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Thermodynamics-I

Chapter : 01 (Fundamental Concepts)

1.2 Definitions and Fundamental Ideas of Thermodynamics

As with all sciences, thermodynamics is concerned with the mathematical modeling of the real world. In order that the mathematical deductions are consistent, we need some precise definitions of the basic concepts. The following is a discussion of some of the concepts we will need. Several of these will be further amplified in the lectures and in other handouts. If you need additional information or examples concerning these topics, they are described clearly and in-depth in (SB&VW). They are also covered, although in a less detailed manner, in Chapters 1 and 2 of the book by Van Ness.

1.2.1 The Continuum Model

Matter may be described at a molecular (or microscopic) level using the techniques of statistical mechanics and kinetic theory. For engineering purposes, however, we want ``averaged" information, i.e., a macroscopic, not a microscopic, description. There are two reasons for this. First, a microscopic description of an engineering device may produce too much information to example, of For standard manage. air at temperature and pressure contains 10^{16} molecules (VW, S & B:2.2), each of which has a position and a velocity. Typical engineering applications involve more than 10^{20} molecules. Second, and more importantly, microscopic positions and velocities are generally not useful for determining how macroscopic systems will act or react unless, for instance, their total effect is integrated. We therefore neglect the fact that real substances are composed of discrete molecules and model matter from the start as a smoothed-out continuum. The information we have about a continuum represents the microscopic information averaged over a volume. Classical thermodynamics is concerned only with continua.

1.2.2 The Concept of a System

A thermodynamic **system** is a quantity of matter of fixed identity, around which we can draw a boundary (see Figure <u>1.3</u> for an example). The boundaries may be fixed or moveable. Work or heat can be transferred across the system boundary. Everything outside the boundary is the **surroundings**.

When working with devices such as engines it is often useful to define the system to be an identifiable volume with *flow* in and out. This is termed a **control volume**. An example is shown in Figure <u>1.5</u>.

A **closed system** is a special class of system with boundaries that matter cannot cross. Hence the principle of the conservation of mass is automatically satisfied whenever we employ a closed system analysis. This type of system is sometimes termed a **control mass**.







Figure 1.4: Boundary around electric motor (system)



Figure 1.5: Sample control volume

1.2.3 The Concept of a ``State''

The **thermodynamic state** of a system is defined by specifying values of a set of measurable **properties** sufficient to determine all other properties. For fluid systems, typical properties are pressure, volume and temperature. More complex systems may require the specification of more unusual properties. As an example, the state of an electric battery requires the specification of the amount of electric charge it contains.

Properties may be **extensive** or **intensive**. Extensive properties are additive. Thus, if the system is divided into a number of sub-systems, the value of the property for the whole system is equal to the sum of the values for the parts. *Volume* is an extensive property. Intensive properties do not depend on the quantity of matter present. *Temperature* and *pressure* are intensive properties.

Specific properties are extensive properties per unit mass and are denoted by lower case letters. For example:

specific volume = V/m = v.

Specific properties are intensive because they do not depend on the mass of the system.

The properties of a **simple system** are uniform throughout. In general, however, the properties of a system can vary from point to point. We can usually analyze a general system by sub-dividing it (either conceptually or in practice) into a number of simple systems in each of which the properties are assumed to be uniform.

It is important to note that properties describe states *only* when the system is in equilibrium.

Muddy Points

Specific properties (MP $\underline{1.1}$)

What is the difference between extensive and intensive properties? (MP $\underline{1.2}$)

1.2.4 The Concept of ``Equilibrium''

The state of a system in which properties have definite, unchanged values as long as external conditions are unchanged is called an equilibrium state.



A system in thermodynamic equilibrium satisfies:

- 1. mechanical equilibrium (no unbalanced forces)
- 2. thermal equilibrium (no temperature differences)
- 3. chemical equilibrium.

1.2.5 The Concept of a ``Process''

If the state of a system changes, then it is undergoing a **process**. The succession of states through which the system passes defines the **path** of the process. If, at the end of the process, the properties

have returned to their original values, the system has undergone a **cyclic process** or a **cycle**. Note that even if a system has returned to its original state and completed a cycle, the state of the surroundings may have changed.

1.2.6 Quasi-Equilibrium Processes

We are often interested in charting thermodynamic processes between states on thermodynamic coordinates. Recall from the end of Section <u>1.2.3</u>, however, that properties define a state only when a system is in equilibrium. If a process involves finite, unbalanced forces, the system can pass through non-equilibrium states, which we cannot treat. An extremely useful idealization, however, is that only ``infinitesimal" unbalanced forces exist, so that the process can be viewed as taking place in a series of ``quasi-equilibrium" states. (The term *quasi* can be taken to mean ``as if;" you will see it used in a number of contexts such as quasi-one-dimensional, quasi-steady, etc.) For this to be true the process must be slow in relation to the time needed for the system to come to equilibrium internally. For a gas at conditions of interest to us, a given molecule can undergo roughly 10^{10} molecular collisions per second, so that, if ten collisions are needed to come to equilibrium, the equilibration time is on the order of 10^{-9} seconds. This is generally much shorter than the time scales associated with the bulk properties of the flow (say the time needed for a fluid particle to move some significant fraction of the length of the device of interest). Over a large range of parameters, therefore, it is a very good approximation to view the thermodynamic processes as consisting of such a succession of equilibrium states, which we can chart. [VW, S& B: 2.3-2.4]

The figures below demonstrate the use of thermodynamics coordinates to plot isolines, lines along

which a property is constant. They include constant temperature lines, or isotherms, on a -

v diagram, constant volume lines, or **isochors** on a $T - {p \over v}$ diagram, and constant pressure lines, or **isobars**, on a T - v diagram for an ideal gas.

Real substances may have phase changes (water to water vapor, or water to ice, for example), which we can also plot on thermodynamic coordinates. We will see such phase changes plotted and used for liquid-vapor power generation cycles in Chapter <u>8</u>. A preview is given in Figure <u>1.15</u> at the end of this chapter.





1.2.7 Equations of state

It is an experimental fact that two properties are needed to define the state of any pure substance in equilibrium or undergoing a steady or quasi-steady process. [VW, S & B: 3.1, 3.3]. Thus for a simple compressible gas like air,

$$P = P(v,T)$$
, or $v = v(P,T)$, or $T = T(P,v)$,

where v is the volume per unit mass, In words, if we know v and T we know P, etc.

$$f(P, v, T) = 0$$

Any of these is equivalent to an equation , which is known as an equation of state. The equation of state for an ideal gas, which is a very good approximation to real gases at conditions that are typically of interest for aerospace applications $1-2^{-2}$, is

 $P\bar{v} = \mathcal{R}T,$

where \bar{v} is the volume per mol of gas and \mathcal{R} is the ``Universal Gas 8.31 kJ/kmol-K

Constant,"

A form of this equ $\mathcal{M}n$ which is more useful in fluid flow problems is obtained if we divide by the molecular weight, :

Pv = RT, or $P = \rho RT$

 \mathcal{R}/\mathcal{M}

where R is , which has a different value for different gases due to the different molecular

R = 0.287 kJ/kg-K

weights. For air at room conditions,

1.3 Changing the State of a System with Heat and Work

Changes in the state of a system are produced by interactions with the environment through *heat* and *work*, which are two different modes of energy transfer. During these interactions, equilibrium (a static or quasi-static process) is necessary for the equations that relate system properties to one-another to be valid.

1.3.1 Heat

Heat is energy transferred due to temperature differences only.

- 1. Heat transfer can alter system states;
- 2. Bodies don't ``contain" heat; heat is identified as it comes across system boundaries;
- 3. The amount of heat needed to go from one state to another is path dependent;
- 4. Adiabatic processes are ones in which no heat is transferred.

1.3.2 Zeroth Law of Thermodynamics

With the material we have discussed so far, we are now in a position to describe the Zeroth Law. Like the other laws of thermodynamics we will see, the Zeroth Law is based on observation. We start with two such observations:

- 1. If two bodies are in contact through a thermally-conducting boundary for a sufficiently long time, no further observable changes take place; *thermal equilibrium* is said to prevail.
- 2. Two systems which are individually in thermal equilibrium with a third are in thermal equilibrium with each other; all three systems have the same value of the property called *temperature*.

These closely connected ideas of temperature and thermal equilibrium are expressed formally in the ``Zeroth Law of Thermodynamics:"

Zeroth Law: There exists for every thermodynamic system in equilibrium a property called temperature. Equality of temperature is a necessary and sufficient condition for thermal equilibrium.

The Zeroth Law thus *defines a property* (temperature) and *describes its behavior*^{1,3}.

Note that this law is true regardless of how we measure the property temperature. (Other relationships we work with will typically require an absolute scale, so in these notes we use either

 $K = 273.15 + {}^{\circ}C$ $R = 459.9 + {}^{\circ}F$ the Kelvin or Rankine scales. Temperature scales will be discussed further in Section 6.2.) The zeroth law is depicted schematically in Figure 1.8.



Figure 1.8: The zeroth law schematically

1.3.3 Work

[VW, S & B: 4.1-4.6]

Section 1.3.1 stated that *heat* is a way of changing the energy of a system by virtue of a temperature difference only. Any other means for changing the energy of a system is called *work*. We can have push-pull work (e.g. in a piston-cylinder, lifting a weight), electric and magnetic work (e.g. an electric motor), chemical work, surface tension work, elastic work, etc. In defining work, we focus on the effects that the system (e.g. an engine) has on its surroundings. Thus we define work as being positive when the system does work on the surroundings (energy leaves the system). If work is done on the system (energy added to the system), the work is negative.

