

Thermodynamics
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Lecture No 25
Pure Substance

In the previous lecture, we introduced the first law of thermodynamics. For a cyclic process, $\oint \delta Q = \oint \delta W$ in SI units. For a system undergoing a non-cyclic process, the difference between the heat transferred and the work done is the change in energy of the system. Work and heat are two different things. We will see how they are different when we look at the second law of thermodynamics. Before that, let's look at the properties of a pure substance.

A pure substance is a substance which has uniform composition as well as chemical aggregation throughout the process under consideration. We are interested in the composition and chemical aggregation of the substance only for the duration of the process.

We discussed that the state of a system is defined in terms of its properties, e.g., pressure, temperature, volume, energy, enthalpy, etc. How many properties do we need to define the state of a system? The number of properties needed to define the state uniquely depends on the type of substance which constitutes the system. For example, for a chemically reacting system (e.g. methane burning in oxygen forming carbon dioxide and water), we may need a certain number of properties such as temperature, pressure or mass. For a falling body, we may need a different set of properties such as the height through which the body falls, its temperature, etc.

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- **'Pure substance'** is a substance which has **uniform composition and chemical aggregation** throughout the process under consideration.



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- The state of a system is defined in terms of its properties
- The number of properties needed to define the state uniquely depends on the type of substance which constitutes the system
- e.g. Chemically reacting system
- e.g. Falling body



(Refer Slide Time 3:40)

Quiz

1. Is air a pure substance? ✓ ✗
2. Is a combusting H_2-O_2 mixture a pure substance? ✗
3. Is a mixture of steam and water a pure substance? ✓



Figure 1.

Let's try to answer the questions shown in Fig. 1.

1. Is air a pure substance?

Air is a mixture of around 76 % nitrogen by mass, 23% of oxygen by mass and some other gases. At room temperature and atmospheric pressure, air is a mixture of all these gases. For time being, assume it is just the mixture of nitrogen and oxygen. The composition of air is uniform. If we start cooling the air, at around -183 degree Celsius, oxygen will become liquid first. Hence, we have a mixture of liquid oxygen and gaseous nitrogen. The compositions are different. Hence, at this temperature, the air is not a pure substance. However, for the most practical applications, we do not have such low temperatures, and air behaves as a pure substance. Hence, air is or is not a pure substance based on the conditions during the process.

2. Is a combusting $H_2 - O_2$ mixture a pure substance?

After combustion, we are left with liquid water as a product of the chemical reaction between H_2 and O_2 . The composition changes during the process. Hence, a combusting $H_2 - O_2$ mixture is not a pure substance.

3. Is mixture of steam and water a pure substance?

The chemical composition of steam (water in vapour form) and liquid water are the same. As far as the chemical composition does not change during the process, a mixture of steam and water is a pure substance.

We are interested in finding out the properties of such pure substances during a process.

(Refer Slide Time 7:39)

- Why is this important?
- The **two-property** rule is applicable
- “The state of a pure substance of given mass can be specified in terms of two independent properties, in the absence of effects due to gravity, motion, electricity, magnetism, elastic deformation, etc.”



We can use a two-property rule for a system consisting of a pure substance (which in some sense a reduction of the Gibb’s phase rule). It is stated as following: the state of a pure substance of given mass can be specified in terms of two independent properties in the absence of effects due to gravity, motion, electricity, magnetism, elastic deformation, etc.

Our goal while solving the tutorial problems is to find these two independent properties which define the state of a system (made of a pure substance) under consideration. These two properties can then be used to find other properties because the state of the system is known.

(Refer Slide Time 10:10)



- What does this mean?
 - If the substance has only one mode of energy storage –namely, that of internal energy, two independent properties are adequate to define its state (for given mass)

– e.g. Pure substance in piston cylinder arrangement

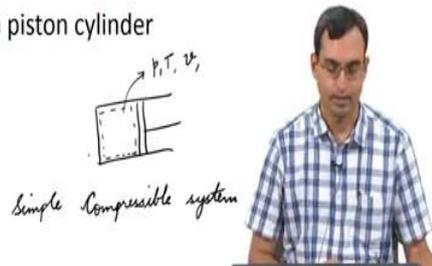


Figure 2.

While implementing the two-property rule, we assume that there is only one mode of energy storage, and it is the internal energy (because all other forms of energy are not there if we look at the statement of the two-property rule).

Consider a piston-cylinder assembly consisting of air as shown in Fig. 2. The conditions are such that the air is a pure substance here. If we know two independent properties such as pressure and temperature (which are intensive) of this system, we can define the state of the system and find out other properties such as specific volume, absolute internal energy or enthalpy (with respect to some datum).

We will often come across a simple compressible system containing a pure substance. For such a system, electric, magnetic or gravity forces and changes in potential and kinetic energy are not considered in the analysis.

(Refer Slide Time 13:08)

- Relationships between various properties for different types of pure substances
 - (i) ideal gas
 - (ii) mixture of ideal gases
 - (iii) steam/ water substance. H_2O
vapour + liquid



Figure 3.

According to two-property rule, once we know two independent properties of a system, the state of the system can be defined. Using these two properties, we can find other properties through property relations.

Based on these property relations, we can classify the substances as shown in Fig. 3: ideal gas, a mixture of ideal gases, steam/water substance (for the purpose of this course, we are going to restrict ourselves to these substances).

We will cover the concept of ideal gas and a mixture of ideal gas a little later in the course. We already saw that steam (water vapor) or water or a mixture of steam and water is a pure substance. There can be other sort of mixtures such liquid ammonia and gaseous ammonia.