy.

It was pointed out long ago in the very influential book by Lewis and Randall [1] that, "aside from the logical and mathematical sciences, there are three great branches of natural science which stand apart by reason of the variety of far-reaching deductions drawn from a small number of primary postulates. They are mechanics, electromagnetics, and thermodynamics." While thermodynamics (from the Greek word *therme*, for heat) is often thought by students to be quite esoteric and uninteresting, it can actually be of great practical use, as will be seen later in this text.

2.2 The Mechanical Equivalent of Heat

Thermodynamics originated from the observation that there is a relation between two different forms of energy, heat, and mechanical work.

The first step was the observation by Count Rumford (Benjamin Thompson) in 1798 that the friction of a blunt borer in a cannon caused an increase in the cannon's temperature, and that the increase in temperature was related to the amount of mechanical work done. The quantitative relationship between the amount of

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mechanical work done on a body and the resultant increase in its temperature was determined by James Prescott Joule in the mid nineteenth century. He found that this relation is

$$1\,cal = 4.184\,Joules \tag{2.1}$$

The thermochemical calorie, the unit quantity of heat, is defined as the amount of heat that must be added to one gram of water to raise its temperature 1 °C. The Joule, a measure of energy, can be expressed in either electrical or mechanical terms:

$$1\,Joule = 1\,watt\ sec = 1\,volt\ coulomb \tag{2.2}$$

or

$$1\,Joule = 1\,Newton\ meter = 1\,kg\ m^2 sec^{-2} \tag{2.3}$$

The amount of heat required to raise the temperature of any material 1 °C is called its *heat capacity*, or its *specific heat*. In the latter case, the amount of heat per unit weight, the dimensions are J kg^{-1} K^{-1}.

2.3 The First Law of Thermodynamics—Conservation of Energy

In a closed system energy cannot either be created or destroyed. It can only be converted from one type to another type. This is called the *first law of thermodynamics*, or the *law of the conservation of energy*. It can be expressed as

$$\Delta U = q + w \tag{2.4}$$

where U is the internal energy of a material or a system, assuming that it is not in motion, and therefore has no kinetic energy, q is heat absorbed by the system, and w is work done on the system by external forces. In the case of a simple solid, U can be thought of as the sum of the energy of all of its interatomic bonds. It does not have an absolute value, but is always compared to some reference value.

2.4 Enthalpy

Another important quantity is the *enthalpy H*, which is sometimes called the *heat content*. The name came from the Greek *enthalpein*, to warm. This is defined by the equation

$$H = U + pv \tag{2.5}$$

where p is the applied pressure and v the volume. The product pv is generally quite small for solids in the conditions that will be met in this text.

If a system (e.g., a material) undergoes a change in state, such as melting or a chemical reaction, there will be a change in enthalpy ΔH. A positive value of ΔH means that heat is absorbed, and the reaction is described as *endothermic*. On the other hand, if heat is evolved, ΔH is negative, the internal energy is reduced, and the reaction is called *exothermic*. The latter is always the case for spontaneous processes. This change in heat content when a reaction takes place is called the *latent heat* of the reaction.

H, U, and the pv product all have the dimensions of energy, kJ/mol. Their values are always compared to a reference *standard state*. For pressure, the standard state is 1 bar, or 0.1 MPa. The conventional reference temperature is 298.15 K, or 25 °C.

The standard state that is generally used for all solid substances is their chemically pure form at a pressure of 1 bar and a specified temperature. This is indicated by the use of the index "^{0}." At a temperature of 298.15 K and a pressure of one bar, the value of H^0 is zero for all pure materials.

2.5 Entropy

A further important quantity in discussions of thermodynamics is the *entropy* (from the Greek word *trope*, a deviation or change). Entropy, S, is a measure of disorder, or randomness. What this means will become evident in the examples to be discussed below.

2.5.1 Thermal Entropy

At a temperature of absolute zero (0 K) the structure of a solid material is fixed, or "frozen." When the temperature is increased by adding heat, or thermal energy, its constituent particles begin to vibrate in place, acquiring local kinetic energy, similarly to the energy in a swinging pendulum or vibrating spring. The magnitude of this vibrational, or motional, kinetic energy, or heat, is proportional to the temperature. The proportional factor is called the *thermal entropy*, S_{th}. This can be simply written as

$$q = TS_{th} \tag{2.6}$$

This can be rearranged to define the thermal entropy, the randomness of the positions of the vibrating particles at any time:

$$S_{th} = q/T \tag{2.7}$$

It can be seen that the product TS_{th} also has the dimension of energy.

One can find more sophisticated discussions of the origin and physical meaning of thermal entropy in a number of places, such as [1, 2], but such greater depth is not necessary here.

2.5.2 Configurational Entropy

A different type of randomness also has to be considered in materials systems. In addition to the vibratory motion of the fundamental particles present, there can also be some degree of disorder in the arrangement of the particles, i.e., atoms and electrons, in a material. This is sometimes called the configurational, or structural, entropy, S_{conf}. It is a measure of the uniformity or regularity of the internal structure, or the arrangement of the particles in a crystal structure, and also has the dimension of energy/T.

The magnitude of this type of entropy changes when there is a change in crystal structure of a solid, the solid melts to become a liquid, or a chemical reaction takes place in which the entropies of the reactants and the products are different.

The total entropy, indicated here simply by the symbol S, is the sum of the thermal entropy and the configurational entropy:

$$S = S_{th} + S_{conf} \tag{2.8}$$

2.6 The Energy Available to Do Work

The driving force for reactions or other changes to take place is always a reduction in energy. This is relatively easy to understand in the case of mechanical systems, where the total energy is generally divided into two types, potential energy and kinetic energy. It may seem to be a bit more complicated in chemical systems, however.