Consider a simple compressible substance, for example, a gas (the system), exerting a force on the surroundings via a piston, which moves through some distance, l (Figure <u>1.9</u>). The work $W_{\text{on surr.}}$ done *on* the surroundings, , is

 $dW_{
m on\ surr.}$ = Force on surr. $\times dl$

$$dW_{\text{on surr.}} = \frac{\text{Force on surr.}}{\text{Area}} \times (\text{Area} \times dl)$$

 $dW_{\text{on surr.}}$ = pressure of surr. × dVolume

- T /

 $dW_{\rm on \ surr.} = p_x \times dV$

therefore

$$W_{\text{on surr.}} = \int_{V_1}^{V_2} p_x dV.$$

Why is the pressure p_x instead of p_s ? Consider $p_x = 0$ (vacuum). No work is done on the surroundings even though p_s changes and the system volume changes.

Use of p_x instead of p_s is often inconvenient because it is usually the state of the system that we are interested in. The external pressure can only be related to the system pressure if $p_x \approx p_s$. For this to occur, there cannot be any friction, and the process must also be slow enough so that pressure differences due to accelerations are not significant. In other words, we require a ``quasipasite p_s $\approx p_x$ $p_x = p_s \pm dp$ static" process, . Consider .

$$W = \int_{V_1}^{V_2} p_x dV = \int_{V_1}^{V_2} (p_s \pm dp) dV = \int_{V_1}^{V_2} p_s dV \pm dp dV.$$

 $\frac{dp}{dp}$ is small (the process is quasi-static),

$$W = \int_{V_1}^{V_2} p_s dV,$$

and the work done by the system is the same as the work done on the surroundings.

Under these conditions, we say that the process is ``reversible." The conditions for reversibility are that:

1. If the process is reversed, the system *and the surroundings* will be returned to the original states.

dp

2. To reverse the process we need to apply only an infinitesimal . A reversible process can be altered in direction by infinitesimal changes in the external conditions (see Van Ness, Chapter 2).

Remember this result, that we can only relate work done on surroundings to system pressure for reversible) processes. the case of ``free expansion," quasi-static (or In a $p_{x} = 0$ p_s is not related to p_x (and thus, not related to the work) because the where (vacuum), system is not in equilibrium.

We can write the above expression for work done by the system in terms of the specific volume, v,

$$W = m \int_{v_1}^{v_2} p_s dv.$$

where m is the mass of the system. Note that if the system volume *expands* against a force, work is done *by the system*. If the system volume *contracts* under a force, work is done *on the system*.



Figure 1.9: A closed system (dashed box) against a piston, which moves into the surroundings



Figure 1.10: Work during an irreversible process

For simple compressible substances *in reversible processes*, the work done can be represented as the area under a curve in a pressure-volume diagram, as in Figure 1.11(a).



Figure 1.11: Work in P - V coordinates

Key points to note are the following:

- 1. Properties only depend on states, but work is path dependent (depends on the path taken between states); therefore work is not a property, and not a state variable. W_{1-2}
- 2. When we say , the work between states 1 and 2, we need to specify the path.

$$\int pdV$$

3. For *irreversible* (non-reversible) processes, we cannot use ; either the work must be given or it must be found by another method.

Muddy Points

How do we know when work is done? (MP $\underline{1.3}$)

1.3.3.1 Example: Work on Two Simple Paths

Consider Figure <u>1.12</u>, which shows a system undergoing quasi-static processes for which we can $\int p dV$ calculate work interactions as



Figure 1.12: Simple processes

$$W = 2p_0(2V_0 - V_0) = 2p_0V_0$$

Along Path a:

$$W = p_0(2V_0 - V_0) = p_0V_0$$

Along Path b:

Practice Questions

Given a piston filled with air, ice, a bunsen burner, and a stack of small weights, describe

- 1. how you would use these to move along either path a or path b above, and
- 2. how you would physically know the work is different along each path.

1.3.3.2 Example: Work Done During Expansion of a Gas

Consider the quasi-static, isothermal expansion of a thermally ideal gas from p_1 , V_1 , p_2 , V_2 , as shown in Figure <u>1.13</u>. To find the work we must know the path. Is it specified? Yes, the path is specified as isothermal.



Figure 1.13: Quasi-static, isothermal expansion of an ideal gas

The equation of state for a thermally ideal gas is

 $pV = n\mathcal{R}T,$

where n is the number of moles, \mathcal{R} is the Universal gas constant, and V is the total system volume. We write the work as above, substituting the ideal gas equation of state,

$$W = \int_{V_1}^{V_2} \frac{n\mathcal{R}T}{V} dV \qquad = n\mathcal{R}T \int_{V_1}^{V_2} \frac{dV}{V} \qquad = n\mathcal{R}T \ln\left(\frac{V_2}{V_1}\right)$$

also for $T={
m constant}$, ${\displaystyle {{p_1V_1=p_2V_2}}\over }$, so the work done by the system is

$$W = n\mathcal{R}T\ln\left(\frac{V_2}{V_1}\right) = n\mathcal{R}T\ln\left(\frac{p_1}{p_2}\right)$$

or in terms of the specific volume and the system mass,

$$W = mRT \ln\left(\frac{v_2}{v_1}\right) = mRT \ln\left(\frac{p_1}{p_2}\right).$$

1.3.4 Work vs. Heat - which is which?

We can have one, the other, or both: it depends on what crosses the system boundary (and thus, on how we define our system). For example consider a resistor that is heating a volume of water (Figure 1.14):



Figure 1.14: A resistor heating water

- 1. If the water is the system, then the state of the system will be changed by heat transferred from the resistor.
- 2. If the system is the water *and* the resistor combined, then the state of the system will be changed by electrical work.

1.4 Muddiest Points on Chapter 1

MP 1..1 Specific properties

Energy, volume, enthalpy are all extensive properties. Their value depends not only on the temperature and pressure but also on ``how much," i.e., what the mass of the system is. The internal energy of two kilograms of air is twice as much as the internal energy of one kilogram of air. It is very often useful to work in terms of properties that do not depend on the mass of the system, and for this purpose we use the specific volume, specific energy, specific enthalpy, etc., which are the values of volume, energy, and enthalpy for a unit mass (kilogram) of the substance. For system mass m, the relations between quantities а of the two are: V = mv U = mu H = mh

MP 1..2 What is the difference between extensive and intensive properties?

Intensive properties are properties that do not depend on the quantity of matter. For example, pressure and temperature are intensive properties. Energy, volume and enthalpy are all extensive properties. Their value depends on the mass of the system. For example, the enthalpy of a certain

mass of a gas is doubled if the mass is doubled; the enthalpy of a system that consists of several parts is equal to the sum of the enthalpies of the parts.

MP 1..3 How do we know when work is done?

A rigorous test for whether work is done or not is whether a weight could have been raised in the process under consideration. I will hand out some additional material to supplement the notes on this point, which seems simple, but can be quite subtle to unravel in some situations.



Figure 1.15: Pressure-temperature-volume surface for a substance that expands on freezing (from VW, S & B: 3.7)

Chapter : 02 (Laws of Perfect Gases)

2.1 Perfect Gas

The terms perfect gas and ideal gas are sometimes used interchangeably, depending on the particular field of physics and engineering. Sometimes, other distinctions are made, such as between thermally perfect gas and calorically perfect gas, or between imperfect, semi-perfect, perfect, and ideal gases.

2.2 Laws of Perfect Gases

A perfect gas (or an ideal gas) may be defined as a state of a substance, whose evaporation from its liquid state is complete. It may be noted that if its evaporation is partial, the substance is called vapor. A vapor contains some particles of liquid in suspension. The behavior of super-heated vapors is similar to that of a perfect gas.

The physical properties of a gas are controlled by the following three variables :

- 1. Pressure exerted by the gas,
- 2. Volume occupied by the gas, and
- 3. Temperature of the gas.

The behavior of a perfect gas, undergoing any change in these three variables, is governed by the following laws :

1. Boyles law. This law was formulated by Robert Boyle in 1662. It states, "The absolute pressure of a given mass of a perfect gas varies inversely as its volume, when the temperature remains constant." Mathematically,

The more useful form of the above equation is :

p1v1 = p2v2 = p3v3 = .. = Constant

where suffixes 1, 2 and 3 refer to different sets of conditions.

2. Charles' law. This law was formulated by a Frenchman Jacques A.C. Charles in about 1787. It may be stated in two different forms :

(i) "The volume of a given mass of a perfect gas varies directly as its absolute temperature, when the absolute pressure remains constant." Mathematically,

where suffixes 1, 2 and 3 refer to different sets of conditions.

(ii) "All perfect gases change in volume by 1 / 273 th of its original volume at 0° C for every 1° C change in temperature, when the pressure remains constant."

Let

Vo = Volume of a given mass of gas at 0° C, and Vt = Volume of the same mass of gas at t° C.

Then, according to the above statement,

where

 $T = Absolute temperature corresponding to t^{\circ} C.$ To = Absolute temperature corresponding to 0° C.

