

“Thermodynamics”.

In Section 1 of this course you will cover these topics:

- Concepts Of Thermodynamics
- Properties Of Substances
- Conservation Of Mass

Topic : Concepts Of Thermodynamics

Topic Objective:

At the end of this topic student would be able to:

- Learn the laws of thermodynamics
- Learn the Thermodynamic potentials
- Understand the Thermodynamic systems
- Learn Thermodynamic instruments

Definition/Overview:

Thermodynamics: In physics, thermodynamics is the study of the conversion of heat energy into different forms of energy (in particular, mechanical, chemical, and electrical energy); different energy conversions into heat energy; and its relation to macroscopic variables such as temperature, pressure, and volume. Its underpinnings, based upon statistical predictions of the collective motion of particles from their microscopic behavior, are the field of statistical thermodynamics, a branch of statistical mechanics. Roughly, heat means "energy in transit" and dynamics relates to "movement"; thus, in essence thermodynamics studies the movement of

energy and how energy instills movement. Historically, thermodynamics developed out of need to increase the efficiency of early steam engines.

The starting point for most thermodynamic considerations are the laws of thermodynamics, which postulate that energy can be exchanged between physical systems as heat or work. They also postulate the existence of a quantity named entropy, which can be defined for any system. In thermodynamics, interactions between large ensembles of objects are studied and categorized. Central to this are the concepts of *system* and *surroundings*. A system is composed of particles, whose average motions define its properties, which in turn are related to one another through equations of state. Properties can be combined to express internal energy and thermodynamic potentials, which are useful for determining conditions for equilibrium and spontaneous processes.

Key Points:

1. History

The history of thermodynamics as a scientific discipline generally begins with Otto von Guericke who, in 1650, built and designed the world's first vacuum pump and created the world's first ever vacuum (known as the Magdeburg hemispheres). Guericke was driven to make a vacuum in order to disprove Aristotle's long-held supposition that 'nature abhors a vacuum'. Shortly after Guericke, the Irish physicist and chemist Robert Boyle had learned of Guericke's designs and, in 1656, in coordination with English scientist Robert Hooke, built an air pump. Using this pump, Boyle and Hooke noticed a correlation between pressure, temperature, and volume. In time, Boyle's Law was formulated, which states that pressure and volume are inversely proportional. Then, in 1679, based on these concepts, an associate of Boyle's named Denis Papin built a bone digester, which was a closed vessel with a tightly fitting lid that confined steam until a high pressure was generated.

Later designs implemented a steam release valve that kept the machine from exploding. By watching the valve rhythmically move up and down, Papin conceived of the idea of a piston and

a cylinder engine. He did not, however, follow through with his design. Nevertheless, in 1697, based on Papin's designs, engineer Thomas Savery built the first engine. Although these early engines were crude and inefficient, they attracted the attention of the leading scientists of the time.

Their work led 127 years later to Sadi Carnot, the "father of thermodynamics", who, in 1824, published *Reflections on the Motive Power of Fire*, a discourse on heat, power, and engine efficiency. The paper outlined the basic energetic relations between the Carnot engine, the Carnot cycle, and Motive power. This marks the start of thermodynamics as a modern science. The term thermodynamics was coined by James Joule in 1849 to designate the science of relations between heat and power. By 1858, "thermo-dynamics", as a functional term, was used in William Thomson's paper *An Account of Carnot's Theory of the Motive Power of Heat*. The first thermodynamic textbook was written in 1859 by William Rankine, originally trained as a physicist and a civil and mechanical engineering professor at the University of Glasgow.

2. The laws of thermodynamics

In thermodynamics, there are four laws that do not depend on the details of the systems under study or how they interact. Hence these laws are very generally valid, can be applied to systems about which one knows nothing other than the balance of energy and matter transfer. Examples of such systems include Einstein's prediction of spontaneous emission around the turn of the 20th century, and ongoing research into the thermodynamics of black holes.

3. Thermodynamic potentials

As can be derived from the energy balance equation (or Burks' equation) on a thermodynamic system there exist energetic quantities called thermodynamic potentials, being the quantitative measure of the stored energy in the system. The five most well known potentials are:

Internal energy

Helmholtz free energy

Enthalpy

Gibbs free energy

Grand potential

Other thermodynamic potentials can be obtained through Legendre transformation. Potentials are used to measure energy changes in systems as they evolve from an initial state to a final state. The potential used depends on the constraints of the system, such as constant temperature or pressure. Internal energy is the internal energy of the system, enthalpy is the internal energy of the system plus the energy related to pressure-volume work, and Helmholtz and Gibbs energy are the energies available in a system to do useful work when the temperature and volume or the pressure and temperature are fixed, respectively.

4. Thermodynamic systems

An important concept in thermodynamics is the system. Everything in the universe except the system is known as surroundings. A system is the region of the universe under study. A system is separated from the remainder of the universe by a boundary which may be imaginary or not, but which by convention delimits a finite volume. The possible exchanges of work, heat, or matter between the system and the surroundings take place across this boundary. Boundaries are of four types: fixed, moveable, real, and imaginary.

Basically, the boundary is simply an imaginary dotted line drawn around a volume of something when there is going to be a change in the internal energy of that something. Anything that passes across the boundary that effects a change in the internal energy of the something needs to be accounted for in the energy balance equation. That something can be the volumetric region surrounding a single atom resonating energy, such as Max Planck defined in 1900; it can be a body of steam or air in a steam engine, such as Sadi Carnot defined in 1824; it can be the body of a tropical cyclone, such as Kerry Emanuel theorized in 1986 in the field of atmospheric thermodynamics; it could also be just one nuclide (i.e. a system of quarks) as some are theorizing presently in quantum thermodynamics.

For an engine, a fixed boundary means the piston is locked at its position; as such, a constant volume process occurs. In that same engine, a moveable boundary allows the piston to move in and out. For closed systems, boundaries are real while for open system boundaries are often imaginary.

5. Thermodynamic instruments

Main article: Thermodynamic instruments

There are two types of thermodynamic instruments, the meter and the reservoir. A thermodynamic meter is any device which measures any parameter of a thermodynamic system. In some cases, the thermodynamic parameter is actually defined in terms of an idealized measuring instrument. For example, the zeroth law states that if two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other. This principle, as noted by James Maxwell in 1872, asserts that it is possible to measure temperature. An idealized thermometer is a sample of an ideal gas at constant pressure. From the ideal gas law $PV=nRT$, the volume of such a sample can be used as an indicator of temperature; in this manner it defines temperature. Although pressure is defined mechanically, a pressure-measuring device, called a barometer may also be constructed from a sample of an ideal gas held at a constant temperature. A calorimeter is a device which is used to measure and define the internal energy of a system.

A thermodynamic reservoir is a system which is so large that it does not appreciably alter its state parameters when brought into contact with the test system. It is used to impose a particular value of a state parameter upon the system. For example, a pressure reservoir is a system at a particular pressure, which imposes that pressure upon any test system that it is mechanically connected to. The Earth's atmosphere is often used as a pressure reservoir.

It is important that these two types of instruments are distinct. A meter does not perform its task accurately if it behaves like a reservoir of the state variable it is trying to measure. If, for example, a thermometer were to act as a temperature reservoir it would alter the temperature of the system being measured, and the reading would be incorrect. Ideal meters have no effect on the state variables of the system they are measuring.

Topic : Properties Of Substances**Topic Objective:**

At the end of this topic student would be able to:

- Learn the concept of Bare particular
- Learn the concept of Inherence relation
- Understand the Indiscernibility
- Learn the Identity of indiscernibles

Definition/Overview:

Substance: Substance is a core concept of ontology and metaphysics. Indeed, philosophies may be divided into monist philosophies, and dualist or pluralist philosophies. Monistic views, often associated with immanence, hold that there is only one substance, sometimes called God or Being. Dualist and pluralist views hold that two or more types of substances do exist, and that these can be placed in an ontological hierarchy. Platonism or Aristotelianism considers that there are various substances, while stoicism and Spinoza hold that there is only one substance. Substance theory, or substance attribute theory, is an ontological theory about objecthood, positing that a substance is distinct from its properties.

Key Points:**1. Criticisms of the concept of substance**

The Eastern Orthodox Church, drawing from the philosophy of Plotinus and neoplatonism, has traditionally been critical of substance theory as understood from the lense of aristotelianism and thomism.

Friedrich Nietzsche and, after him, Martin Heidegger, Michel Foucault and Gilles Deleuze rejected the notion of "substance", and in the same movement the concept of subject contained within the framework of Platonic idealism. For this reason, Althusser's "anti-humanism" and Foucault's statements were criticized, by Jrgen Habermas and others, for misunderstanding that this led to a fatalist conception of social determinism. For Habermas, only a subjective form of liberty could be conceived, to the contrary of Deleuze who talks about "a life", as an impersonal and immanent form of liberty.

For Heidegger, Descartes means by "substance" that by which "we can understand nothing else than an entity which is in such a way that it need no other entity in order to be." Therefore, only God is a substance as ens perfectissimus (most perfect being). Heidegger showed the inextricable relationship between the concept of substance and of subject, which explains why, instead of talking about "man" or "humankind", he speaks about the Dasein, which is not a simple subject, nor a substance.

2. Bare particular

In substance theory, a bare particular of an object is the element without which the object would not exist, that is, its substance, which exists independent from its properties, even if it is physically impossible for it to lack properties entirely. It is "bare" because it is considered without its properties and "particular" because it is not abstract. The properties that the substance has are said to inhere in the substance.

In substance theory of the mind, the objects are minds.

3. Inherence relation

Another primitive concept in substance theory is the inherence relation between a substance and its properties. For example, in the sentence, "The apple is red," substance theory says that red inheres in the apple. Substance theory considers to be clear the meaning of the apple having the property of redness or the property of being juicy, and that a property's inherence in a substance is similar to, but not identical with, being part of the substance. Thus, Aristotle wrote:

"By being 'present in a subject' I do not mean present as parts are present in a whole, but being incapable of existence apart from the said subject.

The inverse relation is participation. Thus in the example above, just as red inheres in the apple, so the apple participates in red.

4. Indiscernibility

The indiscernibility argument from the substance theorist targets those bundle theorists who are also metaphysical realists. Metaphysical realism uses repeatable entities known as universals exemplified by concrete particulars to explain the phenomenon of attribute agreement. Substance theorists then say that bundle theory and metaphysical realism can only coexist by introducing an identity of indiscernibles creed, which substance theorists suggest is incoherent. The identity of indiscernibles says that any concrete particular that is numerically different from another must have its own qualitative properties, or attributes.

Since bundle theory states that all concrete particulars are merely constructions or 'bundles' of attributes, or qualitative properties, the substance theorist's indiscernibility argument claims that the ability to recognize numerically different concrete particulars, such as concrete objects, requires those particulars to have discernible qualitative differences in their attributes and that the metaphysical realist who is also a bundle theorist must therefore concede to the existence of 'discernible (numerically different) concrete particulars', the 'identity of indiscernibles', and a 'principle of constituent identity'.

5. Discernible concrete particulars

Necessarily, for any complex objects, a and b, if for any entity, c, c is a constituent of a if and only if c is a constituent of b, then a is numerically identical with b.

The indiscernibility argument points out that if bundle theory and discernible concrete particulars theory explain the relationship between attributes, then the identity of indiscernibles theory must also be true:

6. Identity of indiscernibles

Necessarily, for any concrete objects, a and b, if for any attribute, A , A is an attribute of a if and only if A is an attribute of b, then a is numerically identical with b.

The indiscernibles argument then asserts that the identity of indiscernibles is false. For example, two different pieces of printer paper can be side by side, numerically different from each other. However, the argument says, all of their qualitative properties can be the same (e.g. both can be white, rectangular-shaped, 9 x 11 inches...). Thus, the argument claims, bundle theory and metaphysical realism cannot both be correct.

However, bundle theory combined with trope theory (as opposed to metaphysical realism) is immune to the indiscernibles argument. The immunity stems from the fact that each trope (attribute) can only be held by one concrete particular, thus qualitative indiscernible objects can exist while being numerically identical and the identity of indiscernibles therefore does not hold.

7. Bundle theory

In direct opposition to substance theory is bundle theory' whose most basic premise is that all concrete particulars are merely constructions or 'bundles' of attributes, or qualitative properties: Necessarily, for any concrete entity, a, if for any entity, b, b is a constituent of a, then b is an attribute.

The bundle theorist's principal objections to substance theory concern the bare particulars of a substance, which substance theory considers independently of the substance's properties. The bundle theorist objects to the notion of a thing with no properties, claiming that one cannot conceive of such a thing and citing John Locke, who described a substance as "a something, I know not what." To the critic, as soon as one has any notion of a substance in mind, a property accompanies that notion. That is, to the critic it is not only physically impossible to encounter a bare particular without properties, but the very notion of a thing without properties is so strange that he cannot even form such a notion.

Topic : Conservation Of Mass**Topic Objective:**

At the end of this topic student would be able to:

- Learn the Law of Conservation of Mass
- Learn about The mass associated with chemical amounts of energy is too small to measure

Definition/Overview:

Conservation of Mass: The law of conservation of mass/matter, also known as law of mass/matter conservation says that the mass of a closed system will remain constant, regardless of the processes acting inside the system. An equivalent statement is that mass cannot be created/destroyed, although it may be rearranged in space, and changed into different types of particles. This implies that for any chemical process in a closed system, the mass of the reactants must equal the mass of the products. This is also the central idea behind the first law of thermodynamics.

The law of "matter" conservation (in the sense of conservation of particles) may be considered as an approximate physical law that holds only in the classical sense, before the advent of special relativity and quantum mechanics. Another difficulty with conservation of "matter" is that "matter" is not a well-defined word in science, and when particles which all consider to be "matter" (such as electrons and positrons) are annihilated to make photons (which are often not considered matter) then conservation of matter does not hold, even in closed systems.

Mass is also not generally conserved in open systems, when various forms of energy are allowed into, or out of, the system. However, the law of mass conservation for closed systems, as viewed over time from any single inertial frame, continues to hold in modern physics. The reason for this

is that relativistic equations show that even massless particles such as photons still add mass to closed systems, allowing mass (though not matter) to be conserved in all processes where energy does not escape the system.

The historical concept of both matter and mass conservation is widely used in many fields such as chemistry, mechanics, and fluid dynamics. In modern physics, only mass conservation for closed systems continues to hold exactly.

Key Points:

1. Historical development and importance

Beginnings of the theory of conservation of mass were stated by Epicurus. In describing the nature of the universe he wrote: "the sum total of things was always such as it is now, and such it will ever remain," and that nothing is created from nothing, and nothing that disappears ceases to exist.