Some time ago, the driving force for a chemical reaction was called the *affinity*. For example, if A and B tend to react to form a product AB, the amount of energy released would be the *affinity* of that reaction. But since the work of J. Willard Gibbs [3, 4] it has been recognized that the driving force for any process, and also therefore the maximum amount of work that can be obtained from it, is a change in the quantity G, where

$$G = H - TS \tag{2.9}$$

The name now generally given to G is the *Gibbs free energy*, although it is sometimes called the *Gibbs energy*. In parts of Europe it is called the *free enthalpy*. It is also equivalent to the *exergy*, a term introduced in 1956 by Zoran Rant [5], that is used in some branches of engineering.

It is obvious that the energy that is available to be used to do either mechanical or electrical work is less than the heat (total energy) H present by the amount of energy tied up in the entropy, TS.

The Gibbs free energy G will appear many times in this text, for it plays a significant role in many applications. Changes or differences in G, not in H or U, constitute the driving forces for many processes and reactions.

2.7 The Temperature Dependence of *G*, *H*, and *S*

The temperature dependences of the Gibbs free energy G, the enthalpy H, and the total entropy S for a simple metal, pure aluminum, are shown in Fig. 2.1.

It can be seen that there is a discontinuity in both the enthalpy H and the entropy S, but not the Gibbs free energy G, at the melting point, 933.45 K. The entropy increases by 11.48 J K^{-1} mol^{-1}, for the liquid aluminum structure has a greater value of configurational entropy than solid aluminum. There is also a corresponding discontinuity in the enthalpy of 10.70 kJ mol^{-1} at that temperature since the process of melting is endothermic, requiring the input of heat at the melting point to convert aluminum from solid to liquid.

The difference between the gradual changes in both H and S with temperature and their discontinuities when melting or other phase changes occur will be discussed further in Chaps. 3 and 4, which deal with the storage of heat. In the one case one considers changes in *sensible heat*, and in the other, the important quantity is the *latent heat* of the reaction.

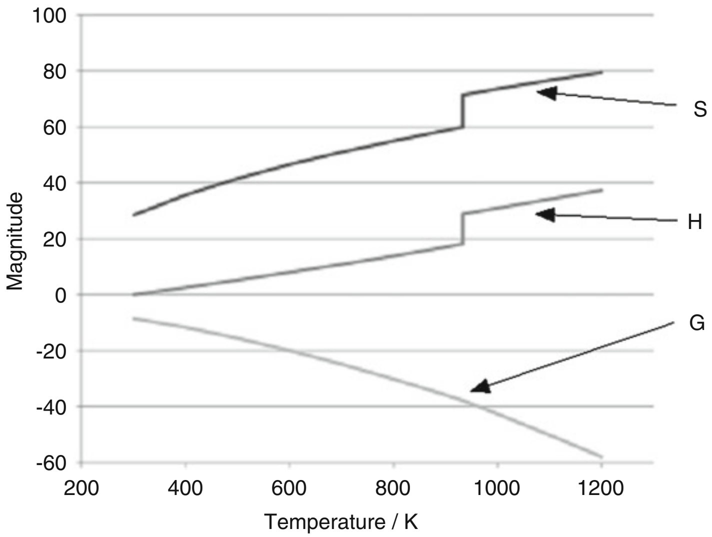

Fig. 2.1 Thermodynamic data for pure aluminum. Dimensions are J/K mol for S, and kJ/mol for H and G

2.8 Irreversible and Reversible Storage Modes

There are two general types of energy storage to be considered. In one type, energy that is already present, or stored, is available to be used once. In the other, energy can be both used and replaced, i.e., the energy is stored reversibly.

2.9 The Carnot Limitation

Considerations of the thermodynamics of energy systems often include discussions of the so-called *Carnot limitation*. It is applicable to energy conversion processes that involve heat engines, and results in the desire to have such devices operate at as high a temperature as possible, producing products at as low a temperature as possible.

The maximum efficiency that can be obtained from any process that involves the input of energy at one (higher) temperature, and its exhaust at another (lower) temperature is given by

$$\varepsilon_{\max} = \frac{T_H - T_L}{T_H} = 1 - \frac{T_L}{T_H} \tag{2.10}$$

There is also a theoretical limit to the maximum power that can be obtained from such a heat engine [6]:

$$\varepsilon_{\max\, power} = 1 - \sqrt{\frac{T_L}{T_H}} \tag{2.11}$$

Large-scale practical power plant efficiencies are now quite close to this limit.

This Carnot limitation is not applicable to other types of energy conversion systems that do not involve temperature changes. As a result, isothermal energy conversion systems can have significantly greater efficiencies. This is a great inherent advantage of the use of fuel cells and batteries, for example.

2.10 Energy Quality

In many applications, not only is the amount of energy important, but also its *quality*. Energy in certain forms can be much more useful than energy in other forms. In cases involving the storage and use of thermal energy, the temperature is important.

As mentioned earlier, the amount of useful energy, that can do work, G is related to the total energy or heat content, the enthalpy H, by Eq. (2.9).

The energy quality can be defined as the ratio G/H,

$$\frac{G}{H} = \frac{\Delta T}{T} = 1 - \frac{T_0}{T} \tag{2.12}$$

where T is the temperature in question, and T_0 is the ambient temperature. The energy quality is thus greater the larger the value of T.

In electrochemical systems the quality of stored energy is dependent upon the voltage. High voltage energy is more useful than low voltage energy. This will be discussed in Chap. 9.

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