Chapter 2. Structure of Thermodynamics

2.1. Classify the following thermodynamic systems in the five categories defined in Section 2.1:

a. A solid bar of copper.
b. A glass of ice water.
c. A yttria stabilized zirconia furnace tube.
d. A styrofoam coffee cup.
e. A eutectic alloy turbine blade rotating at 20,000 rpm.

If you find it necessary to qualify your answer by defining the system more precisely, state your assumptions.

<u>Answer to 2.1.</u>

In each case it is necessary to make some assumptions about the kind of processes that may be of interest in the problem. The simplest situation is assumed in each of the following.

a. Pure solid copper is a unary, homogeneous, closed, non-reacting otherwise simple system.

b. Ice water consists of two phases, solid and liquid; both phases are fixed composition. This system may be treated as a unary, heterogeneous, closed, non-reacting otherwise simple system.

c. In this material system the yttria (Y_2O_3) is present as second phase particles distributed throughout a matrix of ZrO_2. It may be treated as a multicomponent (binary if the components are taken to be Y_2O_3 and ZrO_2) heterogeneous (two phases), closed, non-reacting otherwise simple system.

d. Styrofoam is a polymer of fixed composition. It may be appropriate to treat it as a unary, homogeneous, closed, non-reacting otherwise simple system. If, for example, the system is defined to include the porosity then additional (gaseous) components will be present in these two phases.

e. A eutectic system consists of alternating layers of two phases, each of which is a solid solution. The problem also imposes a centrifugal field on the rotating part. Thus, this is a multicomponent, heterogeneous, closed, non-reacting system in a centrifugal field.

2.2. It is not an overstatement to say that without state functions thermodynamics would be useless. Discuss this assertion.

<u>Answer to 2.2.</u>

If there were no state functions (like T, P, V, composition), i.e., properties that depend only upon the current condition of the system, and not on how it arrived at that condition) then the behavior of all aspects of matter would depend explicitly upon the **history** of the system. There would be no variables that, by themselves, explicitly describe the current condition of any system. Thus, even the history experienced by the system could not be described in terms of some sequence of change of its properties.

2.3. Determine which of the following properties of a thermodynamic system are extensive properties and which are intensive.

a. The mass density.
b. The molar density.
c. The number of gram atoms of aluminum in a chunk of alumina.
d. The potential energy of the system in a gravitational field.
e. The molar concentration of NaCl in a salt solution.
f. The heat absorbed by a the gas in a cylinder when it is compressed.

<u>Answer to 2.3.</u>

a. The mass density is the ratio of the mass of a system to its volume; it is **intensive**.

b. The molar density is the ratio of the number of moles to the volume; it is **intensive**.

c. The number of gram atoms is a property of the system as a whole; it is an **extensive** property.

d. The potential energy of the system is a property of the system as a whole; it is thus an **extensive** property.

e. The molar concentration is the ratio of number of moles to the volume if the system; it is an **intensive** property.

f. The heat absorbed is a property of the system as a whole; it is an **extensive** property.

All of the properties identified as intensive also share the characteristic that they may be defined at a point within the system, and indeed may vary from point to point.

2.4. Why is **heat** a **process variable**?

<u>Answer to 2.4.</u>

Heat is fundamentally a flow of energy. Heat is transferred between two systems, or between parts of the same system; this rearrangement of the distribution of energy is necessarily accompanied by changes in at least some of the properties of the systems involved. Such a change is by definition a ***process.***

2.5. Write the total differential of the function

$$z = 12\,u^3\,v\cos(x)$$

a. Identify the coefficients of the three differentials in

this expression as appropriate partial derivatives.
b. Show that three Maxwell relations hold among these coefficients

Answer to 2.5.

a. Write the total differential of the function z:

$$dz = Mdu + Ndv + Pdx$$

where

$$M = \left(\frac{\partial z}{\partial u}\right)_{v,x} = 36u^2 v\ \cos(x)$$

$$N = \left(\frac{\partial z}{\partial v}\right)_{u,x} = 12\,u^3 \cos(x)$$

$$P = \left(\frac{\partial z}{\partial x}\right)_{u,v} = -\,12\,u^3 v\ \sin(x)$$

b. Evaluate the cross derivatives:

$$\left(\frac{\partial M}{\partial v}\right)_{u,x} \stackrel{?}{=} \left(\frac{\partial N}{\partial u}\right)_{v,x}$$

$$\left(\frac{\partial(36\,u^2 v\ \cos x)}{\partial v}\right)_{u,x} \stackrel{?}{=} \left(\frac{\partial(12\,u^3\ \cos x)}{\partial u}\right)_{v,x}$$