An early yet incomplete theory of the conservation of mass was stated by Nasir al-Din al-Tusi in the 13th century. He wrote that a body of matter is able to change, but is not able to disappear. The law of conservation of mass was first clearly formulated by Antoine Lavoisier in 1789, which is often for this reason referred to as a father of modern chemistry. However, Mikhail Lomonosov had previously expressed similar ideas in 1748 and proved them in experiments. Others who anticipated the work of Lavoisier include Joseph Black, Henry Cavendish, and Jean Rey.

Historically, the conservation of mass and weight was kept obscure for millennia by the buoyant effect of the Earth's atmosphere on the weight of gases. For example, since a piece of wood weighs less after burning, this seemed to suggest that some of its mass disappears, or is transformed or lost. These effects were not understood until careful experiments in which chemical reactions such as rusting were performed in sealed glass ampules, wherein it was found that the chemical reaction did not change the weight of the sealed container. The vacuum pump also helped to allow the effective weighing of gases using scales.

Once understood, the conservation of mass was of key importance in changing alchemy to modern chemistry. When chemists realized that substances never disappeared from measurement with the scales (once buoyancy effects were held constant, or had otherwise been accounted for), they could for the first time embark on quantitative studies of the transformations of substances. This in turn led to ideas of chemical elements, as well as the idea that all chemical processes and transformations (including both fire and metabolism) are simple reactions between invariant amounts or weights of these elements.

2. The mass associated with chemical amounts of energy is too small to measure

The change in mass of certain kinds of open systems where no atoms or massive particles are allowed to escape, but other types of energy (such as light or heat) were allowed to enter or escape, went unnoticed in the 19th century, because the mass-change associated with addition or loss of the fractional amounts of heat and light associated with chemical reactions, was very small.

In relativity, the theoretical connection of all energy with mass was made by Albert Einstein in 1905. However, Einstein pointed out that the change in mass of systems for which the chemical amounts of energy were allowed in or out of systems, was predicted by his theory to be so small that it could not be measured with available instruments. Einstein speculated that the energies associated with radioactive phenomena were so large as compared with the mass producing them, that they might be measured as loss of a fraction of mass in systems, once they were removed. This later indeed proved to be possible, and proved a successful test of Einstein's theory.

3. Criticisms

The conventional statement of the law of conservation of mass - that matter can neither be created nor destroyed - has been subject to wide criticism due to its apparent absurdity in stating that matter cannot be created-as it is not possible to define an entity which cannot be created - and also due to its self-contradiction in stating that matter cannot be destroyed either. Critics have suggested that the statement of the law of conservation of mass be modified to reflect the fact that it merely defines the scope of the physical science, rather than purporting to make a universal statement which is obviously contradicted by the existence of matter in the universe.

4. Mass conservation remains correct if energy is not lost

The conservation of relativistic mass implies the viewpoint of a single observer (or the view from a single inertial frame) since changing inertial frames may result in a change of the total energy (relativistic energy) for systems, and this quantity determines the relativistic mass.

The principle that the mass of a system of particles must be equal to the sum of their rest masses, even though true in classical physics, may be false in special relativity. The reason that rest masses cannot be simply added is that this does not take into account other forms of energy, such as kinetic and potential energy, and massless particles such as photons, all of which may (or may not) affect the mass of systems. For moving massive particles in a system, examining the rest masses of the various particles also amounts to introducing many different inertial observation frames (which is prohibited if total system energy and momentum are to be conserved), and also when in the rest frame of one particle, this procedure ignores the momenta of other particles, which affect the system mass if the other particles are in motion in this frame.

For the special type of mass called invariant mass, changing the inertial frame of observation for a whole closed system has no effect on the measure of invariant mass of the system, which remains both conserved and invariant even for different observers who view the entire system. Invariant mass is a system combination of energy and momentum, which is invariant for any observer, because in any inertial frame, the energies and momenta of the various particles always add to the same quantity. The invariant mass is the relativistic mass of the system when viewed in the center of momentum frame. It is the minimum mass which a system may exhibit in all possible inertial frames.

The conservation of both relativistic and invariant mass applies even to systems of particles created by pair production, where energy for new particles may come from kinetic energy of other particles, or from a photon as part of a system. Again, neither the relativistic nor the invariant mass of closed systems changes when new particles are created. However, different inertial observers will disagree on the value of this conserved mass, if it is the relativistic mass. However, all observers agree on the value of the conserved mass, if the mass being measured is the invariant mass.

The mass-energy equivalence formula requires closed systems, since if energy is allowed to escape a system, both relativistic mass and invariant mass will escape also.

The formula implies that bound systems have an invariant mass (rest mass for the system) less than the sum of their parts, if the binding energy has been allowed to escape the system after the system has been bound. This may happen by converting system potential energy into some other kind of active energy, such as kinetic energy or photons, which easily escape a bound system. The difference in system masses, called a mass defect, is a measure of the binding energy in bound systems in other words, the energy needed to break the system apart. The greater the mass defect, the larger the binding energy. The binding energy (which itself has mass) must be released (as light or heat) when the parts combine to form the bound system, and this is the reason the mass of the bound system decreases when the energy leaves the system.. The total invariant mass is actually conserved, when the mass of the binding energy that has escaped, is taken into account.

5. Fluid Dynamics

Finally, at the bottom of the slide, we consider the changes for a fluid that is moving through our domain. There is no accumulation or depletion of mass, so mass is conserved within the domain. Since the fluid is moving, defining the amount of mass gets a little tricky. Let's consider an amount of fluid that passes through point "a" of our domain in some amount of time t. If the fluid passes through an area A at velocity V, we can define the volume Vol to be:

$$\text{Vol} = A * V * t$$

A units check gives area x length/time x time = area x length = volume. Thus the mass at point "a" m_a is simply density ρ times the volume at "a".

$$m_a = (\rho * A * V * t)_a$$

If we compare the flow through another point in the domain, point "b," for the same amount of time t, we find the mass at "b" m_b to be the density times the velocity times the area times the time at "b":

$$m_b = (\rho * A * V * t)_b$$

From the conservation of mass, these two masses are the same and since the times are the same, we can eliminate the time dependence.

$$(\rho * A * V)_a = (\rho * A * V)_b$$

or

$$\rho * A * V = \text{constant}$$

The conservation of mass gives us an easy way to determine the velocity of flow in a tube if the density is constant. If we can determine (or set) the velocity at some known area, the equation tells us the value of velocity for any other area. In our animation, the area of "b" is one half the area of "a." Therefore, the velocity at "b" must be twice the velocity at "a." If we desire a certain velocity in a tube, we can determine the area necessary to obtain that velocity. This information is used in the design of wind tunnels. The quantity density times area times velocity has the dimensions of mass/time and is called the mass flow rate. This quantity is an important parameter in determining the thrust produced by a propulsion system. As the speed of the flow approaches the speed of sound the density of the flow is no longer a constant and we must then use a compressible form of the mass flow rate equation. The conservation of mass equation also occurs in a differential form as part of the Navier-Stokes equations of fluid flow.

In Section 2 of this course you will cover these topics:

- Conservation Of Energy
- Entropy And The Second Law Of Thermodynamics
- Second-Law Analysis Of Thermodynamic Systems

Topic : Conservation Of Energy

Topic Objective:

At the end of this topic student would be able to:

- Learn the Law of Conservation of Energy
- Learn about the first law of thermodynamics
- Learn about Mechanics
- Understand the Noether's theorem
- Understand the Quantum theory

Definition/Overview:

Conservation of Energy: The law of conservation of energy states that the total amount of energy in an isolated system remains constant. A consequence of this law is that energy cannot be created or destroyed. The only thing that can happen with energy in an isolated system is that it can change form, that is to say for instance kinetic energy can become thermal energy. Because energy is associated with mass in the Einstein's theory of relativity, the conservation of energy also implies the conservation of mass in isolated systems (that is, the mass of a system cannot change, so long as energy is not permitted to enter or leave the system).

Another consequence of this law is that perpetual motion machines can only work if they deliver no energy to their surroundings, or if they produce more energy than is put into them without losing mass (and thus eventually disappearing), and are therefore impossible.

Key Points:**1. History**

Ancient philosophers as far back as Thales of Miletus had inklings of the conservation of some underlying substance of which everything is made. However, there is no particular reason to identify this with what we know today as "mass-energy" (for example, Thales thought it was water). In 1638, Galileo published his analysis of several situations including the celebrated "interrupted pendulum" which can be described (in modern language) as conservatively converting potential energy to kinetic energy and back again. However, Galileo did not state the process in modern terms and again cannot be credited with the crucial insight. It was Gottfried Wilhelm Leibniz during 1676-1689 who first attempted a mathematical formulation of the kind of energy which is connected with motion (kinetic energy). Leibniz noticed that in many mechanical systems (of several masses, m_i each with velocity v_i),

was conserved so long as the masses did not interact. He called this quantity the vis viva or living force of the system. The principle represents an accurate statement of the approximate conservation of kinetic energy in situations where there is no friction. Many physicists at that time held that the conservation of momentum, which holds even in systems with friction, as defined by the momentum:

Was the conserved vis viva. It was later shown that, under the proper conditions, both quantities are conserved simultaneously such as in elastic collisions.

It was largely engineers such as John Smeaton, Peter Ewart, Karl Hotzmann, Gustave-Adolphe Hirn and Marc Seguin who objected that conservation of momentum alone was not adequate for practical calculation and who made use of Leibniz's principle. The principle was also championed by some chemists such as William Hyde Wollaston. Academics such as John Playfair were quick to point out that kinetic energy is clearly not conserved. This is obvious to a modern analysis based on the second law of thermodynamics but in the 18th and 19th centuries, the fate of the lost energy was still unknown. Gradually it came to be suspected that the heat inevitably generated by motion under friction, was another form of vis viva. In 1783, Antoine Lavoisier and Pierre-Simon Laplace reviewed the two competing theories of vis viva and caloric theory. Count Rumford's 1798 observations of heat generation during the boring of cannons added more weight to the view that mechanical motion could be converted into heat, and (as importantly) that the conversion was quantitative and could be predicted (allowing for a universal conversion constant between kinetic energy and heat). Vis viva now started to be known as energy, after the term was first used in that sense by Thomas Young in 1807.

The recalibration of vis viva to

Which can be understood as finding the exact value for the kinetic energy to work conversion constant, was largely the result of the work of Gaspard-Gustave Coriolis and Jean-Victor Poncelet over the period 1819-1839. The former called the quantity *quantité de travail* (quantity of

work) and the latter, travail mécanique (mechanical work), and both championed its use in engineering calculation.

In a paper *ber die Natur der Wärme*, published in the *Zeitschrift für Physik* in 1837, Karl Friedrich Mohr gave one of the earliest general statements of the doctrine of the conservation of energy in the words: "besides the 54 known chemical elements there is in the physical world one agent only, and this is called Kraft [energy or work]. It may appear, according to circumstances, as motion, chemical affinity, cohesion, electricity, light and magnetism; and from any one of these forms it can be transformed into any of the others."

A key stage in the development of the modern conservation principle was the demonstration of the mechanical equivalent of heat. The caloric theory maintained that heat could neither be created nor destroyed but conservation of energy entails the contrary principle that heat and mechanical work are interchangeable.

The mechanical equivalence principle was first stated in its modern form by the German surgeon Julius Robert von Mayer. Mayer reached his conclusion on a voyage to the Dutch East Indies, where he found that his patients' blood was a deeper red because they were consuming less oxygen, and therefore less energy, to maintain their body temperature in the hotter climate. He had discovered that heat and mechanical work were both forms of energy, and later, after improving his knowledge of physics, he calculated a quantitative relationship between them.

Meanwhile, in 1843 James Prescott Joule independently discovered the mechanical equivalent in a series of experiments. In the most famous, now called the "Joule apparatus", a descending weight attached to a string caused a paddle immersed in water to rotate. He showed that the gravitational potential energy lost by the weight in descending was equal to the thermal energy (heat) gained by the water by friction with the paddle.

Over the period 1840-1843, similar work was carried out by engineer Ludwig A. Colding though it was little known outside his native Denmark.

Both Joule's and Mayer's work suffered from resistance and neglect but it was Joule's that, perhaps unjustly, eventually drew the wider recognition.

In 1844, William Robert Grove postulated a relationship between mechanics, heat, light, electricity and magnetism by treating them all as manifestations of a single "force" (energy in modern terms). Grove published his theories in his book *The Correlation of Physical Forces*. In

1847, drawing on the earlier work of Joule, Sadi Carnot and mile Clapeyron, Hermann von Helmholtz arrived at conclusions similar to Grove's and published his theories in his book *ber die Erhaltung der Kraft*. The general modern acceptance of the principle stems from this publication. In 1877, Peter Guthrie Tait claimed that the principle originated with Sir Isaac Newton, based on a creative reading of propositions 40 and 41 of the *Philosophiae Naturalis Principia Mathematica*. This is now generally regarded as nothing more than an example of Whig history.

2. The first law of thermodynamics

Entropy is a function of a quantity of heat which shows the possibility of conversion of that heat into work.

For a thermodynamic system with a fixed number of particles, the first law of thermodynamics may be stated as:

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

where Q is the amount of energy added to the system by a heating process, W is the amount of energy lost by the system due to work done by the system on its surroundings and dU is the increase in the internal energy of the system.

The δ 's before the heat and work terms are used to indicate that they describe an increment of energy which is to be interpreted somewhat differently than the dU increment of internal energy. Work and heat are processes which add or subtract energy, while the internal energy U is a particular form of energy associated with the system. Thus the term "heat energy" for Q means "that amount of energy added as the result of heating" rather than referring to a particular form of energy. Likewise, the term "work energy" for W means "that amount of energy lost as the result of work". The most significant result of this distinction is the fact that one can clearly state the amount of internal energy possessed by a thermodynamic system, but one cannot tell how much energy has flowed into or out of the system as a result of its being heated or cooled, nor as the result of work being performed on or by the system. In simple terms, this means that energy cannot be created or destroyed, only converted from one form to another.

For a simple compressible system, the work performed by the system may be written

$$\delta W = P dV$$

Where P is the pressure and dV is a small change in the volume of the system, each of which are system variables. The heat energy may be written

Where T is the temperature and dS is a small change in the entropy of the system. Temperature and entropy are also system variables.

3. Mechanics

In mechanics, conservation of energy is usually stated as

$$E = T + V,$$

Where T is kinetic and V potential energy.

