Chapter 3
Thermal Energy Storage

3.1 Introduction

It was mentioned in Chap. 1 that a significant portion of the total energy use is for temperature control and lighting in living and working spaces. Energy use for lighting purposes comprises between 20 and 50 % of the total energy used in homes, and varies appreciably with both location and time of the year, of course. This is expected to decrease substantially as the result of the use of fluorescent and light-emitting-diode (LED) devices in the future.

Residential and commercial heating and cooling needs are currently mostly taken care of by the use of gas or electric heating and electrically powered air conditioning. This energy requirement can also be reduced appreciably by various measures. Among these is the reduction of heat transfer to and from the environment by the use of better insulation. Another is to make use of thermal energy storage systems. Thermal energy storage is also used in large-scale power plants, although that will not be included here. Discussions of these matters can be found in several places [1–4].

Household hot water systems in the United States typically have a gas- or electrically-heated water heater and storage tank, from which water is distributed using pipes throughout the dwelling. There is thus heat loss from the distribution piping as well as through the insulation on the storage tank. A different system is used in parts of Europe, where energy is more expensive. This involves local heating of water where, and only when, it is needed. Thus there are essentially no storage losses.

In addition to the storage of heat in order to maintain something at a high temperature, the main topic of this chapter, thermal energy storage methods are also sometimes used to maintain cold temperatures for the storage of food or for other chiller applications. Information about this type of application can be found in [3].

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There are two general types of thermal storage mechanisms. As will be seen below, one is based upon the use of the *sensible heat* in various solid and/or liquid materials. The other involves the *latent heat* of phase change reactions.

3.2 Sensible Heat

Energy can be added to a material by simply heating it to a higher temperature. The energy that is involved in changing its temperature is called "sensible heat," and its amount is simply the product of the specific heat and the temperature change.

This sensible heat can be transferred to another, cooler, material, or to the environment, by radiation, convection, or conduction. Thus this is a method for storing energy in the form of heat, and transferring it again. A simple example is the traditional procedure of using a hot rock or a hot water bottle to pre-warm a bed before going to sleep.

This type of energy storage has also been used to control the temperature in living or working spaces. In some cases the amount of storage material that is needed can be quite large, so that there is the obvious concern about its cost. This results in the use of relatively simple and inexpensive materials. Data on the thermal capacity of some examples are presented in Table 3.1.

The amount of heat q that can be transferred from a given mass of material at one temperature to another at a lower temperature is given by

$$q = \rho C_P V \Delta T \tag{3.1}$$

where ρ is the density, C_p the specific heat at constant pressure, and V the volume of the storage material. ΔT is the temperature difference.

Each of the materials in Table 3.1 has some advantages and some disadvantages. The specific heat of water is more than twice that of most of the other materials, but it is only useful over a limited temperature range (5–95 °C). Thus water appears

Table 3.1 Thermal properties of some common materials

Material	Density (kg $m^{-3)}$	Specific heat (J kg^{-1} K^{-1})	Volumetric thermal capacity (10^6 J m^{-3} K^{-1})
Clay	1458	879	1.28
Brick	1800	837	1.51
Sandstone	2200	712	1.57
Wood	700	2390	1.67
Concrete	2000	880	1.76
Glass	2710	837	2.27
Aluminum	2710	896	2.43
Steel	7840	465	3.68
Magnetite	5177	752	3.69
Water	988	4182	4.17

attractive for systems involved in the control of living space heating and cooling. An example of this was mentioned in Chap. 1.

On the other hand, some of the inexpensive bulk solids can be used over a wider range of temperature, and they can be more compact, due to their higher densities. An additional factor that may be important in some cases is the thermal conductivity of the storage material, for that influences the rate at which heat can be either absorbed or extracted.

No matter how well the system is insulated, there are always some losses when using this method. Thus the insulation or thermal isolation of the storage material can be quite important, particularly if the storage period is substantial.

The rate of heat loss to the surroundings is proportional to the surface area, and also to the temperature difference, but the total amount of thermal storage is proportional to the volume of any storage container. Therefore, it is more effective to use large vessels with shapes that are not far from spherical.

3.3 Latent Heat

A different mechanism for the storage of energy involves using *phase transitions* with no change in the chemical composition. It was shown in Fig. 2.1 of Chap. 2 that there is a jump in the value of the entropy, and a corresponding change in the enthalpy, or heat content, but not of the Gibbs free energy, at the melting point of aluminum, a simple metal. This is characteristic of phase transitions in elements and compounds that melt *congruently*; that is, the solid and liquid phases have the same chemical composition. There are also phase transitions in which both phases are solids. As an example, there is a transition between the alpha and beta phases in titanium at 882 °C. The alpha, lower temperature, phase has a hexagonal crystal structure, whereas the beta phase has a body-centered cubic crystal structure. Because they have different crystal structures they have different values of configurational entropy, and there is a corresponding difference in their enthalpy values.

