Physics Lecture Notes - 5

Thermodynamics

Thermodynamics is a branch of physics that deals with heat, work, and temperature, and their relation to energy, radiation, and physical properties of matter. The behavior of these quantities is governed by the four laws of thermodynamics which convey a quantitative description using measurable macroscopic physical quantities.

The field of thermodynamics can be broadly applied to various fields of science and engineering, including mechanical, chemical, and electrical engineering, as well as chemistry and materials science.

Heat and Work

Heat and work are two different ways of transferring energy. For example, heat can be transferred by conduction, convection, and radiation. Work, on the other hand, is energy transferred by a force acting over a distance.

Heat

Heat (Q) is a form of energy that is transferred from a body at a higher temperature to a body at a lower temperature due to the difference in temperature. This energy transfer occurs until both bodies reach thermal equilibrium (i.e., they have the same temperature). Heat is a process quantity, not a state quantity, which means it is not inherent in a system but is related to a process that changes the system's state.

For example, let's consider a metal rod that is heated at one end. As the molecules at the hot end vibrate, they transfer kinetic energy to the neighboring molecules, and this transfer continues along the rod, eventually heating the cooler end. This is a simple instance of heat transfer.

Heat Transfer Methods

There are three modes of heat transfer: conduction, convection, and radiation. We will consider each in turn.

Conduction

Conduction is the heat transfer due to microscopic collisions of particles and movement of electrons within a body. The heat travels through the body but the bulk system does not. Fourier's law expresses heat conduction as

$$Q = -kA\frac{dT}{dx}$$

where:

- Q is the heat transferred per unit time,

- k is the thermal conductivity of the material,

- A is the cross-sectional area through which heat is transferred,

- dT/dx is the temperature gradient in the direction of flow.

Convection

Convection is the heat transfer by the macroscopic movement of a fluid. This can occur naturally due to buoyancy effects, or it can be forced by a pump or fan. Newton's law of cooling can be used to describe convective heat transfer:

$$Q = hA(T_{\text{surface}} - T_{\text{fluid}})$$

where:

- Q is the heat transferred per unit time,

- h is the heat transfer coefficient,

- A is the surface area through which heat is transferred,

- T_{surface} and T_{fluid} are the temperatures of the surface and fluid, respectively.

Radiation

Radiation is the heat transfer by electromagnetic waves, particularly infrared radiation. All bodies emit radiation, and the Stefan-Boltzmann law describes the power per unit area radiated by a black body in terms of its temperature:

$$P = \sigma e A T^4$$

where:

- P is the power radiated per unit area,

- σ is the Stefan-Boltzmann constant,

- e is the emissivity of the body (with 1.0 being a perfect black body),

- A is the surface area of the body,

- T is the absolute temperature of the body.

Example: Consider an ideal gas that is heated by a heater. Suppose that $2.5 \times 10^4 \, J$ of heat is added. What is the change in internal energy of the system if no work is done?

Internal energy is a quantity which is directly related to the temperature of the substance. If we heat the gas, the temperature of the gas will increase, in other words, the internal energy of the gas will increase. In this case, the change in internal energy of the system is the same as the heat added:

$$\Delta U = Q = 2.5 \times 10^4 \, J$$

Work

Work (W) in the context of thermodynamics is the energy transferred by a force acting through a distance. Like heat, work is also a process quantity and is dependent on the path taken to change the system's state.

In thermodynamics, the work done by a gas during expansion or contraction is often what is considered. Work done by a system (like a gas) on its surroundings is usually considered to be a negative quantity, as it results in a decrease in the system's internal energy.

Work in thermodynamics is a measure of the energy transfer that occurs when an object is moved by an external force along a displacement. It is a form of energy, just like heat, but it is typically associated with systems where there is a change in volume under the effect of an external force, such as in a piston.

In the context of a quasi-static process, the infinitesimal work done (dW) by a system against an external pressure P_{ext} can be given by:

$$dW = -P_{ext}dV$$

where:

- dW is the infinitesimal work done,

- P_{ext} is the external pressure,

- dV is the infinitesimal change in volume.