A little consideration will show, that the volume of a gas goes on decreasing by 1/273th of its original volume for every 1°C decrease in temperature. It is thus obvious, that at a temperature of -273° C, the volume of the gas would become zero. The temperature at which the volume of a gas becomes zero is called absolute zero temperature.

3. Gay Lussac law. This law states, "The absolute pressure of a given mass of a perfect gas varies directly as its absolute temperature, when the volume remains constant." Mathematically

where suffixes 1, 2 and 3.... refer to different sets of conditions.

Note : In dealing with a perfect gas, the values of pressure and temperature are expressed in absolute units.

2.3 General Equation

The Ideal gas law is the equation of state of a hypothetical ideal gas. It is a good approximation to the behaviour of many gases under many conditions, although it has several limitations. The ideal gas equation can be written as

PV = nRT

Where,

- P is the pressure of the ideal gas.
- V is the volume of the ideal gas.
- n is the amount of ideal gas measured in terms of moles.
- R is the **universal gas constant**.

• T is the temperature.

According to the Ideal Gas equation-

The product of Pressure & Volume of a gas bears a constant relation with the product of Universal gas constant and the temperature.

i.e. pv=nRT

2.4 Universal Gas Constant (R)

When the <u>molecular mass</u> of any gas is multiplied by its specific gas constant (R), it is observed that the product R is always the same for all gases. This product is called universal gas constant and it is denoted as R.

Note: From the SI system the value of the universal gas constant is 8.314 kJ/mole.K

2.5 Specific Heat

The specific heat is the amount of <u>heat</u> per unit mass required to raise the <u>temperature</u> by one degree Celsius. The relationship between heat and temperature change is usually expressed in the form shown below where c is the specific heat. The relationship does not apply if a <u>phase change</u> is encountered, because the heat added or removed during a phase change does not change the temperature.

Chapter : 03 (Thermodynamics processes)

Thermodynamic Processes

Everyone is hot. Or rather, everyone has heat. Every atom and molecule in your body undergoes constant random motions that are impossible to predict. Those random motions are what we call heat energy.

Thermodynamics is the study of the movement of heat. If you touch a block of ice, it isn't always pleasant unless it's a really hot day. If you touch a hot pan out of the oven you'll burn yourself. Both of those things happen because of how fast heat is moving. The heat from the hot pan moves into your hand rapidly, and when touching an ice cube, you lose your own body heat fast. Heat transfers from hot places to cold places - or in other words, heat spreads out. Extreme heat or cold can damage our tissues, so it's a pretty important thing to understand. It's also how we've been able to build refrigerators and large insulated coolers to take to the beach.

These are examples of the many things we can do with heat if we understand how it moves within or between systems. A system is just a particular object or area we're looking at. Our system could be the inside of a thermos flask, or it could be the whole human body or just our skin, or the gas inside a piston. We choose the system we want to look at for convenience.

Then we can look at how heat moves in, out and within that system. We can look at how the system changes. A **thermodynamic process** is any process that involves heat energy moving within a system or between systems. In this lesson, we're going to look at the four types of thermodynamic processes.

The Four Types of Thermodynamic Processes

The four types of thermodynamic process are isobaric, isochoric, isothermal and adiabatic. Those terms are pretty hard to understand just from the names, so let's break them down one at a time.

Isobaric Process

An **isobaric process** is one where the pressure of the system (often a gas) stays constant. '**Iso**' means the same, and '**baric**' means pressure. Pressure is related to the amount of force that the molecules apply to the walls of the container. Imagine that you have a gas inside a movable piston and you heat that gas up. By heating the gas up you make the molecules move faster, which would normally increase the pressure. But at the same time the piston expands, increasing the volume and giving the molecules more room to move. Since the walls of the container are now bigger, the pressure can stay the same even though the molecules are moving faster. That makes it an isobaric process.

Isochoric Process

An **isochoric process** is one where the volume of the system stays constant. Again, **'iso'** means the same and **'choric'** means volume. Volume is the amount of space the material takes up. So this would be like heating a gas in a solid, non-expandable container. The molecules would move faster and the pressure would increase, but the size of the container stays the same.

Isothermal Process

An **isothermal process** is a <u>change</u> of a *system*, in which the <u>temperature</u> remains constant: $\Delta T = 0$. This typically occurs when a system is in contact with an outside thermal reservoir (<u>heat bath</u>), and the change in the system will occur slowly enough to allow the system to continue to adjust to the temperature of the reservoir through <u>heat</u> exchange. In contrast, an <u>adiabatic process</u> is where a system exchanges no heat with its surroundings (Q = 0). In other words, in an isothermal process, the value $\Delta T = 0$ and therefore the change in <u>internal energy</u> $\Delta U = 0$ (only for an ideal gas) but $Q \neq 0$, while in an adiabatic process, $\Delta T \neq 0$ but Q = 0.

Adiabatic Process

The thermodynamic process in which there is no exchange of heat from the system to its surrounding neither during expansion nor during compression.

Adiabatic process can be either **reversible or irreversible.** Following are the essential conditions for adiabatic process to take place:

- System must be perfectly insulated from the surrounding.
- The process must be carried out quickly so that there is sufficient amount of time for heat transfer to take place.



For instance, the <u>gas compression</u> within an engine cylinder is expected to happen so fast that on the compression process time scale, a minimum amount of the energy of the system could be produced and sent out in the form of heat.

Despite the cylinders being not insulated and having a conductive nature, the process is deemed to be adiabatic. The same could be considered to be true for the enlargement process of such a system.

Adiabatic Process Equation

Following is the adiabatic process equation:

 $PV^{\gamma} = constant$

Where,

- P is the pressure of the system
- V is the volume of the system
- γ is the adiabatic index and is defined as the ratio of heat capacity at constant pressure C_p to heat capacity at constant volume C_v

Reversible Adiabatic Process

A Reversible Adiabatic Process is also called an Isentropic Process. It is an idealized <u>thermodynamic process</u> that is adiabatic and in which the work transfers of the system are frictionless; there is no transfer of heat or of matter and the process is reversible. Such an idealized process is useful in engineering as a model of and basis of comparison for real processes.

Chapter : 04 (Laws of Thermodynamics)

Zeroth Law of Thermodynamics:

The Thermodynamics Zeroth Law states that if two systems are at the same time in thermal equilibrium with a third system, they are in equilibrium with each other. If an object with a higher temperature comes in contact with an object of lower temperature, it will transfer heat to the lower temperature object. The objects will approach the same temperature and in the absence of loss to other objects, they will maintain a single constant temperature. Therefore, thermal equilibrium is attained.



If objects 'A' and 'C' are in thermal equilibrium with 'B', then object 'A' is in thermal equilibrium with object 'C'. Practically this means all three objects are at the same temperature and it forms the basis for comparison of temperatures.

The First Law of thermodynamics

The **increase** of the *internal energy* of a system is equal to the sum of the *heat* added **to** the system plus the *work* done **on** the system.

In symbols:

$$dU = dQ + dW. 7.1.1$$

You may regard this, according to taste, as any of the following

A fundamental law of nature of the most profound significance;

or A restatement of the law of conservation of energy, which you knew already;

- or A recognition that heat is a form of energy.
- or A definition of *internal energy*

Note that some authors use the symbol E for internal energy. The majority seem to use U, so we shall use U here. Note also that some authors write the first law as dU = dQ - dW, so you have to be clear what the author means by dW. A scientist is likely to be interested in what happens to a system when you do work on it, and is likely to define dW as the work done on the system, in which case dU = dQ + dW. An engineer, in the other hand, is more likely to be asking how much work can be done by the system, and so will prefer dW to mean the work done by the system, in which case

dU = dQ - dW.

The internal energy of a system is made up of many components, any or all of which may be increased when you add heat **to** the system or do work **on** it. If the system is a gas, for example, the internal energy includes the translational, vibrational and rotational kinetic energies of the molecules. It also includes potential energy terms arising from the forces between the molecules, and it may also include excitational energy if the atoms are excited to energy levels above the ground state. It may be difficult to calculate the total internal energy, depending on which forms of energy you take into account. And of course the *potential* energy terms are always dependent on what state you define to have zero potential energy. Thus it is really impossible to define the total internal energy of a system uniquely. What the first law tells us is the *increase* in internal energy of a system when heat is added **to** it and work is done **on** it.

Note that internal energy is a *function of state*. This means, for example in the case of a gas, whose *state* is determined by its pressure, volume and temperature, that the internal energy is uniquely determined (apart from an arbitrary constant) by P, V and T – i.e. by the state of the gas. It also means that in going from one state to another (i.e. from one point in PVT space to another), the change in the internal energy is *route-independent*. The internal energy may be changed by performance of work or by addition of heat, or some combination of each, but, whatever combination of work and energy is added, the change in internal energy depends only upon the initial and final states. This means, mathematically, that dU is an *exact differential* (see Chapter 2, Section 2.1). The differentials dQ and dW, however, are *not* exact differentials.

Note that if work is done on a Body by forces in the Rest of the Universe, and heat is transferred to the Body from the Rest of the Universe (also known as the Surroundings of the Body), the internal energy of the Body increases by dQ + dW, while the internal energy of the Rest of the Universe

(the Surroundings) decreases by the same amount. Thus the internal energy of the Universe is constant. This is an equivalent statement of the First Law. It is also sometimes stated as "Energy can neither be created nor destroyed".