Actually this is the particular case of the more general conservation law

and

Where L is the Lagrangian function. For this particular form to be valid, the following must be true:

The system is scleronomous (neither kinetic nor potential energy are explicit functions of time)

The kinetic energy is a quadratic form with regard to velocities.

The potential energy doesn't depend on velocities.

4. Noether's theorem

The conservation of energy is a common feature in many physical theories. From a mathematical point of view it is understood as a consequence of Noether's theorem, which states every symmetry of a physical theory has an associated conserved quantity; if the theory's symmetry is time invariance then the conserved quantity is called "energy". The energy conservation law is a consequence of the shift symmetry of time; energy conservation is implied by the empirical fact that the laws of physics do not change with time itself. Philosophically this can be stated as "nothing depends on time per se". In other words, if the theory is invariant under the continuous symmetry of time translation then its energy (which is canonical conjugate quantity to time) is conserved. Conversely, theories which are not invariant under shifts in time (for example, systems with time dependent potential energy) do not exhibit conservation of energy unless we consider them to exchange energy with another, external system so that the theory of the enlarged system becomes time invariant again. Since any time-varying theory can be embedded within time-invariant meta-theory energy conservation can always be recovered by a suitable re-

definition of what energy is. Thus conservation of energy for finite systems is valid in all modern physical theories, such as special and general relativity and quantum theory (including QED).

5. Relativity

With the invention of special relativity by Albert Einstein, energy was proposed to be one component of an energy-momentum 4-vector. Each of the four components (one of energy and three of momentum) of this vector is separately conserved in any given inertial reference frame. Also conserved is the vector length (Minkowski norm), which is the rest mass. The relativistic energy of a single massive particle contains a term related to its rest mass in addition to its kinetic energy of motion. In the limit of zero kinetic energy (or equivalently in the rest frame of the massive particle, or the center-of-momentum frame for objects or systems), the total energy of particle or object (including internal kinetic energy in systems) is related to its rest mass via the famous equation $E = mc^2$. Thus, the rule of conservation of energy in special relativity was shown to be a special case of a more general rule, alternatively called the conservation of mass and energy, the conservation of mass-energy, the conservation of energy-momentum, the conservation of invariant mass or now usually just referred to as conservation of energy. In general relativity conservation of energy-momentum is expressed with the aid of a stress-energy-momentum pseudotensor.

6. Quantum theory

In quantum mechanics, energy is defined as proportional to the time derivative of the wave function. Lack of commutation of the time derivative operator with the time operator itself mathematically results in an uncertainty principle for time and energy: the longer the period of time, the more precisely energy can be defined (energy and time become a conjugate Fourier pair).

However, there is a deep contradiction between quantum theory's historical estimate of the vacuum energy density in the universe and the vacuum energy predicted by the cosmological constant. The estimated energy density difference is of the order of 10^{120} times. The consensus is developing that the quantum mechanical derived zero-point field energy density does not conserve the total energy of the universe, and does not comply with our understanding of the

expansion of the universe. Intense effort is going on behind the scenes in physics to resolve this dilemma and to bring it into compliance with an expanding universe.

Topic : Entropy And The Second Law Of Thermodynamics

Topic Objective:

At the end of this topic student would be able to:

- Learn the concept of Entropy
- Learn the concept of Versions of The Law
- Learn the concept of Energy dispersal
- Learn the concept of Entropy and the second law

Definition/Overview:

The second law of thermodynamics (the entropy law or law of entropy) was formulated in the middle of the last century by Clausius and Thomson following Carnot's earlier observation that, like the fall or flow of a stream that turns a mill wheel, it is the "fall" or flow of heat from higher to lower temperatures that motivates a steam engine. The key insight was that the world is inherently active, and that whenever an energy distribution is out of equilibrium a potential or thermodynamic "force" (the gradient of a potential) exists that the world acts spontaneously to dissipate or minimize. All real-world change or dynamics is seen to follow, or be motivated, by this law. So whereas the first law expresses that which remains the same, or is time-symmetric, in all real-world processes the second law expresses that which changes and motivates the change, the fundamental time-asymmetry, in all real-world process. Clausius coined the term "entropy" to refer to the dissipated potential and the second law, in its most general form, states that the world acts spontaneously to minimize potentials (or equivalently maximize entropy), and

with this, active end-directedness or time-asymmetry was, for the first time, given a universal physical basis. The balance equation of the second law, expressed as $S > 0$, says that in all natural processes the entropy of the world always increases, and thus whereas with the first law there is no time, and the past, present, and future are indistinguishable, the second law, with its one-way flow, introduces the basis for telling the difference.

Key Points:

1. Entropy

In many branches of science, entropy is a measure of the disorder of a system. The concept of entropy is particularly notable as it is applied across physics, information theory and mathematics.

In thermodynamics (a branch of physics), entropy, symbolized by S , is a measure of the unavailability of a systems energy to do work. It is a measure of the disorder of molecules in a system, and is central to the second law of thermodynamics and to the fundamental thermodynamic relation, both of which deal with physical processes and whether they occur unexpectedly. Spontaneous changes in isolated systems occur with an increase in entropy. Unexpected changes tend to average out differences in temperature, pressure, density, and chemical potential that may exist in a system and entropy is thus a measure of how great the unexpected changes are.

2. Versions of the Law

There are many ways of stating the second law of thermodynamics, but all are equivalent in the sense that each form of the second law logically implies every other form. Thus, the theorems of thermodynamics can be proved using any form of the second law and third law.

The formulation of the second law that refers to entropy directly is as follows:

In a system, a process that occurs will tend to increase the total entropy of the universe.

Thus, while a system can undergo some physical process that decreases its own entropy, the entropy of the universe (which includes the system and its surroundings) must increase overall. (An exception to this rule is a reversible or "isentropic" process, such as frictionless adiabatic compression.) Processes that decrease total entropy of the universe are impossible. If a system is at equilibrium, by definition no spontaneous processes occur, and therefore the system is at maximum entropy.

Also, due to Rudolf Clausius, is the simplest formulation of the second law, the heat formulation or Clausius statement:

Heat generally cannot spontaneously flow from a material at lower temperature to a material at higher temperature.

Informally, "Heat doesn't flow from cold to hot (without work input)", which is obviously true from everyday experience. For example in a refrigerator, heat flows from cold to hot, but only when aided by an external agent (i.e. the compressor). Note that from the mathematical definition of entropy, a process in which heat flows from cold to hot has decreasing entropy. This can happen in a non-isolated system if entropy is created elsewhere, such that the total entropy is constant or increasing, as required by the second law. For example, the electrical energy going into a refrigerator is converted to heat and goes out the back, representing a net increase in entropy.

The exception to this is in statistically unlikely events where hot particles will "steal" the energy of cold particles enough that the cold side gets colder and the hot side gets hotter, for an instant. Such events have been observed at a small enough scale where the likelihood of such a thing happening is large enough. The mathematics involved in such an event are described by fluctuation theorem.

A third formulation of the second law, by Lord Kelvin, is the heat engine formulation, or Kelvin statement:

It is impossible to convert heat completely into work in a cyclic process.

That is, it is impossible to extract energy by heat from a high-temperature energy source and then convert all of the energy into work. At least some of the energy must be passed on to heat a low-temperature energy sink. Thus, a heat engine with 100% efficiency is thermodynamically impossible.

3. Microscopic systems

Thermodynamics is a theory of macroscopic systems and therefore the second law applies only to macroscopic systems with well-defined temperatures. For example, in a system of two molecules, there is a non-trivial probability that the slower-moving ("cold") molecule transfers energy to the faster-moving ("hot") molecule. Such tiny systems are outside the domain of classical thermodynamics, but they can be investigated in quantum thermodynamics by using statistical mechanics. For any isolated system with a mass of more than a few picograms, probabilities of observing a decrease in entropy approach zero.

4. Energy dispersal

The second law of thermodynamics is an axiom of thermodynamics concerning heat, entropy, and the direction in which thermodynamic processes can occur. For example, the second law implies that heat does not spontaneously flow from a cold material to a hot material, but it allows heat to flow from a hot material to a cold material. Roughly speaking, the second law says that in an isolated system, concentrated energy disperses over time, and consequently less concentrated energy is available to do useful work. Energy dispersal also means that differences in temperature, pressure, and density even out. Again roughly speaking, thermodynamic entropy is a measure of energy dispersal, and so the second law is closely connected with the concept of entropy.

5. Entropy and the second law

An important law of physics, the second law of thermodynamics, states that the total entropy of any isolated thermodynamic system tends to increase over time, approaching a maximum value; and so, by implication, the entropy of the universe (i.e. the system and its surroundings), assumed as an isolated system, tends to increase. Two important consequences are that heat cannot of itself pass from a colder to a hotter body: i.e., it is impossible to transfer heat from a cold to a hot reservoir without at the same time converting a certain amount of work to heat. It is also impossible for any device that can operate on a cycle to receive heat from a single reservoir and produce a net amount of work; it can only get useful work out of the heat if heat is at the same time transferred from a hot to a cold reservoir. This means that there is no possibility of an isolated "perpetual motion" system. Also, from this it follows that a reduction in the increase of

entropy in a specified process, such as a chemical reaction, means that it is energetically more efficient.

In general, according to the second law, the entropy of a system that is not isolated may decrease. An air conditioner, for example, cools the air in a room, thus reducing the entropy of the air. The heat, however, involved in operating the air conditioner always makes a bigger contribution to the entropy of the environment than the decrease of the entropy of the air. Thus the total entropy of the room and the environment increases, in agreement with the second law.

6. Mathematical descriptions

In 1856, the German physicist Rudolf Clausius stated what he called the "second fundamental theorem in the mechanical theory of heat" in the following form:

Where Q is heat, T is temperature and N is the "equivalence-value" of all uncompensated transformations involved in a cyclical process. Later, in 1865, Clausius would come to define "equivalence-value" as entropy. On the heels of this definition, that same year, the most famous version of the second law was read in a presentation at the Philosophical Society of Zurich on April 24th, in which, in the end of his presentation, Clausius concludes:

The entropy of the universe tends to a maximum.

This statement is the best-known phrasing of the second law. Moreover, owing to the general broadness of the terminology used here, e.g. universe, as well as lack of specific conditions, e.g. open, closed, or isolated, to which this statement applies, many people take this simple statement to mean that the second law of thermodynamics applies virtually to every subject imaginable.

This, of course, is not true; this statement is only a simplified version of a more complex description.

In terms of time variation, the mathematical statement of the second law for an isolated system undergoing an arbitrary transformation is:

Where

S is the entropy and

t is time.

It should be noted that statistical mechanics gives an explanation for the second law by postulating that a material is composed of atoms and molecules which are in constant motion. A particular set of positions and velocities for each particle in the system is called a microstate of the system and because of the constant motion, the system is constantly changing its microstate. Statistical mechanics postulates that, in equilibrium, each microstate that the system might be in is equally likely to occur, and when this assumption is made, it leads directly to the conclusion that the second law must hold in a statistical sense. That is, the second law will hold on average, with a statistical variation on the order of $1/N$ where N is the number of particles in the system. For everyday (macroscopic) situations, the probability that the second law will be violated is practically zero. However, for systems with a small number of particles, thermodynamic parameters, including the entropy, may show significant statistical deviations from that predicted by the second law. Classical thermodynamic theory does not deal with these statistical variations.

7. Complex systems

It is occasionally claimed that the second law is incompatible with autonomous self-organization, or even the coming into existence of complex systems. This is a common creationist argument against evolution. The entry self-organization explains how this claim is a misconception. In fact, as hot systems cool down in accordance with the second law, it is not unusual for them to undergo spontaneous symmetry breaking, i.e. for structure to spontaneously appear as the temperature drops below a critical threshold. Complex structures, such as Bnard cells, also spontaneously appear where there is a steady flow of energy from a high temperature input source to a low temperature external sink.

Furthermore, a system that energy flows into and out of may decrease its local entropy provided the increase of the entropy to its surrounding that this process causes is greater than or equal to the local decrease in entropy. A good example of this is crystallization. As a liquid cools, crystals begin to form inside it. While these crystals are more ordered than the liquid they originated from, in order for them to form they must release a great deal of heat, known as the latent heat of fusion. This heat flows out of the system and increases the entropy of its surroundings to a greater extent than the decrease of energy that the liquid undergoes in the formation of crystals.

An interesting situation to consider is that of a supercooled liquid perfectly isolated thermodynamically, into which a grain of dust is dropped. Here even though the system cannot export energy to its surroundings, it will still crystallize. Now however the release of latent heat will contribute to raising its own temperature. If this release of heat causes the temperature to reach the melting point before it has fully crystallized, then it shall remain a mixture of liquid and solid; if not, then it will be a solid at a significantly higher temperature than it previously was as a liquid. In both cases entropy from its disordered structure is converted into entropy of disordered motion

Topic : Second-Law Analysis Of Thermodynamic Systems

Topic Objective:

At the end of this topic student would be able to:

- Learn the concept of Systems in Thermodynamics
- Learn the concept of Systems in equilibrium
- Learn the concept of Open systems

Definition/Overview:

Thermodynamic System: A thermodynamic system, originally called a working substance, is defined as that part of the universe that is under consideration. A real or imaginary boundary separates the system from the rest of the universe, which is referred to as the environment or surroundings (sometimes called a reservoir). A useful classification of thermodynamic systems is based on the nature of the boundary and the quantities flowing through it, such as matter, energy,

work, heat, and entropy. A system can be anything, for example a piston, a solution in a test tube, a living organism, an electrical circuit, a planet, etc.

The first to develop the concept of a "thermodynamic system" was the French physicist Sadi Carnot whose 1824 *Reflections on the Motive Power of Fire* studied what he called the "working substance" (system), i.e. typically a body of water vapor, in steam engines, in regards to the system's ability to do work when heat is applied to it. The working substance could be put in contact with either a heat reservoir (a boiler), a cold reservoir (a stream of cold water), or a piston (to which the working body could do work by pushing on it). In 1850, the German physicist Rudolf Clausius generalized this picture to include the concept of the surroundings, and began referring to the system as a "working body." In his 1850 manuscript *On the Motive Power of Fire*

Key Points:

1. Systems in Thermodynamics

Thermodynamics is conducted under a system-centered view of the universe. All quantities, such as pressure or mechanical work, in an equation refer to the system unless labeled otherwise. Thermodynamics is basically concerned with the flow and balance of energy and matter in a thermodynamic system. Three types of thermodynamic systems are distinguished depending on the kinds of interaction and energy exchange taking place between the system and its surrounding environment:

Isolated systems are completely isolated in every way from their environment. They do not exchange heat, work or matter with their environment. An example of an isolated system would be an insulated rigid container, such as an insulated gas cylinder.