The negative sign indicates that work is done by the system (the system loses energy). If work is done on the system, the sign would be positive. This is in line with the thermodynamic sign convention.

Please note that the above formula applies when the external pressure is constant during the change of volume. If the pressure also changes, then the work done by the system should be calculated by integrating this equation from the initial to the final state:

$$W = - \int_{V_i}^{V_f} P_{ext} dV$$

where V_i and V_f represent the initial and final volumes of the system, respectively.

Ideal Gas

An ideal gas is a theoretical gas composed of a set of randomly moving, non-interacting point particles. The ideal gas concept is useful because it obeys the ideal gas law, a simplified equation of state, and is applicable to many physical situations. However, real gases show small deviations from the ideal behavior and those deviations are accounted for in the real gas models.

Before explaining Ideal Gas Law, we have to remember three fundamental relations in observable quantities of thermodynamics:

Boyle's Law Boyle's law, named after Robert Boyle who proposed it in 1662, states that the pressure and volume of a gas have an inverse relationship when held at a constant temperature. In other words, as the volume of a gas increases, the pressure decreases, and vice versa. It can be mathematically expressed as:

$$P_1 V_1 = P_2 V_2$$

where P_1 and P_2 are the initial and final pressure, and V_1 and V_2 are the initial and final volume.

Charles's Law Charles's law, named after Jacques Charles, describes how gases tend to expand when heated. It states that the volume of a gas is directly proportional to its absolute temperature, provided its pressure remains constant. It can be mathematically represented as:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

where V_1 and V_2 are the initial and final volumes, and T_1 and T_2 are the initial and final absolute temperatures (in Kelvin).

Avogadro's Law Avogadro's law, named after Amedeo Avogadro, states that equal volumes of all gases at the same temperature and pressure contain the

same number of molecules. Thus, the volume of a gas is directly proportional to the number of gas molecules. It can be mathematically expressed as:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

where V_1 and V_2 are volumes of gas, and n_1 and n_2 are the number of moles of the gas.

The Mole Concept

The mole is a fundamental unit in the International System of Units (SI) and is used in chemistry. It is defined as exactly 6.02×10^{23} entities, which could be atoms, molecules, ions, electrons, or other particles. This number is known as Avogadro's number.

A mole of a substance is the amount that contains as many particles or entities as there are atoms in exactly 12 grams of carbon-12. So when we say that one mole of a substance contains $6.02214076 \times 10^{23}$ particles, it is a reference to this fact.

For example, one mole of water (H_2O) contains 6.02×10^{23} water molecules. Similarly, one mole of sodium (Na) contains 6.02×10^{23} sodium atoms. The molar mass of a substance, given in grams per mole (g/mol), is numerically equal to the mass of one molecule of that substance, given in atomic mass units (amu). For instance, the molar mass of water is about 18.015 g/mol, which means one water molecule has a mass of about 18.015 amu.

Ideal Gas Law

The ideal gas law combines the empirical Boyle's Law, Charles's Law, and Avogadro's Law. It can be written as:

$$PV = nRT$$

where:

- P is the pressure of the gas,

- V is the volume occupied by the gas,

- n is the amount of gas in moles,

- R is the ideal gas constant, and

- T is the absolute temperature.

The ideal gas law can be viewed as arising from the kinetic pressure of gas molecules colliding with the walls of a container in accordance with Newton's laws. But these require knowing the velocities of the individual gas particles, which in general is not possible.

Ideal Gas Law Problems

1. An ideal gas occupies a volume of 1.0 cubic meter at a pressure of 100 kPa and a temperature of 300 K. How many moles of gas are present?

2. A gas at 273 K has a volume of 50.0 liters. If the temperature is raised to 300 K and the pressure remains constant, what will the new volume be?

3. If we have 4 moles of gas at a pressure of 5 atm and occupying a volume of 2 liters, what is the temperature of the gas in degrees Celsius?

4. What is the pressure exerted by a gas that occupies 0.03 cubic meters, has a mass of 0.04 kg, and is at a temperature of 400 K? The molar mass of the gas is 28 g/mol.