There are many ways in which you can do work **on** a system. You may compress a gas; you may magnetize some iron; you may charge a battery; you may stretch a wire, or twist it; you may stir a beaker of water.

Some of these processes are *reversible*; others are irreversible or dissipative. The work done in compressing a gas is reversible if it is quasistatic, and the internal and external pressures differ from each other always by only an infinitesimal amount. Charging a lead-acid car battery may be almost reversible; charging or discharging a flashlight battery is not, because it has a high internal resistance, and the chemical reactions are irreversible. Stretching or twisting a wire is reversible as long as you do not exceed the elastic limit. If you do exceed the elastic limit, it will not return to its original length; that is, it exhibits elastic *hysteresis*. When you magnetize a metal sample, you are doing work on it by rotating the little magnetic moments inside the metal. Is this reversible? To answer this, read about the phenomenon of magnetic hysteresis in Chapter 12, Section 12.6, of Electricity and Magnetism.

Work that is reversible is sometimes called *configuration work*. It is also sometimes called PdV *work*, because that is a common example. Work that is not reversible is sometimes called *dissipative work*. Forcing an electric current through a wire is clearly dissipative.

For much of the time, we shall be considering the work that is done **on** a system by *compressing* it. Solids and liquids require huge pressures to change their volumes significantly, so we shall often be considering a *gas*. We imagine, for example, that we have a quantity of gas held in a cylinder by a piston. The work done in compressing it in a reversible process is -PdV. If you are asking yourself "Is *P* the pressure that the gas is exerting on the piston, or the pressure that the piston is exerting on the gas?", remember that we are considering a reversible and quasistatic process, so that the difference between the two is at all stages infinitesimal. Remember also that in calculus, if *x* is some scalar quantity, the expression *dx* doesn't mean vaguely the "change" in *x* (an ill-defined

word), but it means the *increment* or *increase* in x. Thus the symbol dV means the *increase* in volume, which is negative if we are doing work **on** the gas by *compressing* it. In any case whether you adopt the scientist convention or the engineer convention (try both) the first law, when applied to the compression or expansion of a gas, becomes

$$dU = dQ - PdV. 7.2.1$$

7.3 Entropy

Definition: If an infinitesimal quantity of heat dQ is added to a system at temperature *T*, and if no irreversible work is done on the system, the increase in entropy dS of the system is defined by

Question: What are the SI units of entropy?

Note that, since dQ is supposed to be an infinitesimal quantity of heat, any increase in temperature is also infinitesimal. Note also that, as with internal energy, we have defined only what is meant by an *increase* in entropy, so we are not in any position to state what *the* entropy of a system is. (Much later, we shall give evidence that the molar entropy of all substances is the same at the absolute zero of temperature. It may then be convenient to define the zero of the entropy scale as the molar entropy at the absolute zero of temperature. At present, we have not yet shown that there is an absolute zero of temperature, let alone of entropy.)

To the question "What is meant by <u>entropy?</u>" a student will often respond with "Entropy is the state of disorder of a system." What a vague, unquantitative and close to meaningless response that is! What is meant by "disorder"? What could possibly be meant by a statement such as "The state of disorder of this system is 5 joules per kelvin"? Gosh! I would give nought marks out of ten for such a response! Now it *is* true, when we come to the subjects of statistical mechanics, and statistical thermodynamics and mixing theory, that there is a sense in which the entropy of a system is some sort of measure of the state of disorder, in the sense that the more disordered or randomly mixed a system is, the higher its entropy, and random processes do lead to more disorder and to higher entropy. Indeed, this is all connected to the second law of thermodynamics, which we haven't touched upon yet. But please, at the present stage, entropy is defined as I have stated above, and, for the time being, it means nothing less and nothing more. It will have been noted that, in our definition of entropy so far, we specified that no irreversible work be done on the system. (The addition of heat to a system – e.g. by allowing heat to flow naturally into it from a hotter body – is irreversible.) What if some irreversible work *is* done? Let us suppose that we do work on a gas in two ways. (I choose a gas in this discussion, because it is easier to imagine compressing a gas with PdV work than it is with a solid or a liquid, because the compressibility of a solid or a liquid is relatively low. But the same argument applies to any substance.) We compress it with the piston, but, at the same time, we also stir it with a paddle. In that case, the work done **on** the gas is *more* than -PdV. (Remember that -PdV is positive.) If we didn't compress it at all, but only stirred it, dV would be zero, but we would still have done work on

the gas by stirring. Let's suppose the work done **on** the gas is $\delta W = -PdV + \delta W_{irr}$. The part δW_{irr} is the irreversible or dissipative part of the work done **on** the gas; it is unrecoverable as work, and is *irretrievably* converted to heat. You cannot use it to turn the paddle back. Nor can you cool the gas by turning the paddle backwards.

In other words, since dW_{irr} is irreversibly converted to heat, it is just as We can now define the increase of entropy in the irreversible process by $TdS = dQ + dW_{irr}$; that

is, $dS = \frac{dQ \pm dW_{irr}}{T}$.

though it were part of the addition of heat.

In summary,

$$d = dQ + dW$$
$$U = TdS _ PdV$$
$$d$$
$$U$$

and

apply whether there is reversible or irreversible work. But only if there is no irreversible (unrecoverable) work does dQ = TdS and dW = -PdV. If there is any irreversible work, $dW = -PdV + dW_{irr}$ and $dQ = TdS - dW_{irr}$.

Of course there are other forms of reversible work than PdV work; we just use the expansion of gases as a convenient example.

Note that P, V and T are state variables (together, they define the state of the system) and U is a function of state. Thus the *entropy*, too, is a *function of state*. That is to say that the change in entropy as you go from one point in *PVT*-space to another point is route-independent. If you return to the same point that you started at (the same state, the same values of P, V and T), there is no change in entropy, just as there is no change in internal energy.

Definition: The *specific heat capacity* C of a substance is the quantity of heat required to raise the temperature of unit mass of it by one degree. We shall return to the subject of heat capacity in Chapter 8. For the present, we just need to know what it means, in order to do the following exercise concerning entropy.

Exercise. A litre (mass = 1 kg) of water is heated from 0 °C to 100 °C. What is the increase of entropy? Assume that the specific heat capacity of water is $C = 4184 \text{ J kg}^{-1} \text{ K}^{-1}$, that it does not vary significantly through the temperature range of the question, and that the water does not expand significantly, so that no significant amount of work (reversible or irreversible) is done.

Solution. The heat required to heat a mass *m* of a substance through a temperature range dT is mCdT. The entropy gained then is $\frac{mCdT}{2}$. The entropy gained over a finite temperature range is

therefore $mC = \frac{T}{2} = mC \ln(T/T) = 1 \times 4184 \times \ln(373.15/273.15) = 1305 \text{ J K}^{-1}.$ $2 \qquad 1$ $\int_{T_{1}} T$

Т

The Second Law of Thermodynamics

In a famous lecture entitled *The Two Cultures* given in 1959, the novelist C. P. Snow commented on a common intellectual attitude of the day - that true education consisted of familiarity with the humanities, literature, arts, music and classics, and that scientists were mere uncultured technicians and ignorant specialists who never read any of the great works of literature. He described how he had often been provoked by such an attitude into asking some of the self-proclaimed intellectuals if they could describe the Second Law of Thermodynamics – a question to which he invariably received a cold and negative response. Yet, he said, he was merely asking something of about the scientific equivalent of "Have you read a work of Shakespeare?"

So I suggest that, if you have never read a work of Shakespeare, take a break for a moment from thermodynamics, go and read *A Midsummer Night's Dream*, and come back refreshed and ready to complete your well-rounded education by learning the Second Law of Thermodynamics.

We have defined entropy in such a manner that if a quantity of heat dQ is added reversibly to a system at temperature *T*, the increase in the entropy of the system is dS = dQ/T. We also pointed out that if the heat is transferred *irreversibly*, dS > dQ/T.

Now consider the following situation (figure VII.1).



dQ

An isolated system consists of two bodies, A at temperature T_1 and B at temperature T_2 , such that $T_2 > T_1$. Heat will eventually be exchanged between the two bodies, and on the whole more heat will be transferred from B to A than from A to B. That is, there will be a *net* transference of heat, dQ, from B to A. Perhaps this heat is transferred by radiation. Each body is sending forth numerous photons of energy, but there is, on the whole, a net flow of photons from B to A. Or perhaps the two bodies are in contact, and heat is being transferred by conduction. The vibrations in the hot body are more vigorous than those in the cool body, so there will be a net transfer of heat from B to A. However, since the emission of photons in the first case, and the vibrations in the second place, are random, it will be admitted that it is not impossible that at some time more photons may move from A to B than from B to A. Or, in the case of conduction, most of the atoms.

in A happen to be moving to the right while only a few atoms in B are moving to the left in the course of their oscillations. But, while admitting that this is in principle possible and not outside the laws of physics, it is exceedingly unlikely to happen in practice; indeed so unlikely as hardly to be taken seriously. Thus, in any natural, spontaneous process, without the intervention of an External Intelligence, it is almost certain that there will be a net transfer of heat from B to A. And this process, barring the most unlikely set of circumstances, is irreversible.

The hot body will *lose* an amount of entropy dQ/T_2 , while the cool body will *gain* an amount of entropy dQ/T_1 , which is greater than dQ/T_2 . Thus the entropy of the *isolated system as a whole increases* by $dQ/T_1 - dQ/T_2$.