In these cases latent heat is absorbed or supplied at a constant temperature, rather than over a range of temperature, as it is with sensible heat. Isothermal latent heat systems are generally physically much smaller than sensible heat systems of comparable capacity.

A further simple example is water. At low temperatures it is solid, at intermediate temperatures it becomes a liquid, and at high temperatures it converts to a gas. Thus it can undergo two phase transitions, with associated changes in entropy and enthalpy. The Gibbs free energy, or chemical potential, is continuous, for the two phases are in equilibrium with each other at the transition temperature.

From

$$\Delta G = \Delta H - T\Delta S = 0 \tag{3.2}$$

the change in heat content ΔH at the transition temperature is equal to $T\Delta S$ at that temperature.

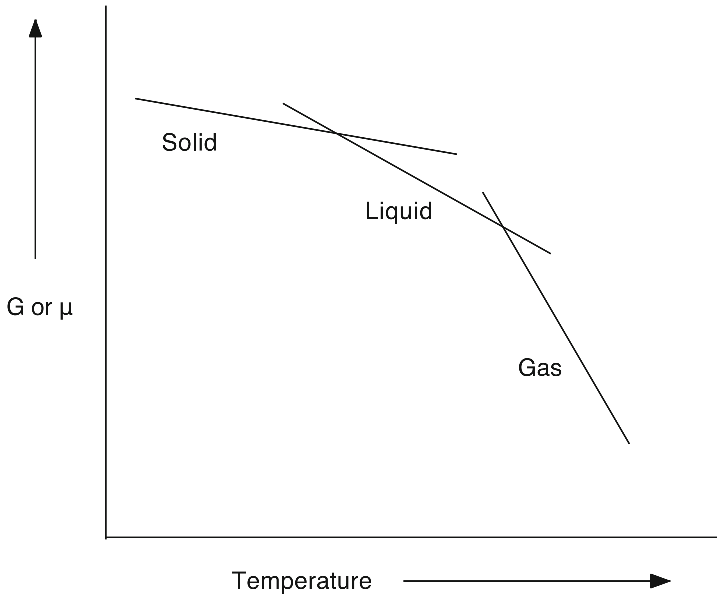

Fig. 3.1 Schematic representation of the temperature dependence of the Gibbs free energy of water

The slope of the temperature dependence of the Gibbs free energy is proportional to the negative value of the entropy, which is different in the different phases, for they have different structures. This is shown schematically in Fig. 3.1.

3.3.1 Inorganic Phase Change Materials

There are a number of other materials that also undergo congruent phase transitions. Data on some simple inorganic materials are given in Table 3.2. There are also many cases in which liquids convert isothermally into two or more phases with different compositions by means of *eutectic reactions* upon cooling, with accompanying heat evolution. Upon heating, heat is absorbed by the reverse reactions. Data on a large number of molten salt eutectic systems can be found in [5].

In addition to the phase changes involved in the conversion of solids into liquids, there are a number of cases in which there is a phase change in the solid state. These involve changes in the crystal structure, and thus changes in the entropy and the heat content at temperatures below their melting points. These materials can be used to store thermal energy at the temperatures of their solid-state phase transitions. Some examples are given in Table 3.3.

There are several features of the data in this table that deserve comment. The total entropy change, and thus the heat absorbed, between the low temperature solid state and the molten state is divided between that which occurs at the solid state

Table 3.2 Heat of fusion data for several simple inorganic materials

Phase	Melting point/°C	Heat of fusion (MJkg^{-1})
NH_4NO_3	170	0.12
$NaNO_3$	307	0.13
NaOH	318	0.15
$Ca(NO_3)_2$	561	0.12
LiCl	614	0.31
$FeCl_2$	670	0.34
$MgCl_2$	708	0.45
KCl	776	0.34
NaCl	801	0.50

Table 3.3 Data on solid-state phase transition and melting entropy for a number of materials

Material	Transition temp./°C	Melting temp./°C	Transition entropy (Jmol^{-1} K^{-1})	Melting entropy (Jmol^{-1} K^{-1})
FeS	138	1190	4.05	21.51
AgI	148	558	14.61	11.33
Ag_2S	177	837	8.86	7.01
Na_2SO_4	247	884	12.5	18.2
Ag_2SO_4	427	660	26.66	19.19
Li_2SO_4	577	860	29.2	7.9
$LiNaSO_4$	518	615	31.2	small

phase transition and that which occurs upon melting. In general, the crystal structures below and above solid state transformations are not very different. As a result, the entropy changes that are involved are not very large, and most of the total entropy changes occur at the melting point. An example of this type that is included in Table 3.3 is FeS.