5. A balloon filled with helium gas occupies 2.5 liters at sea level (1 atm pressure) and at 25 degrees Celsius. How many moles of helium gas are in the balloon?

Solutions to the Ideal Gas Law Problems

1. Using the ideal gas law $PV = nRT$, we solve for n and get $n = \frac{PV}{RT} = \frac{(100 \times 10^3 \, \text{Pa})(1.0 \, \text{m}^3)}{(8.314 \, \text{J/mol·K})(300 \, \text{K})} \approx 4.01 \, \text{mol}$.

2. Using Charles's law ($V_1/T_1 = V_2/T_2$), we solve for V_2 and get $V_2 = \frac{V_1 T_2}{T_1} = \frac{(50.0 \, \text{L})(300 \, \text{K})}{273 \, \text{K}} \approx 54.9 \, \text{L}$.

3. Rearranging the ideal gas law and solving for T, we get $T = \frac{PV}{nR} = \frac{(5 \, \text{atm})(2 \, \text{L})}{(4 \, \text{mol})(0.0821 \, \text{L·atm/mol·K})} \approx 304.4 \, \text{K}$. To convert to Celsius, we subtract 273 from the temperature in Kelvin, getting $304.4 \, \text{K} - 273 \approx 31.4 \, ^\circ\text{C}$.

4. First, we need to convert the mass of the gas to moles using the molar mass, so $n = \frac{0.04 \, \text{kg}}{28 \times 10^{-3} \, \text{kg/mol}} \approx 1.43 \, \text{mol}$. Then, we use the ideal gas law to solve for P and get $P = \frac{nRT}{V} = \frac{(1.43 \, \text{mol})(8.314 \, \text{J/mol·K})(400 \, \text{K})}{0.03 \, \text{m}^3} \approx 15.9 \times 10^3 \, \text{Pa}$.

5. Using the ideal gas law, we solve for n and get $n = \frac{PV}{RT}$ $= \frac{(1 \, \text{atm})(2.5 \, \text{L})}{(0.0821 \, \text{L·atm/mol·K})(298 \, \text{K})} \approx 0.102 \, \text{mol}$.

Kinetic Theory of Gases

The kinetic theory of gases is a statistical theory that relates the macroscopic properties of gases, such as pressure or volume, to their microscopic properties.

According to the kinetic theory of gases, the average kinetic energy of ideal gas particles is directly proportional to absolute temperature only. For an ideal monoatomic gas, this relationship is given as:

$$\frac{3}{2}kT = \frac{1}{2}m\overline{v^2}$$

where:

- k is Boltzmann's constant,

- T is the absolute temperature,

- m is the molecular mass, and

- $\overline{v^2}$ is the mean of the squared speed of the gas molecules.

The equation indicates that the average kinetic energy of gas molecules is determined entirely by the temperature of the gas, not by the type of gas (assuming monatomic ideal gases).

Degrees of Freedom and the Kinetic Theory of Gases

The kinetic theory of gases simplifies the study of gases by modeling them as a large collection of tiny particles (atoms or molecules) that are in constant, random motion.

One important concept in this theory is the degrees of freedom, which is the number of independent ways a particle can move in a system. In a three-dimensional space, a particle has three translational degrees of freedom, corresponding to motion along the x, y, and z axes.

For a monoatomic gas, such as helium or argon, the molecules are point particles and only have translational degrees of freedom. But for diatomic or polyatomic gases, there are additional rotational and vibrational degrees of freedom. For instance, a diatomic gas, like nitrogen (N_2) or oxygen (O_2), has five degrees of freedom at room temperature: three translational and two rotational.

In general, the kinetic energy of a gas is shared equally among its degrees of freedom according to the law of equipartition of energy. This law states that each degree of freedom contributes $\frac{1}{2}kT$ to the average energy of the system, where k is Boltzmann's constant and T is the absolute temperature.

Example: Calculate the average kinetic energy per molecule and per mole for a sample of oxygen gas (O_2) at room temperature (298 K).