From this argument, we readily conclude that any natural, spontaneous and irreversible thermodynamical processes taking place within an isolated system are likely to lead to an increase in entropy of the system. This is perhaps the simplest statement of the Second Law of Thermodynamics.

I have used the phrase "is likely to", although it will be realised that in practice the possibility that the entropy might decrease in a natural process is so unlikely as to be virtually unthinkable, even though it could in principle happen without violating any fundamental laws of physics.

You could regard the Universe as an isolated system. Think of a solid Body sitting somewhere in the Universe. If the Body is hot, it may spontaneously lose heat to the Rest of the Universe. If it is cold, it may spontaneously absorb heat from the Rest of the Universe. Either way, during the course of a spontaneous process, the entropy of the Universe increases.

The transference of heat from a hot body to a cooler body, so that both end at the same intermediate temperature, involves, in effect, the mixing of a set of fast-moving molecules and a set of slow-moving molecules. A similar situation arises if we start with a box having a partition down the middle, and on one side of the partition there is a gas of blue molecules and on the other there is a gas of red molecules. If we remove the partition, eventually the gases will mix into one homogeneous gas. By only a slight extension of the idea of entropy discussed in courses in statistical mechanics, this situation can be described as an increase of entropy – called, in fact, the entropy of mixing. If you saw two photographs, in one of which the blue and red molecules were separated, and in the other the two colours were thoroughly mixed, you would conclude that the latter photograph was probably taken later than the former. But only "probably"; it is conceivable, within the laws of physics, that the velocities of the blue and red molecules separated themselves out without external intervention. This would be allowed perfectly well within the laws of physics. Indeed, if the velocities of all the molecules in the mixed gases were to be reversed, the gases would eventually separate into their two components. But this would seem to be so unlikely as never in practice to happen. The second law says that the entropy of an isolated system is *likely*

(*very* likely!) to increase with time. Indeed it could be argued that the increase of entropy is the criterion that defines the direction of the *arrow of time*. (For more on the arrow of time, see Section 15.12 of the notes on Electricity and Magnetism of this series. Also read the article on the arrow of time by Paul Davis, *Astronomy & Geophysics* (Royal Astronomical Society) **46**, 26 (2005). You'll probably also enjoy H. G. Wells's *The Time Machine*.)

Third Law of Thermodynamics

The **third law of thermodynamics** states as follows, regarding the properties of closed systems in <u>thermodynamic equilibrium</u>:

The <u>entropy</u> of a system approaches a constant value as its temperature approaches <u>absolute zero</u>.

This constant value cannot depend on any other parameters characterizing the closed system, such as pressure or applied magnetic field. At absolute zero (zero kelvin) the system must be in a state with the minimum possible energy. Entropy is related to the number of accessible microstates, and there is typically one unique state (called the ground state) with minimum energy.^[11] In such a case, the entropy at absolute zero will be exactly zero. If the system does not have a well-defined order (if its order is glassy, for example), then there may remain some finite entropy as the system is brought to very low temperatures, either because the system becomes locked into a configuration with non-minimal energy or because the minimum energy state is non-unique. The constant value is called the residual entropy of the system.^[21] The entropy is essentially a state-function meaning the inherent value of different atoms, molecules, and other configurations of particles including subatomic or atomic material is defined by entropy, which can be discovered near 0 K. The Nernst–Simon statement of the third law of thermodynamics concerns thermodynamic processes at a fixed, low temperature.

Chapter : 05 (Ideal and Real Gases)

4.1THE CHARACTERISTIC EQUATION OF STATE

At temperatures that are considerably in excess of critical temperature of a fluid, and also at very low pressure, the vapour of fluid tends to obey the equation

Pv/T = constant = R

In practice, no gas obeys this law rigidly, but many gases tend towards it. An imaginary ideal gas which obeys this law is called a perfect gas, and the equation pv /T = R, is called the characteristic equation of a state of a perfect gas. The constant R is called the gas constant. Each perfect gas has a different gas constant.

Units of R are Nm/kg K or kJ/kg K.Usually, the characteristic equation is written as pv = RT or for m kg, occupying V m³ pV = mRT ...

The characteristic equation in another form, can be derived by using kilogram-mole as a unit.

The kilogram-mole is defined as a quantity of a gas equivalent to M kg of the gas, where M is the molecular weight of the gas (e.g., since the molecular weight of oxygen is 32, then 1 kg mole of oxygen is equivalent to 32 kg of oxygen).

As per definition of the kilogram-mole, for m kg of a gas, we have m = nM

where n = number of moles. Substituting for m from eqn. gives

pV = nMRT or MR = pV nT

According to **Avogadro's hypothesis** the volume of 1 mole of any gas is the same as the volume of 1 mole of any other gas, when the gases are at the same temperature and pressure.

Therefore, V/n is the same for all gases at the same value of p and T. That is the quantity pV/nT is a constant for all gases. This constant is called universal gas constant, and is given the symbol, R0.

i.e., MR = R0 = pV/nT or pV = nR0T.

Since MR = R0, then R = Ro /M

It has been found experimentally that the volume of 1 mole of any perfect gas at 1 bar and 0°C is approximately 22.71 m3. Therefore from eqn.

1

 $R0 = pV/nT = 1 x10^{5}x 22.71/1 x273.15 = 8314.3 Nm/mole K$

Using eqn.the gas constant for any gas can be found when the molecular weight is known.

4.2VAN DER WAALS' EQUATION

Van der Waals' equation (for a real gas) may be written as:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

The constants a and b are specific constants and depend upon the type of the fluid considered, 'v' represents the volume per unit mass and R is the gas constant.

If the volume of one mole is considered then the above equation can be written as

$$\left(p + \frac{a}{v^{-2}}\right) (\overline{v} - b) = R_0 T$$

The units of p, v, T, R, a and b are as follows :p (N/m²), v (m³/kg-mol), T (K) and R = 8314 Nm/kg mol K, a [Nm⁴/(kg-mol)²], b (m³/kgmol).

S.No.	Substance	a Nm4/(kg-mol)2	b m³/kg-mol
1.	Hydrogen (H ₂)	25105	0.0262
2.	Oxygen (O ₂)	139250	0.0314
3.	Carbon dioxide (CO ₂)	362850	0.0423
4.	Helium (He)	3417620	0.0228
5.	Air	135522	0.0362
6.	Water (H ₂ O) vapour	551130	0.0300
7.	Mercury (Hg) vapour	2031940	0.0657

Constants of Van der Waals' Equation

4.3REDUCED PROPERTIES

The ratios of pressure, temperature and specific volume of a real gas to the corresponding critical values are called the **reduced properties**.

$$p_r = \frac{p}{p_c}$$
, $T_r = \frac{T}{T_c}$, $v_r = \frac{v}{v_c}$

4.4 LAW OF CORRESPONDING STATES

If any two gases have equal values of reduced pressure and reduced temperature, then they have same values of reduced volume ; i.e., vR = f(Tr, pr) for all gases and the function is the same. This law is most accurate in the vicinity of the critical point.

4.5 COMPRESSIBILITY CHART

The *compressibility factor* (*Z*) of any gas is a function of only two properties, usually temperature and pressure, so that Z = f(Tr, pr) except near the critical point. The value of *Z* for any real gas may be less or more than unity, depending on pressure and temperature conditions of the gas.

The general compressibility chart is plotted with Z versus pr for various values of Tr. This is constructed by plotting the known data of one or more gases and can be used for any gas. Such a chart is shown in Fig. 8.10. This chart gives best results for the regions well removed from the critical state for all gases.



Fig 4.1 Generalized Compressibility Chart

4.6 DALTON'S LAW

The pressure of a mixture of gases is equal to the sum of the partial pressures of the constituents. The partial pressure of each constituent is that pressure which the gas would exert if it occupied alone that volume occupied by the mixtures at the same temperature. By the consideration of mass, m = mA + mB

By Dalton's law, p = pA + pB

Dalton's law is based on experiment and is found to be obeyed more accurately by gas mixtures at low pressures. The law can be extended to any number of gases,

i.e., $m = mA + mB + mC + \dots$ or $m = \Sigma mi$

where mi = Mass of a constituent.

Similarly $p = pA + pB + pC + \dots$ or $p = \Sigma pi$ where pi = The partial pressure of a constituent

4.7 GIBBS-DALTON LAW

The internal energy, enthalpy, and entropy of a gaseous mixture are respectively equal to the sums of the internal energies, enthalpies, and entropies, of the constituents.

Each constituent has that internal energy, enthalpy and entropy, which it could have if it occupied alone that volume occupied by the mixture at the temperature of the mixture.

This statement leads to the following equations:

mu = $+ \text{ mAuB} + \text{ or mu} = \Sigma \text{ mi ui} \dots \text{ and}$ mAuA

mh = + mBhB + or mh = Σ mi hi ... and mAhA

ms =+ mBsB + or ms $= \Sigma$ mi si mAsA

4.8 VOLUMETRIC ANALYSIS OF A GAS MIXTURE

Let us consider a volume V of a gaseous mixture at a temperature T, consisting of three constituents A, B and C. Let us further assume that each of the constituents is compressed to a pressure p equal to the total pressure of the mixture, and let the *temperature remain constant*. The partial volumes then occupied by the constituents will be VA, VB and VC.