Closed systems are able to exchange energy (heat and work) but not matter with their environment. A greenhouse is an example of a closed system exchanging heat but not work with its environment. Whether a system exchanges heat, work or both is usually thought of as a property of its boundary.

Open systems: exchanging energy (heat and work) and matter with their environment. A boundary allowing matter exchange is called permeable. The ocean would be an example of an open system.

In reality, a system can never be absolutely isolated from its environment, because there is always at least some slight coupling, even if only via minimal gravitational attraction. In analyzing a system in steady-state, the energy into the system is equal to the energy leaving the system.

As an example, consider the system of hot liquid water and solid table salt in a sealed, insulated test tube held in a vacuum (the surroundings). The test tube constantly loses heat (in the form of black-body radiation), but the heat loss progresses very slowly. If there is another process going on in the test tube, for example the dissolution of the salt crystals, it will probably occur so quickly that any heat lost to the test tube during that time can be neglected. (Thermodynamics does not measure time, but it does sometimes accept limitations on the timeframe of a process.)

2. Systems in equilibrium

In isolated systems it is consistently observed that as time goes on internal rearrangements diminish and stable conditions are approached. Pressures and temperatures tend to equalize, and matter arranges itself into one or a few relatively homogeneous phases. A system in which all processes of change have gone practically to completion is considered to be in a state of thermodynamic equilibrium. The thermodynamic properties of a system in equilibrium are unchanging in time. Equilibrium system states are much easier to describe in a deterministic manner than non-equilibrium states.

In thermodynamic processes, large departures from equilibrium during intermediate steps are associated with increases in entropy and increases in the production of heat rather than useful work. It can be shown that for a process to be reversible, each step in the process must be reversible. For a step in a process to be reversible, the system must be in equilibrium throughout the step. That ideal cannot be accomplished in practice because no step can be taken without perturbing the system from equilibrium, but the ideal can be approached by making changes slowly.

3. Open systems

In open systems, matter may flow in and out of the system boundaries. The first law of thermodynamics for open systems states: the increase in the internal energy of a system is equal to the amount of energy added to the system by matter flowing in and by heating, minus the amount lost by matter flowing out and in the form of work done by the system. The first law for open systems is given by:

where U_{in} is the average internal energy entering the system and U_{out} is the average internal energy leaving the system

The region of space enclosed by open system boundaries is usually called a control volume, and it may or may not correspond to physical walls. If we choose the shape of the control volume such that all flow in or out occurs perpendicular to its surface, then the flow of matter into the system performs work as if it were a piston of fluid pushing mass into the system, and the system performs work on the flow of matter out as if it were driving a piston of fluid. There are then two types of work performed: flow work described above which is performed on the fluid (this is also often called PV work) and shaft work which may be performed on some mechanical device.

These two types of work are expressed in the equation:

Substitution into the equation above for the control volume cv yields:

The definition of enthalpy, H , permits us to use this thermodynamic potential to account for both internal energy and PV work in fluids for open systems:

During steady-state operation of a device the expression above may be set equal to zero. This yields a useful expression for the power generation or requirement for these devices in the absence of chemical reactions:

This expression is described by the diagram above.

Mathematical descriptions

In 1856, the German physicist Rudolf Clausius stated what he called the "second fundamental theorem in the mechanical theory of heat" in the following form:

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In terms of time variation, the mathematical statement of the second law for an isolated system undergoing an arbitrary transformation is:

Where

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that the second law must hold in a statistical sense. That is, the second law will hold on average, with a statistical variation on the order of $1/N$ where N is the number of particles in the system. For everyday (macroscopic) situations, the probability that the second law will be violated is practically zero. However, for systems with a small number of particles, thermodynamic parameters, including the entropy, may show significant statistical deviations from that predicted by the second law. Classical thermodynamic theory does not deal with these statistical variations.

4. Available useful work

An important and revealing idealized special case is to consider applying the Second Law to the scenario of an isolated system (called the total system or universe), made up of two parts: a sub-system of interest, and the sub-system's surroundings. These surroundings are imagined to be so large that they can be considered as an unlimited heat reservoir at temperature T_R and pressure P_R so that no matter how much heat is transferred to (or from) the sub-system, the temperature of the surroundings will remain T_R ; and no matter how much the volume of the sub-system expands (or contracts), the pressure of the surroundings will remain P_R .

Whatever changes dS and dS_R occur in the entropies of the sub-system and the surroundings individually, according to the Second Law the entropy S_{tot} of the isolated total system must not decrease:

According to the First Law of Thermodynamics, the change dU in the internal energy of the sub-system is the sum of the heat q added to the sub-system, less any work w done by the sub-system, plus any net chemical energy entering the sub-system $d\sum \mu_i R N_i$, so that:

Where $\mu_i R$ are the chemical potentials of chemical species in the external surroundings.

Now the heat leaving the reservoir and entering the sub-system is

Where we have first used the definition of entropy in classical thermodynamics (alternatively, the definition of temperature in statistical thermodynamics); and then the Second Law inequality from above.

It therefore follows that any net work w done by the sub-system must obey

It is useful to separate the work w done by the subsystem into the useful work w_u that can be done by the sub-system, over and beyond the work $pR dV$ done merely by the sub-system expanding against the surrounding external pressure, giving the following relation for the useful work that can be done:

It is convenient to define the right-hand-side as the exact derivative of a thermodynamic potential, called the availability or exergy X of the subsystem,

The Second Law therefore implies that for any process which can be considered as divided simply into a subsystem, and an unlimited temperature and pressure reservoir with which it is in contact,

i.e. the change in the subsystem's exergy plus the useful work done by the subsystem (or, the change in the subsystem's exergy less any work, additional to that done by the pressure reservoir, done on the system) must be less than or equal to zero.

5. Gibbs and Helmholtz free energies

When no useful work is being extracted from the sub-system, it follows that

with the exergy X reaching a minimum at equilibrium, when $dX=0$.

If no chemical species can enter or leave the sub-system, then the term $\sum \mu_i R N_i$ can be ignored.

If furthermore the temperature of the sub-system is such that T is always equal to T_R , then this gives:

If the volume V is constrained to be constant, then

where A is the thermodynamic potential called Helmholtz free energy, $A=U-TS$. Under constant-volume conditions therefore, $dA < 0$ if a process is to go forward; and $dA=0$ is the condition for equilibrium.

Alternatively, if the sub-system pressure p is constrained to be equal to the external reservoir pressure p_R , then

where G is the Gibbs free energy, $G=U-TS+PV$. Therefore under constant-pressure conditions, if $dG < 0$, then the process can occur spontaneously, because the change in system energy exceeds the energy lost to entropy. $dG=0$ is the condition for equilibrium. This is also commonly written in terms of enthalpy, where $H=U+PV$.

Application

In sum, if a proper infinite-reservoir-like reference state is chosen as the system surroundings in the real world, then the Second Law predicts a decrease in X for an irreversible process and no change for a reversible process.

is equivalent to

This expression together with the associated reference state permits a design engineer working at the macroscopic scale (above the thermodynamic limit) to utilize the Second Law without directly measuring or considering entropy change in a total isolated system.. Those changes have already been considered by the assumption that the system under consideration can reach equilibrium with the reference state without altering the reference state. Efficiency for a process or collection of processes that compares it to the reversible ideal may also be found. This approach to the Second Law is widely utilized in engineering practice, environmental accounting, systems ecology, and other disciplines.

In Section 3 of this course you will cover these topics:

- Gas Cycles
- Exhaust Flow
- Thermodynamic Relationships

Topic : Gas Cycles**Topic Objective:**

At the end of this topic student would be able to:

- Learn the concept of Thermodynamic power cycles
- Learn the concept of Thermodynamic heat pump and refrigeration cycle
- Learn the concept of Carnot cycle
- Learn the concept of Ideal cycle

Definition/Overview:

A thermodynamic cycle is a series of thermodynamic processes transferring heat and work, while varying pressure, temperature, and other state variables, eventually returning a system to its initial state. State Properties depend only on the thermodynamic state and cumulative variation of such properties adds up to zero. Path Quantities, such as heat and work are process dependent, and cumulative heat and work are non-zero. The first law of thermodynamics dictates that the net heat input is equal to the net work output over any cycle. The repeating nature of the process path allows for continuous operation, making the cycle an important concept in thermodynamics. Thermodynamic cycles often use quasistatic processes to model the workings of actual devices. A thermodynamic cycle is a closed loop on a P-V diagram. A P-V diagram's X axis shows volume (V) and Y axis shows pressure (P). The area enclosed by the loop is the work (W) done by the process:

This work is equal to the balance of heat (Q) transferred into the system:

Equation (2) makes a cyclic process similar to an isothermal process: even though the internal energy changes during the course of the cyclic process, when the cyclic process finishes the system's energy is the same as the energy it had when the process began.

If the cyclic process moves clockwise around the loop, then it represents a heat engine, and W will be positive. If it moves counterclockwise then it represents a heat pump, and W will be negative.

Key Points:

1. Thermodynamic power cycles

Thermodynamic power cycles are the basis for the operation of heat engines, which supply most of the world's electric power and run almost all motor vehicles. Power cycles can be divided according to the type of heat engine they seek to model. The most common cycles that model internal combustion engines are the Otto cycle, which models gasoline engines and the Diesel cycle, which models diesel engines. Cycles that model external combustion engines include the Brayton cycle, which models gas turbines, and the Rankine cycle, which models steam turbines.

For example the pressure-volume mechanical work done in the heat engine cycle, consisting of 4 thermodynamic processes, is:

If no volume change happens in process $4 \rightarrow 1$ and $2 \rightarrow 3$, equation (3) simplifies to:

2. Thermodynamic heat pump and refrigeration cycle

Thermodynamic heat pump and refrigeration cycles are the models for heat pumps and refrigerators. The difference between the two is that heat pumps are intended to keep a place warm and refrigerators designed to cool it. The most common refrigeration cycle is the vapor compression cycle, which models systems using refrigerants that change phase. The absorption refrigeration cycle is an alternative that absorbs the refrigerant in a liquid solution rather than evaporating it. Gas refrigeration cycles include the reversed Brayton cycle and the Hampson-Linde cycle. Regeneration in gas refrigeration allows for the liquefaction of gases.

3. Carnot cycle

The Carnot cycle is a cycle composed of the totally reversible processes of isentropic compression and expansion and isothermal heat addition and rejection. The thermal efficiency of a Carnot cycle depends only on the temperatures in Kelvins of the two reservoirs in which heat transfer takes place, and for a power cycle is:

Where T_L is the lowest cycle temperature and T_H the highest. For Carnot refrigeration cycles the coefficient of performance for a heat pump is:

And for a refrigerator the coefficient of performance is:

The second law of thermodynamics limits the efficiency and COP for all cyclic devices to levels at or below the Carnot efficiency. The Stirling cycle and Ericsson cycle are two other reversible cycles that use regeneration to obtain isothermal heat transfer.

4. Ideal cycle

An ideal cycle is constructed out of:

TOP and BOTTOM of the loop: a pair of parallel isobaric processes

LEFT and RIGHT of the loop: a pair of parallel isochoric processes

5. Otto cycle

An Otto cycle is constructed out of:

TOP and BOTTOM of the loop: a pair of quasi-parallel adiabatic processes

LEFT and RIGHT sides of the loop: a pair of parallel isochoric processes

The adiabatic processes are impermeable to heat: heat flows into the loop through the left pressurizing process and some of it flows back out through the right depressurizing process, and the heat which remains does the work.

6. Stirling cycle

A Stirling cycle is like an Otto cycle, except that the adiabats are replaced by isotherms.

TOP and BOTTOM of the loop: a pair of quasi-parallel isothermal processes

LEFT and RIGHT sides of the loop: a pair of parallel isochoric processes

Heat flows into the loop through the top isotherm and the left isochore, and some of this heat flows back out through the bottom isotherm and the right isochore, but most of the heat flow is through the pair of isotherms. This makes sense since all the work done by the cycle is done by the pair of isothermal processes, which are described by $Q=W$. This suggests that all the net heat comes in through the top isotherm. In fact, all of the heat which comes in through the left isochore comes out through the right isochore: since the top isotherm is all at the same warmer temperature T_H and the bottom isotherm is all at the same cooler temperature T_C , and since change in energy for an isochore is proportional to change in temperature, then all of the heat coming in through the left isochore is cancelled out exactly by the heat going out the right isochore.

7. State functions and entropy

If Z is a state function then the balance of Z remains unchanged during a cyclic process:

Entropy is a state function and is defined as

So that

Then it is clear that for any cyclic process,

Meaning that the entropy net entropy over a cycle is 0.

Topic : Exhaust Flow

Topic Objective:

At the end of this topic student would be able to:

- Learn the concept of Vapor Cycle Theory
- Learn the concept of Ideal Rankine cycle
- Understand the concept of Vapor-compression cycle
- Learn the concept of Vapor absorption cycle

Definition/Overview:

Vapor Cycle Theory: Refrigerant used in the vapor cycle refrigeration system occurs as both a liquid and as a vapor. Conversion from a liquid to a vapor will occur at temperatures above 21F (34C) at sea level. If the refrigerant pressure is increased, conversion to a vapor will occur at higher temperatures. Maximum heat transfer efficiency occurs when the refrigerant is at the boiling point (the point at which the liquid will vaporize). The refrigerant must be delivered to the evaporator as a liquid if it is to absorb large quantities of heat. Since it leaves the evaporator in the form of a vapor, some way of condensing the vapor is necessary. To condense the refrigerant vapor, the heat surrendered by the vapor during condensation must be transferred to some other medium. For this purpose, water or air is ordinarily used. The water or air must be at a temperature lower than the condensing temperature of the refrigerant. At any given pressure, the condensing and vaporizing temperature of a fluid are the same. If a refrigerant that vaporizes at 40F (5C) is to be condensed at the same temperature, water or air at a lower temperature is needed. Obviously, if water or air at this lower temperature were available, mechanical refrigeration would not be required. As the temperature of available water or air is usually always higher than the temperature of the boiling refrigerant in the evaporator, the refrigerant must be condensed after it leaves the evaporator. To condense the vapor, its pressure must be increased to a point that its condensing temperature will be above the temperature of the water or air available for condensing purposes. For this purpose a compressor is needed. After the pressure of the refrigerant vapor has been increased sufficiently, it may be liquefied in the condenser with comparatively warm water or air.