An O_2 molecule, being diatomic, has five degrees of freedom at room temperature. Using the equipartition theorem, the average energy per molecule is given by:

$$E = \frac{f}{2}kT = \frac{5}{2}kT.$$

To find the energy per mole, we multiply the energy per molecule by Avogadro's number (N_A):

$$E = \frac{5}{2}RT,$$

where R is the universal gas constant, $R = N_A k$.

Note that at higher temperatures, additional degrees of freedom can become excited, such as vibrational modes. This means that the degrees of freedom can depend on the temperature of the system, which is important in many thermodynamic calculations.

Zeroth Law of Thermodynamics

The Zeroth Law of Thermodynamics states that if two thermodynamic systems are each in thermal equilibrium with a third, then they are in thermal equilibrium with each other. Essentially, this law allows us to define temperature and assures that temperature is a transitive property: If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then A is in thermal equilibrium with C.

Example:

Consider three systems A, B, and C. System A has a temperature of $20°C$, and System B is at $30°C$. System C is brought into contact with System A until they are in thermal equilibrium, and the final temperature is $20°C$. Then, System C is brought into contact with System B until they are in thermal equilibrium, with a final temperature of $30°C$.

The question is: Are System A and System B in thermal equilibrium?

Solution

According to the Zeroth Law of Thermodynamics, if two systems are both in thermal equilibrium with a third system, then they are in thermal equilibrium with each other. Here, System C is in thermal equilibrium with both System A and System B.

However, when System A was in thermal equilibrium with System C, the temperature was $20°C$, and when System B was in thermal equilibrium with System C, the temperature was $30°C$. Therefore, the temperatures of Systems A and B are different when in thermal equilibrium with the same third system

(System C), which implies that Systems A and B are not in thermal equilibrium with each other. This illustrates the transitive property of thermal equilibrium, which is the essence of the Zeroth Law of Thermodynamics.

First Law of Thermodynamics

The first law of thermodynamics is often referred to as the law of energy conservation. It states that the change in the internal energy ΔU of a system is equal to the heat Q added to the system minus the work W done by the system. Mathematically, it is expressed as:

$$\Delta U = Q - W$$

or, the transferred heat energy to the system is converted into increase in internal energy of the system and work done by the system:

$$Q = \Delta U + W$$

This law implies that energy cannot be created or destroyed. It can only change forms, and it can flow from one place to another. The internal energy of a system can be understood as the total kinetic and potential energy of all particles in the system.

Consider an ideal gas that expands in a cylinder and pushes a piston. This is a common example of a system that does work (on the piston). If the gas is heated, causing it to expand, then the amount of work done by the gas is the force applied by the gas times the distance through which the force is applied (which is the distance the piston moves).

An ideal gas in a cylinder expands, pushing a piston. The force exerted by the gas is equivalent to a pressure P over a cross-sectional area A, and the piston is displaced by a small distance dx. Then the small amount of work dW done by the gas is given by $dW = PAdx = PdV$, where $dV = Adx$ is the small change in volume.

Therefore, in an infinitesimal process, the work done by the system (gas) is given by:

$$dW = PdV$$

If the process is reversible, then the ideal gas law can be used $PV = nRT$, where n is the number of moles of gas, R is the ideal gas constant, and T is the temperature. Therefore, for a finite change, we can integrate to find the total work done:

$$W = \int_{V_i}^{V_f} P \, dV = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln\left(\frac{V_f}{V_i}\right)$$

where V_i and V_f are the initial and final volumes, respectively.

Problems and Solutions

Problem 1   A system undergoes a process in which its volume changes from $V_i = 1\,m^3$ to $V_f = 3\,m^3$. The pressure of the system remains constant at $P = 2\,\text{atm} = 2 \times 10^5\,\text{Pa}$. Calculate the work done by the system during this process.

Solution 1   Since the pressure is constant, the work done by the system can be calculated using the formula $W = P\Delta V$. Therefore, the work done by the system is $W = P\Delta V = 2 \times 10^5\,\text{Pa} \times (3\,m^3 - 1\,m^3) = 4 \times 10^5\,J$.