$m = m_A + m_B + m_C = \Sigma m_i$	V _A	V _Ē	Vc
$\mathbf{p} = \mathbf{p}_{A} + \mathbf{p}_{B} + \mathbf{p}_{C} = \sum \mathbf{p}_{I}$	p m _a	р m _в	p m _c
$n = n_A + n_B + n_C = \sum n_I$	n _A	n _B	n _c

Now using the eqn. pV = mRT, we get

$$m_A = \frac{p_A V}{R_A T}$$
 and
$$m_A = \frac{p V_A}{R_A T}$$

Now equating the two values for m_A , we have

$$\frac{p_A V}{R_A T} = \frac{p V_A}{R_A T} \quad i.e., \quad p_A V = p V_A$$
$$V_A = \frac{p_A}{p} V$$

or

In general therefore,

$$V_{i} = \frac{p_{i}}{p}V$$

i.e.,
$$\Sigma V_{i} = \sum \frac{p_{i}V}{p} = \frac{V}{p}\Sigma p_{i}$$

We know

,
$$p = \Sigma p_i$$
, therefore,
 $\Sigma V_i = V$

Thus, the volume of a mixture of gases is equal to the sum of the volumes of the individual constituents when each exists alone at the pressure and temperature of the mixture. This is the statement of another empirical law, the law of partial volumes, sometimes called **Amagat's law** or Leduc's law.

The analysis of mixtures, often, is simplified if it is carried out in moles. The mole is given by the equation

$$n = \frac{m}{M}$$

where, n = Number of moles,

m = Mass of gas, and

M = Molecular weight.

According to **Avogadro's law**, the number of moles of any gas is proportional to the volume of the gas at a given pressure and temperature. Referring to Fig. ,the volume V contains n moles of the mixture at p and T. In Fig., the gas A occupies a volume VA at p and T, and this volume contains nA moles. Similarly there are nB moles of gas B in volume VB and nC moles of gas C in volume VC.

$$\Sigma V_i = V$$
$$V_A + V_B + V_C = V$$

The total number of moles in the vessel must equal the sum of the moles of the individual constituents,

 $n = n_A + n_B + n_C = \Sigma n_i$

4.9 THE APPARENT MOLECULAR WEIGHT AND GAS CONSTANT

An apparent molecular weight is defined by the equation

M = m/n

where, m = Mass of the mixture, and

n = Number of moles of mixture.

The apparent gas constant (similarly as above) is defined by the equation

$$R = \frac{R_0}{M}$$

It can be assumed that a mixture of perfect gases obeys all the perfect gas laws. In order to determine the gas constant for the mixture in terms of the gas constants of the constituents let us consider the equation pV = mRT both for the mixture and for a constituent as follows

and

$$pV = mRT$$

$$p_iV = m_iR_iT$$

$$\Sigma p_iV = \Sigma m_iR_iT$$

$$\therefore$$

$$V\Sigma p_i = T \Sigma m_iR_i$$

$$pV = T \Sigma m_iR_i$$

$$pV = mRT = T \Sigma m_iR_i$$

$$pV = mRT = T \Sigma m_iR_i$$

$$mR = \Sigma m_iR_i$$
or
$$R = \Sigma \frac{m_i}{m} R_i$$

where $\frac{m_i}{m}$ = mass fraction of a constituent.

We know pi V = ni R0T, and vi = pi/p x v

Combining two equations and applied to the mixture (i.e., pV = nR0T), we have

$$\frac{p_i V}{p V} = \frac{n_i R_0 T}{n R_0 T}$$
$$\frac{p_i}{p} = \frac{n_i}{n}$$

On combining this with eqn. (9.8), we get

$$\frac{p_i}{p} = \frac{n_i}{n} = \frac{V_i}{V}$$

This means that the molar analysis is identical with the volumetric analysis, and both are equal to the ratio of the partial pressure to the total pressure.

The apparent molecular weight can be also be determined by the following method. Let us apply characteristic equation to each constituent and to mixture, we have

$$m_i = \frac{p_i V}{R_i T}$$
$$m = \frac{p V}{R T}$$

Also
$$m = \Sigma m_i$$

 $\therefore \qquad \frac{pV}{RT} = \sum \frac{p_i V}{R_i T}$
 $\therefore \qquad \frac{p}{R} = \sum \frac{p_i}{R_i}$

Using the relation $R = \frac{R_0}{M}$, and substituting, we have rM = rM.

or

$$i.e.,$$
 $\frac{pM}{R_0} = \sum \frac{p_i M_i}{R_0}$
 $pM = \sum p_i M_i$
 $M = \sum \frac{p_i}{p} M_i$

Also

$$M = \sum \frac{V_i}{V} M_i$$
 and
$$M = \sum \frac{n_i}{n} M_i$$

4.10 SPECIFIC HEATS OF A GAS MIXTURE

$$\begin{split} C_v &= \sum \frac{n_i}{n} C_{vi} \\ C_p &= \sum \frac{n_i}{n} C_{pi}. \end{split}$$

Chapter : 06 (Properties of Steam)

FORMATION OF STEAM

The process of formation of steam is shown in fig.



IMPORTANT TERMS RELATING STEAM FORMATION

Sensible heat of water (hf). It is defined as the quantity of heat absorbed by 1 kg of water when it is heated from 0°C (freezing point) to boiling point. It is also called total heat (or enthalpy) of water or liquid heat invariably. It is reckoned from 0°C where sensible heat is taken as zero. If 1 kg of water is heated from 0°C to 100°C the sensible heat added to it will be $4.18 \times 100 = 418$ kJ but if water is at say 20°C initially then sensible heat added will be $4.18 \times (100 - 20) = 334.4$ kJ. This type of heat is denoted by letter hf and its value can be directly read from the steam tables. Note. The value of specific heat of water may be taken as 4.18 kJ/kg K at low pressures but at high pressures it is different from this value.

Latent heat or hidden heat (hfg). It is the amount of heat required to convert water at a given temperature and pressure into steam at the same temperature and pressure. It is expressed by the symbol hfg and its value is available from steam tables. The value of latent heat is not constant and varies according to pressure variation.

Dryness fraction (**x**). The term dryness fraction is related with wet steam. It is defined as the ratio of the mass of actual dry steam to the mass of steam containing it. It is usually expressed by the symbol 'x' or 'q'. If ms = Mass of dry steam contained in steam considered, and mw = Weight of water particles in suspension in the steam considered,

$$x = \frac{m_s}{m_s + m_w}$$

Thus if in 1 kg of wet steam 0.9 kg is the dry steam and 0.1 kg water particles then x = 0.9.

Total heat or enthalpy of wet steam (h). It is defined as the quantity of heat required to convert 1 kg of water at 0°C into wet steam at constant pressure. It is the sum of total heat of water and the latent heat and this sum is also called enthalpy.

In other words, h = hf + xhfg

If steam is dry and saturated, then x = 1 and hg = hf + hfg.

Superheated steam. When steam is heated after it has become dry and saturated, it is called superheated steam and the process of heating is called superheating. Superheating is always

carried out at constant pressure. The additional amount of heat supplied to the steam during superheating is called as 'Heat of superheat' and can be calculated by using the specific heat of superheated steam at constant pressure (cps), the value of which varies from 2.0 to 2.1 kJ/ kg K depending upon pressure and temperature.

If Tsup., Ts are the temperatures of superheated steam in K and wet or dry steam, then (Tsup - Ts) is called 'degree of superheat'.

The total heat of superheated steam is given by hsup = hf + hfg + cps (Tsup - Ts) ...(3.4)

Superheated steam behaves like a gas and therefore it follows the gas laws. The value of n for this type of steam is 1.3 and the law for the adiabatic expansion is pv1.3 = constant.

The advantages obtained by using 'superheated' steam are as follows :

(i) By superheating steam, its heat content and hence its capacity to do work is increased without having to increase its pressure.

(ii) Superheating is done in a superheater which obtains its heat from waste furnace gases which would have otherwise passed uselessly up the chimney.

(iii) High temperature of superheated steam results in an increase in thermal efficiency.

(iv) Since the superheated steam is at a temperature above that corresponding to its pressure, it can be considerably cooled during expansion in an engine before its temperature falls below that at which it will condense and thereby become wet. Hence, heat losses due to condensation of steam on cylinder walls etc. are avoided to a great extent.

Volume of wet and dry steam. If the steam has dryness fraction of x, then 1 kg of this steam will contain x kg of dry steam and (1 - x) kg of water. If vf is the volume of 1 kg of water and vg is the volume of 1 kg of perfect dry steam (also known as specific volume), then volume of 1 kg of wet steam = volume of dry steam + volume of water.

= xvg + (1 - x)vf

Note. The volume of vf at low pressures is very small and is generally neglected.

Thus is general, the volume of 1 kg of wet steam is given by, xvg and

= vf + xvfg

= vf + xvfg + vfg - vfg = (vf + vfg) - (1 - x)vfg =

7. Volume of superheated steam. As superheatlike a perfect gas its volume can be found out in t gases.

If, vg = Specific volume of dry steam at pressure

Ts = Saturation temperature in K,

Tsup = Temperature of superheated steam in K, ar

vsup = Volume of 1 kg of superheated steam at pr

$$\frac{p \cdot v_g}{T_s} = \frac{p \cdot v_{\sup}}{T_{\sup}}$$
$$v_{sup} = \frac{v_g T_{sup}}{T_s}$$

8. ENTROPY OF WET STEAM.

The total entropy of wet steam is the sum of entropy of water (sf) and entropy of evaporation (sfg).