But there are some materials in which the higher temperature solid phase has a crystal structure in which one of the atomic species has an unusual vibrational amplitude or inter-site mobility. When that phase is stable it has a high value of entropy. Thus the entropy change in its formation is large. Two examples of this are shown in Table 3.3, AgI and Ag_2S. Silver ions have an unusually large vibrational amplitude and high mobility in the higher temperature phases of both of these materials. AgI is called a *fast ionic conductor*, and Ag_2S is a *fast mixed conductor*. The difference is that Ag_2S is an electronic, as well as an ionic, conductor, whereas AgI is an electronic insulator.

Na_2SO_4 and Ag_2SO_4 are two additional examples of materials with this type of behavior. In these cases the sodium and silver ions are relatively mobile, and the SO_4 tetrahedral groups are essentially static parts of the crystal structure.

However, there are some other materials in which the type of structural disorder that leads to large values of entropy is quite different. Whereas atomic or ionic motion in most solids, including AgI and Ag_2S, involves species either jumping into adjacent crystallographic vacancies or between dilutely occupied interstitial positions, some materials have been found in which atomic motion occurs in coordinated groups. That is, groups of atoms move together. This type of atomic motion occurs in a group of lithium sulfates. It was found that these materials can also have unusually high values of ionic conductivity, different from that of the sodium and silver analogs [6, 7]. The structural reason for this is that there is rotation of SO_4 groups within the "static" crystal structure that assists in the longer-range transport of the lithium ions. This was first described as a *cogwheel mechanism*, but it is now generally referred to as a *paddlewheel mechanism* [8]. These materials also exhibit a high degree of mechanical plasticity, and are sometimes also called *plastic crystals*. Reviews of this topic can be found in [9, 10].

It can be seen in Table 3.3 that the entropy changes related to the solid state structural changes in the paddlewheel materials are significantly greater than the entropy changes upon melting. They are thus particularly attractive as heat storage components if the temperature is appropriate. Materials that have large values of latent heat related to solid-state phase transitions are discussed in [11].

3.3.2 Organic Phase Change Materials

In addition to these inorganic materials, it is also possible to take advantage of analogous behavior in organic materials. Data for some simple organic materials with large values of the heat of fusion are shown in Table 3.4, and the thermal properties of fatty acids and two simple aromatic materials are presented in Tables 3.5 and 3.6.

Table 3.4 Data relating to some organic phase change materials

Material	Melting temperature (°C)	Heat of fusion (kJ kg^{-1})
Paraffin wax	64	173.6
Polyglycol E 400	8	99.6
Polyglycol E 600	22	127.2
Polyglycol E 6000	66	190.0

Table 3.5 Data relating to some fatty acids used as phase change materials

Material	Melting temperature (°C)	Heat of fusion (kJ kg^{-1})
Stearic acid	69	202.5
Palmitic acid	64	185.4
Capric acid	32	152.7
Caprylic acid	16	148.5

Table 3.6 Some aromatics used as phase change materials

Material	Melting temperature (°C)	Heat of fusion (kJ kg^{-1})
Biphenyl	71	19.2
Naphthalene	80	147.7

3.4 Quasi-Latent Heat

Chemical reactions generally result in the generation or absorption of heat, similar to the thermal effects related to phase transitions in materials in which there are no changes in chemical composition. The thermal effects related to chemical reactions are often described in terms of *quasi-latent heat*. They will be discussed in Chap. 4.

3.5 Heat Pumps

Although they are not involved in the storage of heat, the topic of this chapter, it seems desirable to briefly discuss *heat pumps*. They can be used to move heat from one location to another. There are two general types of such systems. One involves the input of mechanical work to move low temperature heat from one location to another location at a higher temperature.

In a second type, which is sometimes called a chemical heat pump, the important feature is the temperature dependence of a chemical reaction. An example of this method is a system involving metal hydride materials in two locations, one that is at a high temperature in which there is heat input, and one that is cooler. Heat is moved by the movement of a chemical species, such as hydrogen, from one location to another.

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