Key Points:**1. Ideal Rankine cycle**

The Rankine cycle is a thermodynamic cycle which converts heat into work. The heat is supplied externally to a closed loop, which usually uses water as the working fluid. This cycle generates about 80% of all electric power used throughout the world. Including virtually all solar thermal,

biomass, coal and nuclear power plants. It is named after William John Macquorn Rankine, a Scottish polymath. A Rankine cycle describes a model of the operation of steam heat engines most commonly found in power generation plants. Common heat sources for power plants using the Rankine cycle are coal, natural gas, oil, and nuclear.

The Rankine cycle is sometimes referred to as a practical Carnot cycle as, when an efficient turbine is used, the TS diagram will begin to resemble the Carnot cycle. The main difference is that a pump is used to pressurize liquid instead of gas. This requires about 100 times less energy than that compressing a gas in a compressor (as in the Carnot cycle).

The efficiency of a Rankine cycle is usually limited by the working fluid. Without the pressure going super critical the temperature range the cycle can operate over is quite small, turbine entry temperatures are typically 565C (the creep limit of stainless steel) and condenser temperatures are around 30C. This gives a theoretical Carnot efficiency of around 63% compared with an actual efficiency of 42% for a modern coal-fired power station. This low turbine entry temperature (compared with a gas turbine) is why the Rankine cycle is often used as a bottoming cycle in combined cycle gas turbine power stations.

The working fluid in a Rankine cycle follows a closed loop and is re-used constantly. The water vapor often seen billowing from power stations is generated by the cooling systems (not from the closed loop Rankine power cycle) and represents the waste heat that could not be converted to useful work. Note that steam is invisible until it comes in contact with cool, saturated air, at which point it condenses and forms the white billowy clouds seen leaving cooling towers. While many substances could be used in the Rankine cycle, water is usually the fluid of choice due to its favorable properties, such as nontoxic and unreactive chemistry, abundance, and low cost, as well as its thermodynamic properties.

One of the principal advantages it holds over other cycles is that during the compression stage relatively little work is required to drive the pump, due to the working fluid being in its liquid phase at this point. By condensing the fluid to liquid, the work required by the pump will only consume approximately 1% to 3% of the turbine power and so give a much higher efficiency for a real cycle. The benefit of this is lost somewhat due to the lower heat addition temperature. Gas turbines, for instance, have turbine entry temperatures approaching 1500C. Nonetheless, the efficiencies of steam cycles and gas turbines are fairly well matched.

2. Vapor-compression cycle

The vapor-compression cycle is used in most household refrigerators as well as in many large commercial and industrial refrigeration systems. Figure 1 provides a schematic diagram of the components of a typical vapor-compression refrigeration system.

The thermodynamics of the cycle can be analyzed on a diagram as shown in Figure 2. In this cycle, a circulating refrigerant such as Freon enters the compressor as a vapor. From point 1 to point 2, the vapor is compressed at constant entropy and exits the compressor superheated. From point 2 to point 3 and on to point 4, the superheated vapor travels through the condenser which first cools and removes the superheat and then condenses the vapor into a liquid by removing additional heat at constant pressure and temperature. Between points 4 and 5, the liquid refrigerant goes through the expansion valve (also called a throttle valve) where its pressure abruptly decreases, causing flash evaporation and auto-refrigeration of, typically, less than half of the liquid.

That results in a mixture of liquid and vapor at a lower temperature and pressure as shown at point 5. The cold liquid-vapor mixture then travels through the evaporator coil or tubes and is completely vaporized by cooling the warm air (from the space being refrigerated) being blown by a fan across the evaporator coil or tubes. The resulting refrigerant vapor returns to the compressor inlet at point 1 to complete the thermodynamic cycle.

The above discussion is based on the ideal vapor-compression refrigeration cycle, and does not take into account real-world effects like frictional pressure drop in the system, slight thermodynamic irreversibility during the compression of the refrigerant vapor, or non-ideal gas behavior (if any).

More information about the design and performance of vapor-compression refrigeration systems is available in the classic "Perry's Chemical Engineers' Handbook".

3. Vapor absorption cycle

In the early years of the twentieth century, the vapor absorption cycle using water-ammonia systems was popular and widely used. After the development of the vapor compression cycle, the vapor absorption cycle lost much of its importance because of its low coefficient of performance

(about one fifth of that of the vapor compression cycle). Today, the vapor absorption cycle is used mainly where fuel for heating is available but electricity is not, such as in recreational vehicles that carry LP gas. It's also used in industrial environments where plentiful waste heat overcomes its inefficiency.

The absorption cycle is similar to the compression cycle, except for the method of raising the pressure of the refrigerant vapor. In the absorption system, the compressor is replaced by an absorber which dissolves the refrigerant in a suitable liquid, a liquid pump which raises the pressure and a generator which, on heat addition, drives off the refrigerant vapor from the high-pressure liquid. Some work is required by the liquid pump but, for a given quantity of refrigerant, it is much smaller than needed by the compressor in the vapor compression cycle. In an absorption refrigerator, a suitable combination of refrigerant and absorbent is used. The most common combinations are ammonia (refrigerant) and water (absorbent), and water (refrigerant) and lithium bromide (absorbent).

4. Equations

Each of the first four equations is easily derived from the energy and mass balance for a control volume. The fifth equation defines the thermodynamic efficiency of the cycle as the ratio of net power output to heat input. As the work required by the pump is often around 1% of the turbine work output, equation 5 can be simplified.

Topic : Thermodynamic Relationships

Topic Objective:

At the end of this topic student would be able to:

- Learn the concept of Set of Thermodynamic Variables
- Understand the Gibbs Equation
- Understand the Thermodynamic relations

Definition/Overview:

Thermodynamics deals with the interrelationships between the macroscopic variables which describe physical systems. This chapter will explore those relationships in some detail on two levels. The first level concerns the many interrelationships that are of a strictly mathematical nature derivable from a few general principles. The second level of discussion concerns interrelationships that exist in specific systems because of some a priori knowledge concerning the system. This a priori knowledge may consist of experimental or theoretical information. The key point toward understanding for the student will be to separate the general relationships from the specific relationships.

Key Points:**1. The Set of Thermodynamic Variables**

The Thermodynamic Identity of Section 5.09 will serve as the starting point for a discussion of thermodynamic variables. We quote that result:

There are seven variables in this expression. This is typical of thermodynamic problems but is not a general result. Equation (1) is restricted to one mechanical force and one type of particle. Extension to multiple forces acting on the system at one time (gravitational, electric, and magnetic, as examples) can be achieved by adding addition terms to Equation (1) for each of the distinct forces. That equation would look like,

Here the F_i represent the additional forces with the dx_i being the corresponding displacement coordinates.

Equation (1) can be extended to multiple types of particles by recognizing that each type of particle would have its own chemical potential. That extension would like,

The N_j represent the particle numbers of the additional species and the μ_j are their respective chemical potentials.

2. Gibbs Equation the Gibbs free energy is defined as:

$$G = U + pV - TS$$

which is the same as:

$$G = H - TS$$

where:

- U is the internal energy (SI unit: joule)
- p is pressure (SI unit: pascal)
- V is volume (SI unit: m³)
- T is the temperature (SI unit: Kelvin)
- S is the entropy (SI unit: joule per Kelvin)
- H is the enthalpy (SI unit: joule)

Note: H and S are Thermodynamic values found at Standard Temperature and Pressure. The expression for the infinitesimal reversible change in the Gibbs free energy, for an open system, subjected to the operation of external forces X_i , which cause the external parameters of the system a_i to change by an amount da_i , is given by:

$TdS = dq = dU + pdV$ where:

μ_i is the chemical potential of the i th chemical component. (SI unit: joules per particle or joules per mol)

N_i is the number of particles (or number of moles) composing the i th chemical component.

This is one form of Gibbs fundamental equation. In the infinitesimal expression, the term involving the chemical potential accounts for changes in Gibbs free energy resulting from an influx or outflux of particles. In other words, it holds for an open system. For a closed system, this term may be dropped.

Any number of extra terms may be added, depending on the particular system being considered. Aside from mechanical work, a system may, in addition, perform numerous other types of work. For example, in the infinitesimal expression, the contractile work energy associated with a thermodynamic system that is a contractile fiber that shortens by an amount $-dl$ under a force f would result in a term $f dl$ being added. If a quantity of charge $-de$ is acquired by a system at an electrical potential ϕ , the electrical work associated with this is $-\phi de$, which would be included in the infinitesimal expression. Other work terms are added on per system requirements.

Each quantity in the equations above can be divided by the amount of substance, measured in moles, to form molar Gibbs free energy. The Gibbs free energy is one of the most important thermodynamic functions for the characterization of a system. It is a factor in determining outcomes such as the voltage of an electrochemical cell, and the equilibrium constant for a reversible reaction. In isothermal, isobaric systems, Gibbs free energy can be thought of as a "dynamic" quantity, in that it is a representative measure of the competing effects of the enthalpic and entropic driving forces involved in a thermodynamic process.

The temperature dependence of the Gibbs energy for an ideal gas is given by the Gibbs-Helmholtz equation and its pressure dependence is given by:

if the volume is known rather than pressure then it becomes:

or more conveniently as its chemical potential:

In non-ideal systems, fugacity comes into play.

Derivation

The Gibbs free energy total differential in terms of its natural variables may be derived via Legendre transforms of the internal energy. For a system undergoing an internally reversible process that is allowed to exchange matter, heat and work with its surroundings, the differential of the internal energy is given from the first law of thermodynamics as

Because S , V , and N_i are extensive variables, Euler's homogeneous function theorem allows easy integration of dU :

The definition of G from above is

Taking the total differential, we have

Replacing dU with the result from the first law gives

The natural variables of G are then p , T , and $\{N_i\}$. Because some of the natural variables are intensive, dG may not be integrated using Euler integrals as is the case with internal energy. However, simply substituting the result for U into the definition of G gives a standard expression for G :

3. Thermodynamic relations

First, we assume that the magnetic moment M and the external field H together with the temperature T provide a complete characterization of states of our magnetic system. If M and H are conjugate work variables and F is the Helmholtz free energy, then

F is the corresponding Gibbs free energy. It is known from thermodynamics, that F is the thermodynamic potential controlling spontaneous transformations under fixed T and H . Any transformation of this kind can only proceed in the sense of producing a decrease of F , and thermodynamic equilibrium is reached when F attains its globally minimum value. In our magnetic system the internal degrees of freedom, which give rise to these spontaneous transformations, can be represented by the magnetic moment M itself. Here, we assume, that M varies during the relaxation process and the internal processes leading to a certain value and direction of M have characteristic relaxation times much shorter than the time scale over which T varies significantly and the system globally approaches equilibrium. This means, that the system relaxes by passing through a sequence of nonequilibrium states, each characterized by a well-defined value of M . The energy of these intermediate states, for fixed T and H , is given by

This is the Landau free energy. The important difference between F and F_L lies in the role of M . F is a function of M and H only, in which H must be expressed as a function of M and T through the equation of state of the system. On the contrary, F_L is the energy of that particular restriction where the state variable M is forced to take a certain given value, as if it were an external constraint.

The equation of state of the system for the conjugate work variables M and H is given by

and

So far we did not consider the dependence of the magnetization on space coordinates, but magnetic materials exhibit complicated magnetization patterns. Thus, we subdivide our

ferromagnetic body into many elementary volumes, which are small enough with respect to the typical length over which the magnetization varies significantly and at the same time large enough to contain a sufficient number of atoms, so that we can make use of statistical and thermodynamic methods to describe the properties of the volume. We can then calculate the Landau free energy for each elementary volume. At this point the different time scales become obvious again: The assumption, which led to the definition of τ means, that the relaxation time over which individual elementary volumes reach thermal equilibrium with respect to the given local value of the magnetization M is much shorter than the time over which the system as a whole approaches equilibrium through time changes of M .

There are four important contributions to the Landau free energy of a ferromagnetic body: the exchange energy, the magnetocrystalline anisotropy energy, the magnetostatic energy, and the Zeeman energy in an external field.

Another contribution, magnetoelastic energy, which arises from magnetostriction, is omitted for two reasons. When a ferromagnet is magnetized it shrinks (or expands) in the direction of the magnetization. As a result, the volume changes and with it the saturation magnetization, which is defined as the magnetic moment in saturation per unit volume. However, in micromagnetics it is a basic assumption, that the saturation magnetization remains constant. Secondly, a large part of the internal magnetostriction in a ferromagnetic crystal can be expressed in the same mathematical form as magnetocrystalline anisotropy. If the anisotropy constants are taken from experiment, the effect of magnetostriction is already included, and therefore we do not have to consider it in an additional energy term.

In Section 4 of this course you will cover these topics:

- Thermodynamic Behavior Of Real Gases
- Non-Reacting-Gas Mixtures

Topic : Thermodynamic Behavior Of Real Gases**Topic Objective:**

At the end of this topic student would be able to:

- Learn the concept of Classical thermodynamic ideal gas
- Learn the concept of Compressibility factor
- Learn the concept of Generalized compressibility factor graphs for pure gases
- Learn the concept of Compressibility of air

Definition/Overview:

The ideal gas model is a model of matter in which the molecules are treated as non-interacting point particles which are engaged in a random motion that obeys conservation of energy. At standard temperature and pressure, most real gases behave qualitatively like an ideal gas: for example, 22.4 liters of most gases at standard temperature and pressure will contain very nearly 6.022×10^{23} molecules (one mole).

The model tends to fail at lower temperatures or higher pressures, when the molecules come close enough that they start interacting with each other, and not just with their surroundings. This is usually associated with a phase transition. For example, clouds form when the gas of water molecules in the sky drops below the dew point, which causes the water molecules to "stick together" into little droplets. By contrast, at high temperatures and low pressures, the vast majority of familiar substances can be vaporised and will behave more-or-less as an ideal gas. The ideal gas model has been explored in both the Newtonian dynamics (as "kinetic theory") and in quantum mechanics (as a "gas in a box"). The model has also been used to model the behavior of electrons in a metal (in the Drude model and free electron model) and is one of the most important models in statistical mechanics.

Key Points:**1. Classical thermodynamic ideal gas**

The thermodynamic properties of an ideal gas can be described by two equations: The equation of state of a classical ideal gas is given by the ideal gas law.

The internal energy of an ideal gas is given by:

Where:

γ is a constant dependent on temperature (e.g. equal to $3/2$ for a monoatomic gas for moderate temperatures)

U is the internal energy

P is the pressure

V is the volume

n is the amount of gas (moles)

R is the gas constant, $8.314 \text{ JK}^{-1}\text{mol}^{-1}$

T is the absolute temperature

N is the number of particles

k is the Boltzmann constant, $1.38110^{-23}\text{JK}^{-1}$

The probability distribution of particles by velocity or energy is given by the Boltzmann distribution.