In other words, $s_{wet} = s_f + \frac{xh_{fg}}{T_s}$ where s_{wet} = Total entropy of wet steam, s_f = Entropy of water, and

$$\frac{xh_{fg}}{T_s}$$
 = Entropy of evaporation.

If steam is dry and saturated, *i.e.*, x = 1, then

$$s_g = s_f + \frac{h_{fg}}{T_s}$$

9 ENTROPY OF SUPERHEATED STEAM

Total entropy of superheated steam above the freezing point of water.

Ssup = Entropy of dry saturated steam + change of entropy during superheating

$$= s_f + \frac{h_{fg}}{T_s} + c_{ps} \log_e \left(\frac{T_{sup}}{T_s} \right) \\ = s_g + c_{ps} \log_e \left(\frac{T_{sup}}{T_s} \right)$$

THERMODYNAMIC PROPERTIES OF STEAM AND STEAM TABLES

Following are the thermodynamic properties of steam which are tabulated in the form of table:

p = Absolute pressure (bar or kPa);

t s = Saturation temperature (°C) ; hf = Enthalpy of saturated liquid

(kJ/kg); hfg = Enthalpy or latent heat of vapourisation (kJ/kg); hg =

Enthalpy of saturated vapour (steam) (kJ/kg);

sf = Entropy of saturated liquid (kJ/kg K) ; sfg = Entropy of vapourisation

(kJ/kg K) ; sg = Entropy of saturated vapour (steam) (kJ/kg K) ; vf =

Specific volume of saturated liquid (m3/kg);

vg = Specific volume of saturated vapour (steam) (m3/kg). Also, hfg = hg - hf Change of enthalpy during evaporation

sfg = sg - sf Change of entropy during evaporation

vfg = vg - vf Change of volume during evaporation.

The above mentioned properties at different pressures are tabulated in the form of tables as under: The internal energy of steam (u = h - pv) is also tabulated in some steam tables.

ENTHALPY-ENTROPY (h-s) CHART OR MOLLIER DIAGRAM



Chapter : 07 (Steam Generators)

STEAM GENERATION THEORY

To acquaint you with some of the fundamentals underlying the process of steam operation, suppose that you set an open pan of water on the stove and turn on the heat. You find that the heat causes the temperature of the water to increase and, at the same time, to expand in volume. When the temperature reaches the boiling point (212°F or 100°C at sea level), a physical change occurs in the water; the water starts vaporizing. When you hold the temperature at the boiling point long enough, the water continues to vaporize until the pan is dry. A point to remember is that the temperature of water does not increase beyond the boiling point. Even if you add more heat after the water starts to boil, the water cannot get any hotter as long as it remains at the same pressure.

Now suppose you place a tightly fitting lid on the pan of boiling water. The lid prevents the steam from escaping from the pan and this results in a buildup of pressure inside the container. However, when you make an opening in the lid, the steam escapes at the same rate it is generated. As long as water remains in the pan and as long as the pressure remains constant, the temperature of the water and steam remains constant and equal.

The steam boiler operates on the same basic principle as a closed container of boiling water. By way of comparison, it is as true with the boiler as with the closed container that steam formed during boiling tends to push against the water and sides of the vessel. Because of this downward pressure on the surface of the water, a temperature in excess of 212°F is required for boiling. The higher temperature is obtained simply by increasing the supply of heat; therefore, the rules you should remember are as follows:

- 1. All of the water in a vessel, when held at the boiling point long enough, will change into steam. As long as the pressure is held constant, the temperature of the steam and boiling water remains the same.
- 2. An increase in pressure results in an increase in the boiling point temperature of water.
- 3. Degree is defined as a measure of heat intensity.
- 4. Temperature is defined as a measure in degrees of sensible heat. The term sensible heat refers to heat that can be measured with a thermometer.
- 5. Heat is a form of energy measured in *British thermal units (BTU)*. One Btu is the amount of heat required to raise 1 pound of water 1 degree Fahrenheit at sea level.

BOILER FITTINGS and ACCESSORIES

A sufficient number of essential boiler fittings and accessories are discussed in this section to provide a background for further study. As a reminder, and in case you should run across some unit or device not covered here, check the manufacturer's manual for information on the details of its construction and method of operation



The term "fittings" includes various control devices on the boiler. Fittings are vitally important to the economy of operation and safety of personnel and equipment. You must understand fittings if you are to acquire skill in the installation, operation, and servicing of steam boilers.

All boilers require boiler fittings to operate safely. The American Society of Mechanical Engineers (ASME) requires all boiler fittings to be made of materials that withstand the pressure and temperatures that boilers are subject to. All of the boiler fittings discussed are important and must be operated and maintained properly to operate a boiler safely.

TYPES of BOILERS

The Utilities man (UT) is concerned primarily with the fire -tube type of boiler, since it is the type generally used in Seabee operations. However, the water-tube type of boiler may occasionally be used at some activities. The information in this chapter primarily concerns the different designs and construction feature of fire-tube boilers.

The basis for identifying the two types is as follows:

- 1. Water-tube boilers are those in which the products of combustion surround the tubes through which the water flows.
- 2. Fire-tube boilers are those in which the products of combustion pass through the tubes and the water surrounds them.

Water-Tube Boilers

Water-tube boilers may be classified in a number of ways. For our purpose, they are classified as either straight tube or bent tube. These classes are discussed separately in succeeding sections. To avoid confusion, make sure you study carefully each illustration referred to throughout the discussion.

Straight Tube

The straight-tube class of water-tube boilers includes three types:

- 1. Sectional-header cross drum
- 2. Box-header cross drum
- 3. Box-header longitudinal drum

Baffles are usually arranged so gases are directed across the tubes three times before being discharged from the boiler below the drum.

Box-header cross drum boilers are shallow boxes made of two plates—a tube-sheet plate that is bent to form the sides of the box, and a plate containing the handholes that is riveted to the tube-sheet plate. Some are designed so that the front plate can be removed for access to tubes. Tubes enter at right angles to the box header and are expanded and flared in the same manner as the sectional-header boiler. The boiler is usually built with the drum in front. It is supported by lugs fastened to the box headers. This boiler has either cross or longitudinal baffling arranged to divide the boiler into three passes. Water enters the bottom of the drum, flows through connecting tubes to the box header, through the tubes to the rear box header, and back to the drum.

Box-header longitudinal drum boilers have either a horizontal or inclined drum. Box headers are fastened directly to the drum when the drum is inclined. When the drum is horizontal, the front box header is connected to it at an angle greater than 90 degrees. The rear box header is connected to the drum by tubes. Longitudinal or cross baffles can be used with either type.

Bent Tube

Bent tube boilers usually have three drums. The drums are usually of the same diameter and positioned at different levels. The uppermost or highest positioned drum is referred to as the steam drum, while the middle drum is referred to as the water drum, and the lowest, the mud drum. Tube banks connect the drums. The tubes are bent at the ends to enter the drums radially.

Water enters the top rear drum, passes through the tubes to the bottom drum, and then moves up through the tubes to the top front drum. A mixture of steam and water is discharged into this drum. The steam returns to the top rear drum through the upper row of tubes, while the water travels through the tubes in the lower rear drum by tubes extending across the drum, and enters a small collecting header above the front drum.

Many types of baffle arrangements are used with bent-tube boilers. Usually, they are installed so that the inclined tubes between the lower drum and the top front drum absorb 70 to 80 percent of the heat. The water-tube boilers discussed above offer a number of worthwhile advantages. For one thing, they afford flexibility in starting up. They also have a high productive capacity ranging from 100,000 to 1,000,000 pounds of steam per hour. In case of tube failure, there is little danger of a disastrous explosion of

the water-tube boiler. The furnace not only can carry a high overload, it can also be modified for firing by oil or coal. Still another advantage is that it is easy to get into sections inside the furnace to clean and repair them. There are also several disadvantages common to water-tube boilers. One of the main drawbacks is their high construction cost. The large assortment of tubes required for this boiler and the excessive weight per unit weight of steam generated are other unfavorable factors. the water-tube boiler. The furnace not only can carry a high overload, it can also be modified for firing by oil or coal. Still another advantage is that it is easy to get into sections inside the furnace to clean and repair them. There are also several disadvantages common to water-tube boilers. One of the main drawbacks is their high construction cost. The large assortment of tubes required for this boiler and the excessive weight per unit weight of steam generated are other unfavourable factors.



Water Tube Boiler

Fire-Tube Boilers

There are four types of fire-tube boilers—Scotch marine boiler, vertical-tube boiler, horizontal return tubular boiler, and firebox boiler. These four types of boilers are discussed in this section.

Scotch Marine Boiler

The Scotch marine tire-tube boiler is especially suited to Seabee needs. shows a portable Scotch marine tire -tube boiler. The portable unit can be moved easily and requires only a minimal amount of foundation work. A completely self-contained unit, its design includes automatic controls, a steel boiler, and burner equipment. These features are a big advantage because no disassembly is required when you must move the boiler into the field for an emergency.