$$36\,u^2\ \cos x = 36\,u^2\ \cos x$$

$$\left(\frac{\partial M}{\partial x}\right)_{u,v} \stackrel{?}{=} \left(\frac{\partial P}{\partial u}\right)_{v,x}$$

$$\left(\frac{\partial(36\,u^2 v\ \cos x)}{\partial x}\right)_{u,v} \stackrel{?}{=} \left(\frac{\partial(-\,12\,u^3 v\ \sin x)}{\partial u}\right)_{v,x}$$

$$-\,36\,u^2 v\ \sin x = -\,36\,u^2 v\ \sin x$$

$$\left(\frac{\partial N}{\partial x}\right)_{u,v} \stackrel{?}{=} \left(\frac{\partial P}{\partial v}\right)_{u,x}$$

$$\left(\frac{\partial(12\,u^3 \cos x)}{\partial x}\right)_{u,v} \stackrel{?}{=} \left(\frac{\partial(-\,12\,u^3 v \sin x)}{\partial v}\right)_{u,x}$$

$$-\,12\,u^3 \sin x = -\,12\,u^3 \sin x$$

2.6. Describe what the notion of **equilibrium** means to you. List as many attributes as you can think of that would be exhibited by a system that has come to equilibrium. Why do you think these characteristics of a system in equilibrium are important in thermodynamics?

Answer to 2.6.

Attributes of equilibrium:

1. A *state of rest*: state of the system does not change with time.

2. A *stable state*: if the state is displaced from the equilibrium state, it will return to it.

3. A *state of internal uniformity*; (in the absence of external fields) gradients of intensive properties vanish.

The equilibrium state is the final state of every process. The primary goal of thermodynamics is the prediction of the properties of the final equilibrium state for any given initial condition of any system. "How far the system is" from the equilibrium state is a measure of the driving force for processes changing the system toward equilibrium, and controls the rate of approach to the final state of rest.

Chapter 3. The Laws of Thermodynamics

3.1. The laws of thermodynamics are "pervasive". Explain in detail the meaning of this important statement.

Answer to 3.1.

"Pervasive" means that the laws apply

a. In every system
b. At every instant in time
c. In every volume element

in which change is occurring. This characteristic emphasizes the generality, and thus the power, of the laws of thermodynamics.

3.2. List the kinds of energy conversions involved in propelling an automobile.

Answer to 3.2.

Electrical energy (the spark) combines with chemical energy (in the fuel) to produce heat and mechanical work that drives the pistons in the engine block; the mechanical work is then transmitted through the crankshaft and transmission to the axle and the differential that ultimately turns the wheels.

3.3. List the kinds of energy conversions involved in operating a hand calculator.

Answer to 3.3.

Chemical energy stored in a battery is converted to electrical energy that flows through the connectors and integrated circuits along paths determined by mechanical input through the keypad. Depending upon the nature of the display, the pattern of output electrical energy may be used to alter the structure of molecules in a liquid crystal or convert to light energy in an LED array.

3.4. List the kinds of energy conversions involved in using your arm and hand to turn the page in this text.

Answer to 3.4.

Stored chemical energy derived from food products and oxygen is converted to electrical energy which generates patterns in the brain that are transmitted through the neural network to muscles in the arm and hand. These signals induce chemical and electrical changes in the required muscles causing them to contract appropriately; this contraction is converted to the mechanical work involved in the motion of the arm and hand as they move their weight and that of the paper in a gravitational field.

3.5. Suppose the convention were adopted that defines W and W' in the first law of thermodynamics to be the "work done *by* the system *on* the surroundings".

a. Write the first law with this alternate convention.
b. Why do the signs change?

Answer to 3.5.

a.

$$dU = \delta Q - \delta W - \delta W'$$

b. With this convention W is defined to be positive when it is transmitted from the system to the surroundings; thus if W is positive, the internal energy of the system **decreases**.

3.6. Give five examples of the operation of the second law of thermodynamics in your daily experience; they must be different from those given in the text.

Answer to 3.6.

1. The morning coffee cools with time.
2. Sugar dissolves in hot coffee.
3. Left to itself, a pendulum will slow to a stop.
4. Organisms die.
5. An expanding gas cools.

3.7. Biological systems, - organelles, cells, organs, plants and animals,- are highly ordered, yet form spontaneously. Does the formation and growth of biological systems violate the second law of thermodynamics? Explain your answer.

Answer to 3.7.

No, it does not violate the second law of thermodynamics. Their formation and growth are accompanied by changes in their surroundings such that the total change in entropy of the biological system plus its surroundings is positive.

3.8. "Irreversible" is an awkward adjective. Why is this term so appropriate in its application to the description of processes