The ideal gas law is an extension of experimentally discovered gas laws. Real fluids at low density and high temperature approximate the behavior of a classical ideal gas. However, at lower temperatures or a higher density, a real fluid deviates strongly from the behavior of an ideal gas, particularly as it condenses from a gas into a liquid or solid. The deviation is expressed as a compressibility factor.

2. Compressibility factor

The compressibility factor (Z) is a useful thermodynamic property for modifying the ideal gas law to account for the real gas behavior. In general, deviations from ideal behavior become more

significant the closer a gas is to a phase change, the lower the temperature or the larger the pressure. Compressibility factor values are usually obtained by calculation from equations of state (EOS), such as the virial equation which take compound specific empirical constants as input. Alternatively, the compressibility factor for specific gases can be read from generalized compressibility charts. that plot Z as a function of pressure at constant temperature.

The compressibility factor is defined as:

where, p is the pressure, V_m is the molar volume of the gas, T is the temperature, and R is the gas constant.

For an ideal gas the compressibility factor is $Z = 1$ per definition. In many real world applications requirements for accuracy demand that deviations from ideal gas behaviour, i.e. real gas behaviour, is taken into account. The value of Z generally increases with pressure and decreases with temperature. At high pressures molecules are colliding more often, and at low temperatures they are moving less rapidly. This allows attractive forces between molecules to have a noticeable effect, making the volume of the real gas (V_{real}) less than the volume of an ideal gas (V_{ideal}) which causes Z to drop below one. When pressures are lower or temperatures higher, the molecules are freer to move. In this case repulsive forces dominate, making $Z > 1$. The closer the gas is to its critical point or its boiling point, the more Z deviates from the ideal case.

3. Generalized compressibility factor graphs for pure gases

The unique relationship between the compressibility factor and the so-called reduced temperature, T_r , and the so-called reduced pressure, P_r , was first recognized by Johannes Diderik van der Waals in 1873 and is known as the two-parameter principle of corresponding states. The principle of corresponding states expresses the generalization that the properties of a gas which are dependent on intermolecular forces are related to the critical properties of the gas in a universal way. That provides a most important basis for developing correlations of molecular properties.

As for the compressibility of gases, the principle of corresponding states indicates that any pure gas at the same reduced temperature, T_r , and reduced pressure, P_r , should have the same compressibility factor.

The reduced temperature and pressure are defined as:

And

T_c and P_c are known as the critical temperature and critical pressure of a gas. They are characteristics of each specific gas with T_c being the temperature above which it is not possible to liquefy a given gas and P_c is the minimum pressure required to liquefy a given gas at its critical temperature. Together they define the critical point of a fluid above which distinct liquid and gas phases of a given fluid do not exist. The pressure-volume-temperature (PVT) data for real gases varies from one pure gas to another. However, when the compressibility factors of various single-component gases are graphed versus pressure along with temperature isotherms many of the graphs exhibit similar isotherm shapes. In order to obtain a generalized graph that can be used for many different gases, the reduced pressure and temperature, P_r and T_r , are used to normalize the compressibility factor data. Figure 2 is an example of a generalized compressibility factor graph derived from hundreds of experimental P-V-T data points of 10 pure gases, namely methane, ethane, ethylene, propane, n-butane, i-pentane, n-hexane, nitrogen, carbon dioxide and steam. There are more detailed generalized compressibility factor graphs based on as many as 25 or more different pure gases, such as the Nelson-Obert graphs. Such graphs are said to have accuracy within 1-2 percent for Z values greater than 0.6 and within 4-6 percent for Z values of 0.3-0.6. The generalized compressibility factor graphs may be considerably in error for strongly polar gases which are gases for which the centers of positive and negative charge do not coincide. In such cases the estimate for Z may be in error by as much as 15-20 percent. The quantum gases hydrogen, helium, and neon do not conform to the corresponding-states behavior and the reduced pressure and temperature for those three gases should be redefined in the following manner to improve the accuracy of predicting their compressibility factors when using the generalized graphs:

and

4. Compressibility of air

Normal air comprises in crude numbers 80 percent nitrogen N₂ and 20 percent oxygen O₂. Both molecules are small and non-polar (and therefore non-associating). We can therefore expect that the behavior of air within broad temperature and pressure ranges can be approximated as an ideal gas with reasonable accuracy. Experimental values for the compressibility factor confirm this.

Z for air as function of pressure 1-500 bars

75-200 K isotherms 250-1000 K isotherms

[Figure 2: Z for air as function of pressure 1-500 bars]

5. Clausius modelisation

The Clausius equation is a very simple three-parameter equation used to modelize gases.

where

Topic : Non-Reacting-Gas Mixtures

Topic Objective:

At the end of this topic student would be able to:

- Learn the concept of Gas Mixtures
- Learn the concept of Homogeneous Mixtures
- Learn the concept of Colloidal Dispersions
- Learn the concept of Suspensions
- Learn the concept of Mixtures and Compounds

Definition/Overview:

Gas Mixtures: In chemistry, a mixture is a substance made by combining two or more different materials without a chemical reaction occurring. A mixture is very different from a compound. The objects do not bond together in a mixture. A mixture can usually be separated back into its original components. Some examples of mixtures are: fruit salad, ocean water and soil, some examples of heterogeneous mixtures are salt water, iron fillings, sulfur and salt mixed with sand. Mixtures are the product of a mechanical blending or mixing of chemical substances like elements and compounds, without chemical bonding or other chemical change, so that each ingredient substance retains its own chemical properties and makeup.

While there are no chemical changes in a mixture, physical properties of a mixture, such as its melting point, may differ from those of its components. Mixtures can usually be separated by any mechanical means. Mixtures are either homogeneous or heterogeneous.

Key Points:**1. Homogeneous Mixtures**

Homogeneous mixtures are mixtures that have definite, consistent properties. Particles are uniformly spread. For example, any amount of a given mixture has the same composition and properties. Examples are solutions and some alloys (but not all). A homogeneous mixture is a uniform mixture consisting of only one phase. Examples are gasoline and margarine.

A solution is when a homogeneous mixture of one or more substances (the solutes) dissolved in another substance (the solvent). Solutions have all particles within the size of atoms, small molecules or small ions, less than 1 nanometer (nm) in all dimensions. A common example would be a solid dissolving into a liquid (i.e. salt or sugar dissolving in water or gold into

mercury). Liquids dissolve into one another, and sometimes liquids dissolve into gases, for example water vapor and the atmosphere. Common examples include fountain drinks, where carbon dioxide is trapped in the liquid through carbonation. Several solution properties collectively called colligative properties change as a function of solute concentration. Solubility is a compound property.

2. Colloidal Dispersions

Colloids are another type of homogeneous mixture in which the particles of one or more components have at least one dimension in the range of 1 to 1000nm, larger than those in a solution but smaller than those in a suspension. In general, a colloid or colloidal dispersion is a substance with components of one or two phases. It creates the Tyndall effect when light passes through it. A colloid will not settle if left to sit. Jelly, milk, blood, paint, fog, and glue are examples of colloid dispersions.

3. Heterogeneous Mixtures

Heterogeneous mixtures are mixtures with inconsistent, non-uniform composition. The parts of a heterogeneous composition can be mechanically separated from each other. Examples include salad, trail mix and granite.

4. Suspensions

A heterogeneous mixture in which the particles, of at least one component is larger than 1 μ m (1000nm) in at least one dimension, larger than colloidal particles. Unlike colloids, suspensions will eventually settle. An example of a suspension would be sand in water. Particles of suspensions exhibit the Tyndall effect, that is, they are big enough to disperse light.

5. Mixtures and Compounds

A compound is not a mixture. A compound has very different properties than the elements it is made of, but a mixture contains several substances which keep their properties.

The gas constant (also known as the molar, universal, or ideal gas constant, usually denoted by symbol R) is a physical constant which is featured in a large number of fundamental equations in the physical sciences, such as the ideal gas law and the Nernst equation. It is equivalent to the Boltzmann constant, but expressed in units of energy (i.e. the pressure-volume product) per Kelvin per mole (rather than energy per Kelvin per particle).

Its value is:

$$R = 8.314472(15) \text{ J K}^{-1} \text{ mol}^{-1}$$

The two digits in parentheses are the uncertainty (standard deviation) in the last two digits of the value.

The gas constant occurs in the simplest equation of state, the ideal gas law, as follows:

where:

p is the absolute pressure

T is absolute temperature

V is the volume the gas occupies

n is the amount of gas (the number of gas molecules, usually in moles)

V_m is the molar volume

The gas constant has the same units as specific entropy.

6. Air-fuel ratio

Air-fuel ratio (AFR) is the mass ratio of air to fuel present during combustion. When all the fuel is combined with all the free oxygen, typically within a vehicle's combustion chamber, the mixture is chemically balanced and this AFR is called the stoichiometric mixture (often abbreviated to stoich). AFR is an important measure for anti-pollution and performance tuning reasons. Lambda (λ) is an alternative way to represent AFR.

In industrial fired heaters, power plant steam generators, and large gas-fired turbines, the more common term is percent excess combustion air. For example, excess combustion air of 15 percent means that 15 percent more than the required stoichiometric air is being used.

A mixture is the working point that modern engine management systems employing fuel injection attempt to achieve in light load cruise situations. For gasoline fuel, the stoichiometric air/fuel mixture is approximately 14.7 times the mass of air to fuel. Any mixture less than 14.7 to 1 is considered to be a rich mixture, any more than 14.7 to 1 is a lean mixture - given perfect (ideal) "test" fuel (gasoline consisting of solely n-heptane and iso-octane). In reality, most fuels consist of a combination of heptane, octane, a handful of other alkanes, plus additives including detergents, and possibly oxygenators such as MTBE (methyl tert-butyl ether) or ethanol/methanol. These compounds all alter the stoichiometric ratio, with most of the additives pushing the ratio downward (oxygenators bring extra oxygen to the combustion event in liquid form that is released at time of combustions; for MTBE-laden fuel, a stoichiometric ratio can be as low as 14.1:1). Vehicles using an oxygen sensor(s) or other feedback-loop to control fuel to air ratios (usually by controlling fuel volume) will usually compensate automatically for this change in the fuel's stoichiometric rate by measuring the exhaust gas composition, while vehicles without such controls (such as most motorcycles until recently, and cars predating the mid-1980s) may have difficulties running certain boutique blends of fuels (esp. winter fuels used in some areas) and may need to be rejetted (or otherwise have the fueling ratios altered) to compensate for special boutique fuel mixes. Vehicles using oxygen sensors enable the air-fuel ratio to be monitored by means of an air fuel ratio meter.

Lean mixtures produce hotter combustion gases than does a stoichiometric mixture, so much so that pistons can melt as a result. Rich mixtures produces cooler combustion gases than does a stoichiometric mixture, primarily due to the excessive amount of carbon which oxidises to form carbon monoxide, rather than carbon dioxide. The chemical reaction oxidizing carbon to form carbon monoxide releases significantly less heat than the similar reaction to form carbon dioxide. (Carbon monoxide retains significant potential chemical energy. It is itself a fuel whereas carbon dioxide is not.) Lean mixtures, when consumed in an internal combustion engine, produce less power than does the stoichiometric mixture. Similarly, rich mixtures return poorer fuel efficiency than the stoichiometric mixture. (The mixture for the best fuel efficiency is slightly different from the stoichiometric mixture.)

7. Equivalence ratio

The equivalence ratio of a system is defined as the ratio of the fuel-to-oxidizer ratio to the stoichiometric fuel-to-oxidizer ratio. Mathematically,

where, m represents the mass, n represents number of moles, suffix st stands for stoichiometric conditions.

TLALI ratio over fuel-to-oxidizer ratio is that it does not have the same dependence as fuel-to-oxidizer ratio on the units being used. For example fuel-to-oxidizer ratio based on mass of fuel and oxidizer is not same as one define based on number of moles. This is not the case for equivalence ratio. The following example can help clarify the point. Consider a mixture of one mole of ethane (C_2H_6) and one mole of oxygen (O_2).

Fuel-to-oxidizer ratio of this mixture based on the mass of fuel and air is

Fuel-to-oxidizer ratio of this mixture based on the number of moles of fuel and air is

Clearly the two values are not equal. To compare it to the equivalence ratio, we need to determine the fuel-to-oxidizer ratio of ethane and oxygen mixture. For this we need to consider the stoichiometric reaction of ethane and oxygen,

This gives,

Thus we can determine the equivalence ratio of the give mixture as,

or equivalently as,

Another advantage of using the equivalence ratio is that ratios greater than one always represent excess fuel in the fuel-oxidizer mixture than would be required for complete combustion (stoichiometric reaction) irrespective of the fuel and oxidizer being used. While ratios less than 1 represents a deficiency of fuel or equivalently excess oxidizer in the mixture. This is not the case if one uses fuel-to-oxidizer ratio, which will take different values for different mixtures. It should be noted that equivalence ratio is related to ϕ (defined previously) as follows,

In Section 5 of this course you will cover these topics:

- ▀ Thermodynamics Of Chemical Reactions
- ▀ Chemical Equilibrium
- ▀ Introduction To One-Dimensional Compressible Flow

Topic : Thermodynamics Of Chemical Reactions

Topic Objective:

At the end of this topic student would be able to:

- Learn the concept of Chemical Thermodynamics
- Learn the concept of Chemical energy

- Learn the concept of Chemical reactions
- Learn the concept of Chemical affinity

Definition/Overview:

Chemical Thermodynamics: Chemical thermodynamics is the study of the interrelation of heat and work with chemical reactions or with physical changes of state within the confines of the laws of thermodynamics. Chemical thermodynamics involves not only laboratory measurements of various thermodynamic properties, but also the application of mathematical methods to the study of chemical questions and the spontaneity of processes. The structure of chemical thermodynamics is based on the first two laws of thermodynamics. Starting from the first and second laws of thermodynamics, four equations called the "fundamental equations of Gibbs" can be derived. From these four, a multitude of equations, relating the thermodynamic properties of the thermodynamic system can be derived using relatively simple mathematics. This outlines the mathematical framework of chemical thermodynamics. The German physicist Rudolf Clausius, in his Mechanical Theory of Heat, suggested that the principles of thermo-chemistry, e.g. such as the heat evolved in combustion reactions, could be applied to the principles of thermodynamics. Building on the work of Clausius, between the years 1873-76 the American mathematical physicist Willard Gibbs published a series of three papers, the most famous one being the paper On the Equilibrium of Heterogeneous Substances. In these papers, Gibbs showed how the first two laws of thermodynamics could be measured graphically and mathematically to determine both the thermodynamic equilibrium of chemical reactions as well as their tendencies to occur or proceed. Gibbs collection of papers provided the first unified body of thermodynamic theorems from the principles developed by others, such as Clausius and Sadi Carnot. During the early 20th century, two major publications successfully applied the principles developed by Gibbs to chemical processes, and thus established the foundation of the science of chemical thermodynamics. The first was the 1923 textbook Thermodynamics and the Free Energy of Chemical Substances by Gilbert N. Lewis and Merle Randall. This book was

responsible for supplanting the chemical affinity for the term free energy in the English-speaking world. The second was the 1933 book *Modern Thermodynamics by the methods of Willard Gibbs* written by E. A. Guggenheim. In this manner, Lewis, Randall, and Guggenheim are considered as the founders of modern chemical thermodynamics because of the major contribution of these two books in unifying the application of thermodynamics to chemistry.