The Scotch marine boiler has a two -pass (or more) arrangement of tubes that run horizontally to allow the heat inside the tubes to travel back and forth. It also has an internally fired furnace with a cylindrical combustion chamber. Oil is the primary fuel

used to fire the boiler; however, it can also be fired with wood, coal, or gas. A major advantage of the Scotch marine boiler is that it requires less space than a water-tube boiler and can be placed in a room that has a low ceiling.

The Scotch marine boiler also has disadvantages. The shell of the boiler runs from 6 to 8 feet in diameter, a detail of construction that makes a large amount of reinforcing necessary. The fixed dimensions of the internal surface cause some difficulty in cleaning the sections below the combustion chamber. Another drawback is the limited capacity and pressure of the Scotch marine boiler.

An important safety device sometimes used is the fusible plug that provides added protection against low-water conditions. In case of a low-water condition, the fusible plug core melts, allowing steam to escape, and a loud noise is emitted which provides a warning to the operator. On the Scotch boiler the plug is located in the crown sheet, but sometimes it is placed in the upper back of the combustion chamber. Fusible plugs are discussed in more detail later in this chapter. Access for cleaning, inspection, and repair of the boiler watersides is provided through a manhole in the top of the boiler shell and a hand hole in the *water leg*. The manhole opening is large enough for a person to enter the boiler shell for inspection, cleaning, and repairs. On such occasions, always ensure that all valves are secured, locked, and tagged, and that the person in charge knows you are going to enter the boiler. Additionally, always have a person located outside of the boiler standing by to aid you in case of an incident that would require assistance. The hand holes are openings large enough to permit hand entry for cleaning, inspection, and repairs to tubes and headers. shows a horizontal fire-tube boiler used in low-pressure applications. Personnel in the UT rating are assigned to operate and maintain this type of boiler more often than any other type of boiler. Refer to for equipment location.



Fire Tube Boile

Chapter : 08 (Air Standard Cycles)

Air-Standard Cycles

The <u>Rankin</u> cycle is based on a working fluid which changes phase during the cycle, and in which the regions of heat addition and rejection occur at constant temperature. However, the most readily available working fluid is air, which is a <u>superheated gas</u> at normal operating conditions. This results in a series of cycles in which the <u>energy</u> is received and rejected at variable temperature. These cycles can be used to examine the performance of <u>internal combustion engines</u>, e.g. petrol and <u>diesel engines</u> and <u>gas turbines</u>. It should be realised that internal combustion engines and gas turbines are *not* heat engines – because mass flows across the boundaries as air and fuel to enter the engines, and exhaust gases leave. More realistic cycles for these engines are considered in Chapters 16 and 17Chapter 16Chapter 17, respectively. However, it is possible to define 'engines' which can be analysed by end reversible cycles: these 'engines' replace the energy flows brought about by gas flows and combustion by heat transfer processes. Such cycles will be described below.

There are three air-standard cycles:

- 1. constant volume 'combustion' (Otto),
- 2. constant pressure 'combustion' (Diesel) and

dual 'combustion' – this is a combination of constant volume and constant pressure combustion, and results in a slightly more realistic cycle.

These are the heat engine equivalent of the reciprocating engine and different from the actual engine cycle because:

Otto Cycle

The <u>Otto cycle</u> is an air-standard cycle which approximates the processes in petrol or diesel engines. It is based on constant volume heat addition (combustion) and heat rejection processes, and <u>isentropic compression and expansion</u>. The diagram is shown in, where it is superimposed on an actual p–V diagram for a <u>diesel engine</u>.



P-V and T-S Diagram of Otto Cycle

The actual p-V diagram for an engine has rounded corners because of the processes of combustion take place at a finite rate. The Otto cycle has sharp corners because the 'combustion' is switched on and off instantaneously. It can be seen from Fig. 3.10 that the area of the Otto cycle is larger than that of the actual cycle, and this has to be taken into account when analysing engine cycles – the actual engine cycle will always produce less work output than the Otto cycle. A typical engine 'cycle' is defined in . It consists of a compression stroke followed by a period of combustion close to top dead centre (tdc) and then by expansion. These two strokes form the power producing processes, but afterwards the products of combustion have to be replaced by fresh air. This is symbolised in where the exhaust valve is open at the beginning of the exhaust stroke. In a four-stroke engine the piston executes two complete revolutions of the crankshaft, and uses two strokes while the gas is pushed out by the piston on the up stroke, and then the intake valve is opened to enable air to be induced. In a two-stroke engine the intake and exhaust strokes occur at the end and the beginning of the expansion and compression strokes, respectively. These processes are called the *gas exchange processes*, and are one of the main reasons why real engines are not heat engines. The other reason is the combustion process, when the air is used to burn the fuel. This process of combustion means that the fluid in the engine cannot undergo a cycle.

Diesel Cycle

The Diesel cycle also applies to reciprocating engines, and is similar to the Otto cycle except that the heat is applied at constant pressure rather than constant volume. This removes the limitation of infinite rates of combustion implied by the Otto cycle, but still results in an unrealistic combustion pattern. The Diesel cycle is shown in.



P-V and T-S Diagram of Diesel Cycle

Chapter : 09 (Air Compressors)

Introduction

Compression of air and vapour plays an important role in engineering fields. Compression of air is mostly used since it is easy to transmit air compared with vapour.

Uses of compressed air

The applications of compressed air are listed below:

- 1. It is used in gas turbines and propulsion units.
- 2. It is used in striking type pneumatic tools for concrete breaking, clay or rock drilling,
- 3. chipping, caulking, riveting etc.
- 4. It is used in rotary type pneumatic tools for drilling, grinding, hammering etc.
- 5. Pneumatic lifts and elevators work by compressed air.
- 6. It is used for cleaning purposes
- 7. It is used as an atomiser in paint spray and insecticides spray guns.
- 8. Pile drivers, extractors, concrete vibrators require compressed air.
- 9. Air-operated brakes are used in railways and heavy vehicles such as buses and lorries.
- 10. Sand blasting operation for cleaning of iron castings needs compressed air.
- 11. It is used for blast furnaces and air-operated chucks.
- 12. Compressed air is used for starting I.C.engines and also super charging them.

Working principle of a compressor



Air Compressor

A line diagram of a compressor unit is shown in fig:. The compression process requires work input. Hence a compressor is driven by a prime mover. Generally, an electric motor is used as prime mover. Air from atmosphere enters into the compressor It is compressed to a high pressure. Then, this high pressure air is delivered to a storage vessel (reservoir). From the reservoir, it can be conveyed to the desired place through pipe lines.

Some of the energy supplied by the prime mover is absorbed in work done against friction. Some portion of energy is lost due to radiation and coolant. The rest of the energy is maintained within the high pressure air delivered.

Classification of compressors

Air compressors may be classified as follows:



According to design and principle of operation:

- Reciprocating compressors in which a piston reciprocates inside the cylinder.
- Rotary compressors in which a rotor is rotated.

According to number of stages:

- Single stage compressors in which compression of air takes place in one cylinder

 only.
- Multi stage compressors in which compression of air takes place in more than one cylinder.

According to pressure limit:

- 1Low pressure compressors in which the final delivery pressure is less than 10 bar,
 - Medium pressure compressor in which the final delivery pressure is 10 bar to 80 bar $_{\odot}$ and

• High pressure compressors in which the final delivery pressure is 80 to 100 bar.

(a) Low capacity compressor (delivers $0.15m^3$ /s of compressed air),

- (b) Medium capacity compressor (delivers $5m^3$ /s of compressed air) and
- (c) High capacity compressor (delivers more than $5m^3$ /s of compressed air).

According to method of cooling:

- a. Air cooled compressor (Air is the cooling medium) and
- *b.* Water cooled compressor (Water is the cooling medium). According to the nature of installation:
- Portable compressors (can be moved from one place to another).
- Semi-fixed compressors and
- Fixed compressors (They are permanently installed in one place). According to applications:
 - Rock drill compressors (used for drilling rocks),
 - Quarrying compressors (used in quarries),
 - Sandblasting compressors (used for cleaning of cast iron) and
 - Spray painting compressors (used for spray
 - painting). According to number of air cylinders
 - Simplex contains one air cylinder
 - Duplex contains two air cylinders
 - Triplex contains three air cylinders

Rotary Compressors

These compressors are not of reciprocating nature, therefore does not have any pistons and crankshaft. Instead, these compressors have screws, vanes, scrolls, and other devices which rotate and thus compress air. The rotary compressors are classified into screw type, vane type-lobe type, scroll type and other types.





Reciprocating Compressor

These are most commonly used compressors with varying pressure ranges. These are simple in design with almost very little automation. The cylinders of various stages are found in a straight line when seen from top. These compressors are commonly direct driven by electric motors or diesel engines. Refer the attached diagram of the reciprocating in-line compressors.



Single-Acting Compressors:

These are usually reciprocating compressors, which has piston working on air only in one direction. The other end of the piston is often free or open which does not perform any work. The air is compressed only on the top part of the piston. The bottom of the piston is open to crankcase and not utilized for the compression of air.



Double-Acting Compressors:

These compressors are having two sets of suction/intake and delivery valves on both sides of the piston. As the piston moves up and down, both sides of the piston is utilized in compressing the air. The intake and delivery valves operate corresponding to the stroke of the compressor. The compressed air delivery is comparatively continuous when compared to a single-acting air compressor. Thus both sides of the pistons are effectively used in compressing the air.