Key Points:

1. Chemical energy

It is the potential of a chemical substance to undergo a transformation through a chemical reaction or transform other chemical substances. Breaking or making of chemical bonds, involves energy that may be either absorbed or evolved from a chemical system.

Energy that can be released (or absorbed) because of a reaction between a set of chemical substances is equal to the difference between the energy content of the products and the reactants. This change in energy is called the change in internal energy of a chemical reaction.

Where $U_{\text{reactants}}$ is the internal energy of formation of the reactant molecules that can be calculated from the bond energies of the various chemical bonds of the molecules under

consideration and U_{products} is the internal energy of formation of the product molecules.

The internal energy change of a process is equal to the heat change if it is measured under conditions of constant volume, as in a closed rigid container such as a bomb calorimeter.

However, under conditions of constant pressure, as in reactions in vessels open to the atmosphere, the heat change measured is not always equal to the internal energy change, because pressure-volume work also releases or absorbs energy. (The heat change at constant pressure is called the enthalpy change, in this case the enthalpy of formation).

Another useful term is the heat of combustion, it is the energy released due to a combustion reaction and often applied in the study of fuels. Food is similar to hydrocarbon fuel and carbohydrate fuels, and when it is oxidized; its caloric content is similar (though not assessed in the same way as a hydrocarbon fuel).

In **chemical thermodynamics** the term used for the chemical potential energy is chemical potential and for chemical transformation an equation most often used is Gibbs-Duhem equation

2. Chemical reactions

In most cases of interest in chemical thermodynamics there are internal degrees of freedom and processes, such as chemical reactions and phase transitions, which always create entropy unless they are at equilibrium, or are maintained at a "running equilibrium" through "quasi-static" changes by being coupled to constraining devices, such as pistons or electrodes, to deliver and receive external work. Even for homogeneous "bulk" materials, the free energy functions depend on the composition, as do all the extensive thermodynamic potentials, including the internal energy. If the quantities $\{ N_i \}$, the number of chemical species, are omitted from the formulae, it is impossible to describe compositional changes.

Gibbs function

For a "bulk" (unstructured) system they are the last remaining extensive variables. For an unstructured, homogeneous "bulk" system, there are still various extensive compositional variables $\{ N_i \}$ that G depends on, which specify the composition, the amounts of each chemical substance, expressed as the numbers of molecules present or (dividing by Avogadro's number), the numbers of moles

For the case where only PV work is possible

in which μ_i is the chemical potential for the i -th component in the system

The expression for dG is especially useful at constant T and P , conditions which are easy to achieve experimentally and which approximates the condition in living creatures

3. Chemical affinity

While this formulation is mathematically defensible, it is not particularly transparent since one does not simply add or remove molecules from a system. There is always a process involved in changing the composition; e.g., a chemical reaction (or many), or movement of molecules from one phase (liquid) to another (gas or solid). We should find a notation which does not seem to imply that the amounts of the components (N_i) can be changed independently. All real processes obey conservation of mass, and in addition, conservation of the numbers of atoms of each kind. Whatever molecules are transferred to or from should be considered part of the "system".

Consequently we introduce an explicit variable to represent the degree of advancement of a process, a progress variable ξ for the extent of reaction, and to the use of the partial derivative $\left(\frac{\partial G}{\partial \xi}\right)$ (in place of the widely used " ΔG ", since the quantity at issue is not a finite change). The result is an understandable expression for the dependence of dG on chemical reactions (or other processes). If there is just one reaction

If we introduce the stoichiometric coefficient for the i -th component in the reaction

Which tells how many molecules of i are produced or consumed, we obtain an algebraic expression for the partial derivative

where, we introduce a concise and historical name for this quantity, the "affinity", symbolized by A , as introduced by Thophile de Donder in 1923. The minus sign comes from the fact the affinity was defined to represent the rule that spontaneous changes will ensue only when the change in the Gibbs free energy of the process is negative, meaning that the chemical species have a positive affinity for each other. The differential for G takes on a simple form which displays its dependence on compositional change

If there are a number of chemical reactions going on simultaneously, as is usually the case

a set of reaction coordinates $\{ j \}$, avoiding the notion that the amounts of the components (N_i) can be changed independently. The expressions above are equal to zero at thermodynamic equilibrium, while in the general case for real systems, they are negative because all chemical reactions proceeding at a finite rate produce entropy. This can be made even more explicit by introducing the reaction rates $d j/dt$. For each and every physically independent process

This is a remarkable result since the chemical potentials are intensive system variables, depending only on the local molecular milieu. They cannot "know" whether the temperature and pressure (or any other system variables) are going to be held constant over time. It is a purely local criterion and must hold regardless of any such constraints. Of course, it could have been obtained by taking partial derivatives of any of the other fundamental state functions, but nonetheless is a general criterion for $(-T \text{ times})$ the entropy production from that spontaneous process; or at least any part of it that is not captured as external work. We now relax the requirement of a homogeneous bulk system by letting the chemical potentials and the affinity apply to any locality in which a chemical reaction (or any other process) is occurring. By accounting for the entropy production due to irreversible processes, the inequality for dG is now replaced by an equality

or

Any decrease in the Gibbs function of a system is the upper limit for any isothermal, isobaric work that can be captured in the surroundings, or it may simply be dissipated, appearing as T times a corresponding increase in the entropy of the system and/or its surrounding. Or it may go partly toward doing external work and partly toward creating entropy. The important point is that the extent of reaction for a chemical reaction may be coupled to the displacement of some external mechanical or electrical quantity in such a way that one can advance only if the other one also does. The coupling may occasionally be rigid, but it is often flexible and variable.

4. Solutions

In solution chemistry and biochemistry, the Gibbs free energy decrease (ΔG , in molar units, denoted cryptically by ΔG) is commonly used as a surrogate for ($-T$ times) the entropy produced by spontaneous chemical reactions in situations where there is no work being done; or at least no "useful" work; i.e., other than perhaps some PdV . The assertion that all spontaneous reactions have a negative ΔG is merely a restatement of the fundamental thermodynamic relation, giving it the physical dimensions of energy and somewhat obscuring its significance in terms of entropy. When there is no useful work being done, it would be less misleading to use the Legendre transforms of the entropy appropriate for constant T , or for constant T and P , the Massieu functions $-F/T$ and $-G/T$ respectively.

5. Non equilibrium

Generally the systems treated with the conventional chemical thermodynamics are either at equilibrium or near equilibrium. Ilya Prigogine developed the thermodynamic treatment of open systems that are far from equilibrium. In doing so he has discovered phenomena and structures of completely new and completely unexpected types. His generalized, nonlinear and irreversible thermodynamics has found surprising applications in a wide variety of fields.

The non equilibrium thermodynamics has been applied for explaining how ordered structures e.g. the biological systems, can develop from disorder. Even if Onsager's relations are utilized, the classical principles of equilibrium in thermodynamics still show that linear systems close to equilibrium always develop into states of disorder which are stable to perturbations and cannot explain the occurrence of ordered structures.

Prigogine called these systems dissipative systems, because they are formed and maintained by the dissipative processes which take place because of the exchange of energy between the system and its environment and because they disappear if that exchange ceases. They may be said to live in symbiosis with their environment.

The method which Prigogine used to study the stability of the dissipative structures to perturbations is of very great general interest. It makes it possible to study the most varied problems, such as city traffic problems, the stability of insect communities, the development of ordered biological structures and the growth of cancer cells to mention but a few examples.

6. System constraints

In this regard, it is crucial to understand the role of walls and other constraints, and the distinction between independent processes and coupling. Contrary to the clear implications of many reference sources, the previous analysis is not restricted to homogenous, isotropic bulk systems which can deliver only PdV work to the outside world, but applies even to the most structured systems. There are complex systems with many chemical "reactions" going on at the same time, some of which are really only parts of the same, overall process. An independent process is one that could proceed even if all others were unaccountably stopped in their tracks. Understanding this is perhaps a thought experiment in chemical kinetics, but actual examples exist.

A gas reaction which results in an increase in the number of molecules will lead to an increase in volume at constant external pressure. If it occurs inside a cylinder closed with a piston, the equilibrated reaction can proceed only by doing work against an external force on the piston. The extent variable for the reaction can increase only if the piston moves, and conversely, if the piston is pushed inward, the reaction is driven backwards.

Similarly, a redox reaction might occur in an electrochemical cell with the passage of current in wires connecting the electrodes. The half-cell reactions at the electrodes are constrained if no current is allowed to flow. The current might be dissipated as joule heating, or it might in turn run an electrical device like a motor doing mechanical work. An automobile lead-acid battery can be recharged, driving the chemical reaction backwards. In this case as well, the reaction is not an independent process. Some, perhaps most, of the Gibbs free energy of reaction may be delivered as external work.

The hydrolysis of ATP to ADP and phosphate can drive the force times distance work delivered by living muscles, and synthesis of ATP is in turn driven by a redox chain in mitochondria and chloroplasts, which involves the transport of ions across the membranes of these cellular organelles. The coupling of processes here, and in the previous examples, is often not complete. Gas can leak slowly past a piston, just as it can slowly leak out of a rubber balloon. Some reaction may occur in a battery even if no external current is flowing. There is usually a coupling coefficient, which may depend on relative rates, which determines what percentage of the

driving free energy is turned into external work, or captured as "chemical work", a misnomer for the free energy of another chemical process.

Topic : Chemical Equilibrium

Topic Objective:

At the end of this topic student would be able to:

- Learn the concept of Chemical Equilibrium
- Learn the concept of Chemical Reaction
- Learn the concept of Le Chatelier's Principle

Definition/Overview:

Chemical Equilibrium: In a chemical process, chemical equilibrium is the state in which the chemical activities or concentrations of the reactants and products have no net change over time. Usually, this would be the state that results when the forward chemical process proceeds at the same rate as their reverse reaction. The reaction rates of the forward and reverse reactions are generally not zero but, being equal, there are no net changes in any of the reactant or product concentrations. This process is called dynamic equilibrium.

Key Points:**1. Chemical Reaction**

In a chemical reaction, when reactants are mixed together in a reaction vessel (and heated if needed), the whole of reactants do not get converted into the products. After some time (which may be shorter than millionths of a second or longer than the age of the universe), there will come a point when a fixed amount of reactants will exist in harmony with a fixed amount of products, the amounts of neither changing anymore. This is called chemical equilibrium.

The concept of chemical equilibrium was developed after Berthollet (1803) found that some chemical reactions are reversible. For any reaction such as

to be at equilibrium the rates of the forward and backward (reverse) reactions have to be equal.

In this chemical equation with harpoon arrows pointing both ways to indicate equilibrium, A and B are reactant chemical species, S and T are product species, and ν_A , ν_B , ν_S , and ν_T are the stoichiometric coefficients of the respective reactants and products. The equilibrium position of a reaction is said to lie far to the right if, at equilibrium, nearly all the reactants are used up and far to the left if hardly any product is formed from the reactants.

Guldberg and Waage (1865), building on Berthollets ideas, proposed the law of mass action:

where A, B, S and T are active masses and k_+ and k_- are rate constants. Since forward and backward rates are equal:

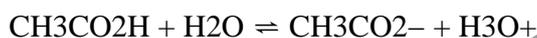
and the ratio of the rate constants is also a constant, now known as an equilibrium constant.

By convention the products from the numerator. However, the law of mass action is valid only for concerted one-step reactions that proceed through a single transition state and is not valid in general because rate equations do not, in general, follow the stoichiometry of the reaction as Guldberg and Waage had proposed. Equality of forward and backward reaction rates, however,

is a necessary condition for chemical equilibrium, though it is not sufficient to explain why equilibrium occurs.

Despite the failure of this derivation, the equilibrium constant for a reaction is indeed a constant, independent of the activities of the various species involved, though it does depend on temperature as observed by the van 't Hoff equation. Adding a catalyst will affect both the forward reaction and the reverse reaction in the same way and will not have an effect on the equilibrium constant. The catalyst will speed up both reactions thereby increasing the speed at which equilibrium is reached.

Although the macroscopic equilibrium concentrations are constant in time reactions do occur at the molecular level. For example, in the case of ethanoic acid dissolved in water and forming ethanoate and hydronium ions,



a proton may hop from one molecule of ethanoic acid on to a water molecule and then on to an ethanoate ion to form another molecule of ethanoic acid and leaving the number of ethanoic acid molecules unchanged. This is an example of dynamic equilibrium. Equilibria, like the rest of thermodynamics, are statistical phenomena, averages of microscopic behavior.

2. Le Chatelier's Principle

Le Chatelier's principle (1884) is a useful principle that gives a qualitative idea of an equilibrium system's response to changes in reaction conditions. If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change. For example, adding more S from the outside will cause an excess of products, and the system will try to counteract this by increasing the reverse reaction and pushing the equilibrium point backward (though the equilibrium constant will stay the same).

If mineral acid is added to the ethanoic acid mixture, increasing the concentration of hydronium ion, the amount of dissociation must decrease as the reaction is driven to the left in accordance with this principle. This can also be deduced from the equilibrium constant expression for the reaction:

if $\{\text{H}_3\text{O}^+\}$ increases $\{\text{CH}_3\text{CO}_2\text{H}\}$ must increase and $\{\text{CH}_3\text{CO}_2^-\}$ must decrease.

A quantitative version is given by the reaction quotient.

J.W. Gibbs suggested in 1873 that equilibrium is attained when the Gibbs energy of the system is at its minimum value (assuming the reaction is carried out under constant pressure). What this means is that the derivative of the Gibbs energy with respect to reaction coordinate (a measure of the extent of reaction that has occurred, ranging from zero for all reactants to a maximum for all products) vanishes, signalling a stationary point. This derivative is usually called, for certain technical reasons, the Gibbs energy change. This criterion is both necessary and sufficient. If a mixture is not at equilibrium, the liberation of the excess Gibbs energy (or Helmholtz energy at constant volume reactions) is the driving force for the composition of the mixture to change until equilibrium is reached. The equilibrium constant can be related to the standard Gibbs energy change for the reaction by the equation

where R is the universal gas constant and T the temperature.

When the reactants are dissolved in a medium of high ionic strength the quotient of activity coefficients may be taken to be constant. In that case the concentration quotient, K_c ,

where $[A]$ is the concentration of A, etc., is independent of the analytical concentration of the reactants. For this reason, equilibrium constants for solutions are usually determined in media of high ionic strength. K_c varies with ionic strength, temperature and pressure (or volume).

Likewise K_p for gases depends on partial pressure. These constants are easier to measure and encountered in high-school chemistry courses.

3. Equilibrium change with addition of reactant () or product ()

For a reactional system at equilibrium: ; .

If are modified activities of constituents, the value of the reaction quotient changes and becomes different from the equilibrium constant:

and

then

If activity of a reagent increases

, the reaction quotient decreases.

then

and

:

The reaction will shift to the right (i.e. in the forward direction, and thus more products will form).

If activity of a product increases

then

and : The reaction will shift to the left (i.e. in the reverse direction, and thus less products will form).

Note that activities and equilibrium constants are dimensionless numbers.

4. Treatment of activity

The expression for the equilibrium constant can be rewritten as the product of a concentration quotient, K_c and an activity coefficient quotient, γ .

[A] is the concentration of reagent A, etc. It is possible in principle to obtain values of the activity coefficients, γ . For solutions, equations such as the Debye-Hückel equation or extensions such as Davies equation or Pitzer equations may be used. Software. However this is not always possible. It is common practice to assume that γ is a constant, and to use the concentration quotient in place of the thermodynamic equilibrium constant. It is also general practice to use the term equilibrium constant instead of the more accurate concentration quotient. This practice will be followed here.

For reactions in the gas phase partial pressure is used in place of concentration and fugacity coefficient in place of activity coefficient. In the real world, for example, when making ammonia in industry, fugacity coefficients must be taken into account. Fugacity, f , is the product of partial pressure and fugacity coefficient. The chemical potential of a species in the gas phase is given by

so the general expression defining an equilibrium constant is valid for both solution and gas phases.

5. Justification for the use of concentration quotients

In aqueous solution, equilibrium constants are usually determined in the presence of an "inert" electrolyte such as sodium nitrate NaNO_3 or Potassium perchlorate KClO_4 . The ionic strength, I , of a solution containing a dissolved salt, X^+Y^- , is given by

Where c stands for concentration, z stands for ionic charge and the sum is taken over all the species in equilibrium. When the concentration of dissolved salt is much higher than the analytical concentrations of the reagents, the ionic strength is effectively constant. Since activity coefficients depend on ionic strength the activity coefficients of the species are effectively independent of concentration. Thus, the assumption that γ is constant is justified. The concentration quotient is a simple multiple of the equilibrium constant.

However, K_c will vary with ionic strength. If it is measured at a series of different ionic strengths the value can be extrapolated to zero ionic strength. The concentration quotient obtained in this manner is known, paradoxically, as a thermodynamic equilibrium constant.

To use a published value of an equilibrium constant in conditions of ionic strength different from the conditions used in its determination, the value should be adjusted Software.

6. Meta-stable mixtures

A mixture may be appearing to have no tendency to change, though it is not at equilibrium. For example, a mixture of SO_2 and O_2 is meta-stable as there is a kinetic barrier to formation of the product, SO_3 .



The barrier can be overcome when a catalyst is also present in the mixture as in the contact process, but the catalyst does not affect the equilibrium concentrations.

Likewise, the formation of bicarbonate from carbon dioxide and water is very slow under normal conditions



but almost instantaneous in the presence of the catalytic enzyme carbonic anhydrase.

7. Pure compounds in equilibria

When pure substances (liquids or solids) are involved in equilibria they do not appear in the equilibrium equation

Applying the general formula for an equilibrium constant to the specific case of ethanoic acid one obtains

It may be assumed that the concentration of water is constant. This assumption will be valid for all but very concentrated solutions. The equilibrium constant expression is therefore usually written as

where now

a constant factor is incorporated into the equilibrium constant.

A particular case is the self-ionization of water itself

The self-ionization constant of water is defined as

It is perfectly legitimate to write $[H^+]$ for the hydronium ion concentration, since the state of solvation of the proton is constant (in dilute solutions) and so does not affect the equilibrium concentrations. K_w varies with variation in ionic strength and/or temperature.

The concentrations of H^+ and OH^- are not independent quantities. Most commonly $[OH^-]$ is replaced by $K_w/[H^+]$ in equilibrium constant expressions which would otherwise hydroxide.

Solids also do not appear in the equilibrium equation. An example is the Boudouard reaction :

for which the equation (without solid carbon) is written as:

8. Multiple equilibria

Consider the case of a dibasic acid H_2A . When dissolved in water, the mixture will contain H_2A , HA^- and A^{2-} . This equilibrium can be split into two steps in each of which one proton is liberated.

K_1 and K_2 are examples of stepwise equilibrium constants. The overall equilibrium constant, D , is product of the stepwise constants.

Note that these constants are dissociation constants because the products on the right hand side of the equilibrium expression are dissociation products. In many systems, it is preferable to use association constants.

γ_1 and γ_2 are examples of association constants. Clearly $\gamma_1 = 1/K_2$ and $\gamma_2 = 1/D$; $\lg \gamma_1 = pK_2$ and $\lg \gamma_2 = pK_2 + pK_1$

Topic : Introduction To One-Dimensional Compressible Flow

Topic Objective:

At the end of this topic student would be able to:

- Learn the concept of Compressible flow
- Learn the concept of Isentropic flow
- Learn the concept of Transonic
- Learn the concept of Supersonic objects
- Learn the concept of Hypersonic
- Learn the concept of Shock Wave

Definition/Overview:

Compressible flow: In fluid dynamics, a flow is considered to be a compressible flow if the density of the fluid changes with respect to pressure. In general, this is the case where the Mach number (defined as the ratio of the flow speed to the local speed of sound) of the flow exceeds 0.3. The Mach 0.3 value is rather arbitrary, but it is used because gas flows with a Mach number below that value introduce less than 5% change in density. Furthermore, the maximum density

change occurs at the stagnation points and the density change in the rest of the flow field will be significantly lower.

The factor that distinguishes a flow from being compressible or incompressible is the fact that in compressible flow the changes in the velocity of the flow can lead to changes in the temperature which are not negligible. On the other hand in case of incompressible flow, the changes in the internal energy (i.e. temperature) are negligible even if the entire kinetic energy of the flow is converted to internal energy (i.e. the flow is brought to rest).

These definitions, though they seem to be inconsistent, are all saying one and the same thing: the Mach number of the flow is high enough so that the effects of compressibility can no longer be neglected.

For subsonic compressible flows, it is sometimes possible to model the flow by applying a correction factor to the answers derived from incompressible calculations or modelling - for example, the Prandtl-Glauert rule:

(a_c is compressible lift curve slope, a_i is the incompressible lift curve slope, and M is the Mach number). Note that this correction only yields acceptable results over a range of approximately $0.3 < M < 0.7$.

For many other flows, their nature is qualitatively different to subsonic flows. A flow where the local Mach number reaches or exceeds 1 will usually contain shock waves. A shock is an abrupt change in the velocity, pressure and temperature in a flow; the thickness of a shock scales with the molecular mean free path in the fluid (typically a few micrometers).

Shocks form because information about conditions downstream of a point of sonic or supersonic flow cannot propagate back upstream past the sonic point.

The behavior of a fluid changes radically as it starts to move above the speed of sound (in that fluid), i.e. when the Mach number is greater than 1. For example, in subsonic flow, a stream tube in an accelerating flow contracts. But in a supersonic flow, a stream tube in an accelerating flow expands. To interpret this in another way, consider steady flow in a tube that has a sudden expansion: the tube's cross section suddenly widens, so the cross-sectional area increases.

In subsonic flow, the fluid speed drops after the expansion (as expected). In supersonic flow, the fluid speed increases. This sounds like a contradiction, but it isn't: the mass flux is conserved but

because supersonic flow allows the density to change, the volume flux is not constant. This effect is utilized in De Laval nozzles.

Key Points:

1. Isentropic flow

An isentropic flow is a flow that is both adiabatic and reversible. That is, no energy is added to the flow, and no energy losses occur due to friction or dissipative effects. For an isentropic flow of a perfect gas, several relations can be derived to define the pressure,

Derivation of the isentropic relations

For a closed system, the total change in energy of a system is the sum of the work done and the heat added,

The work done on a system by changing the volume is,

Where p is the pressure and V the volume. The change in enthalpy () is given by,

Since a reversible process is adiabatic (i.e. no heat transfer occurs), so . This leads to two important observations,

, and

or

=>

The heat capacity ratio can be written as,

For a perfect gas is constant. Hence on integrating the above equation, assuming a perfect gas, we get

i.e.

Using the equation of state for an ideal gas, ,

also, for constant $C_p = C_v + R$ (per mole),

and

Thus for isentropic processes with an ideal gas,

or

Table of isentropic relations for an ideal gas

Derived from:

Where:

= Pressure

- = Volume
- = Ratio of specific heats =
- = Temperature
- = Mass
- = Gas constant for the specific gas =
- = Universal gas constant
- = Molecular weight of the specific gas
- = Density
- = Specific heat at constant pressure
- = Specific heat at constant volume

2. Transonic

Transonic is an aeronautics term referring to a range of velocities just below and above the speed of sound (about mach 0.81.2). It is defined as the range of speeds between the critical mach number, when some parts of the airflow over an aircraft become supersonic, and a higher speed, typically near Mach 1.2, when all of the airflow is supersonic. Between these speeds some of the airflow is supersonic, and some is not.

Most modern jet-powered aircraft spend a considerable amount of time in the transonic state. This is particularly important due to an effect known as wave drag, which is prevalent in these speed ranges. Attempts to combat wave drag can be seen on all high-speed aircraft; most notable is the use of swept wings, but another common form is a wasp-waist fuselage as a side effect of the Whitcomb area rule.

Severe instability can occur at transonic speeds. Shock waves move through the air at the speed of sound. When an object such as an aircraft also moves at the speed of sound, these shock waves build up in front of it to form a single, very large shock wave. During transonic flight, the plane must pass through this large shock wave, as well as contending with the instability caused by air moving faster than sound over parts of the wing and slower in other parts. The difference in speed is due to Bernoulli's principle.

Transonic speeds can also occur at the tips of rotor blades of helicopters and aircraft. However, as this puts severe, unequal stresses on the rotor blade, it is avoided and may lead to dangerous accidents if it occurs. It is one of the limiting factors to the size of rotors, and also to the forward speeds of helicopters (as this speed is added to the forward-sweeping (leading) side of the rotor, thus possibly causing localized transonics).

3. Supersonic objects

Most modern fighter aircraft are supersonic, but Concorde and the Tupolev Tu-144 were the only supersonic passenger aircraft. An aircraft that can still sustain supersonic flight without using an afterburner is called a super-cruise aircraft. Due to its ability to super-cruise for several hours and the relatively high frequency of flight over several decades, Concorde spent more time flying supersonically than all other aircraft put together by a considerable margin. Since Concorde's final retirement flight on November 26, 2003, there are no supersonic passenger aircraft left in service. Some large bombers, such as the Tupolev Tu-160 and Rockwell/Boeing B-1B are also supersonic-capable.

Most modern firearm bullets are supersonic, with rifle projectiles often travelling at speeds approaching and in some cases largely exceeding Mach 3.

Most spacecraft, most notably the Space Shuttle are supersonic at least during portions of their reentry, though the effects on the spacecraft are reduced by low air pressures. During ascent, launch vehicles generally avoid going supersonic below 30 km (~98,400 feet) to reduce air drag. Note that the speed of sound decreases somewhat with altitude, due to lower temperatures found there (typically up to 25 km). At even higher altitudes the temperature starts increasing, with the corresponding increase in the speed of sound.

A wave traveling through a bull whip is also capable of achieving supersonic speeds

4. Hypersonic

In aerodynamics, hypersonic speeds are speeds that are highly supersonic. Since the 1970s, the term has generally been assumed to refer to speeds of Mach 5 (5 times the speed of sound) and above. The hypersonic regime is a subset of the supersonic regime.

Supersonic airflow is very different from subsonic flow. Nearly everything about the way an aircraft flies changes dramatically as it accelerates to supersonic speeds. Even with this strong demarcation, there is still some debate as to the definition of "supersonic". One definition is that the aircraft, as a whole, is traveling at Mach 1 or greater. More technical definitions state that it is only supersonic if the airflow over the entire aircraft is supersonic, which occurs around Mach 1.2 on typical designs. The range Mach 0.75 to 1.2 is therefore considered transonic.

Considering the problems with this simple definition, the precise Mach number at which a craft can be said to be fully hypersonic is even more elusive, especially since physical changes in the airflow (molecular dissociation, ionization) occur at quite different speeds. Generally, a combination of effects become important "as a whole" around Mach 5. The hypersonic regime is often defined as speeds where ramjets do not produce net thrust. This is a nebulous definition in itself, as there exists a proposed change to allow them to operate in the hypersonic regime (the Scramjet).

5: Shock Wave

A shock wave (also called shock front or simply "shock") is a type of propagating disturbance. Like an ordinary wave, it carries energy and can propagate through a medium (solid, liquid or gas) or in some cases in the absence of a material medium, through a field such as the electromagnetic field. Shock waves are characterized by an abrupt, nearly discontinuous change in the characteristics of the medium. Across a shock there is always an extremely rapid rise in pressure, temperature and density of the flow. In supersonic flows, expansion is achieved through an expansion fan. A shock wave travels through most media at a higher speed than an ordinary wave. Unlike solitons (another kind of nonlinear wave), the energy of a shock wave dissipates relatively quickly with distance. Also, the accompanying expansion wave approaches and eventually merges with the shock wave, partially cancelling it out. Thus the sonic boom associated with the passage of a supersonic aircraft is the sound wave resulting from the degradation and merging of the shock wave and the expansion wave produced by the aircraft. When a shock wave passes through matter, the total energy is preserved but the energy which can be extracted as work decreases and entropy increases. This for example creates additional drag force on aircraft with shocks.

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