Problem 2   Consider a system undergoing a cyclic process that consists of two steps. In the first step, the system absorbs 500 J of heat and performs 300 J of work. In the second step, the system releases 400 J of heat and 100 J of work is done on the system. Calculate the total change in internal energy of the system during this cyclic process.

Solution 2   In the first step, the change in internal energy is $\Delta U_1 = Q_1 - W_1 = 500\,J - 300\,J = 200\,J$.

In the second step, the change in internal energy is $\Delta U_2 = Q_2 - W_2 = -400\,J - (-100\,J) = -300\,J$ (heat released and work done on the system are taken as negative).

Therefore, the total change in internal energy during the cyclic process is $\Delta U = \Delta U_1 + \Delta U_2 = 200\,J - 300\,J = -100\,J$. The negative sign indicates that the system has lost energy.

Suppose we add 500 J of heat to a system and it does 200 J of work on the surroundings. The change in internal energy of the system is $\Delta U = Q - W = 500\,\text{J} - 200\,\text{J} = 300\,\text{J}$.

State and Process in Thermodynamics

Thermodynamic State

In thermodynamics, a state of a system is described by its properties that can be measured without knowing how the system got to that condition. These properties are usually macroscopic quantities like pressure (P), volume (V), temperature (T), and internal energy (U).

A system is said to be in a *thermodynamic state* when these macroscopic properties are uniform throughout and do not change with time. The state of a system can be fully described by certain pairs of these properties in equilibrium, for example, P and V, or T and V, or T and P.

Thermodynamic Process

A process is the transformation from one state to another. The path of the process can be depicted on a diagram with the system's properties as coordinates, typically a P-V diagram (pressure-volume diagram) or a T-S diagram (temperature-entropy diagram).

There are different types of processes:

- **Isothermal process:** A process that occurs at constant temperature.

- **Adiabatic process:** A process in which no heat exchange occurs with the surroundings.

- **Isobaric process:** A process that occurs at constant pressure.

- **Isochoric (isovolumetric) process:** A process that occurs at constant volume.

- **Cyclic process:** A process that returns a system to its initial state.

During a process, the state variables change from their initial values to final values. The exact path taken to get from the initial to the final state can be important, as it can affect the amount of work done and heat transferred during the process.

Isothermal Process

An isothermal process occurs at a constant temperature. For an ideal gas, the equation of state for an isothermal process is $PV = \text{constant}$.

Example: Consider 1 mole of an ideal gas at a temperature of 300 K and a volume of 22.4 L. If the gas expands isothermally to a volume of 44.8 L, the final pressure will be half the initial pressure due to Boyle's law.

Adiabatic Process

An adiabatic process is one in which there is no heat exchange with the surroundings. For an ideal gas, the equation of state for an adiabatic process is $PV^{\gamma} = \text{constant}$, where $\gamma = C_P/C_V$ is the heat capacity ratio.

Example: Rapid compression or expansion of a gas can be approximated as an adiabatic process since there isn't enough time for heat exchange with the surroundings.

Isobaric Process

An isobaric process occurs at a constant pressure. The work done during an isobaric process is given by $W = P\Delta V$.

Example: A gas at a pressure of 1 atm expands from a volume of 10 L to 20 L. The work done by the gas is approximately 101.3 J (using $W = P\Delta V$ and converting atm to Pa).

Isochoric Process

An isochoric process occurs at a constant volume. Since the volume is constant, the work done during an isochoric process is zero.

Example: Heating or cooling a gas in a rigid container (where the volume can't change) would constitute an isochoric process.

Cyclic Process

A cyclic process is a sequence of processes that returns a system to its initial state.

Example: The operation of a heat engine involves a cyclic process. The working substance (usually a gas) is cyclically compressed and expanded, and returns to its initial state at the end of each cycle.

Second Law of Thermodynamics

The second law of thermodynamics provides critical insight into the directionality of processes and the concept of irreversibility. This law introduces a principle that seems quite intuitive: the natural tendency of any isolated system is to degenerate into a more disordered state.

Mathematically, we express the second law of thermodynamics using heat engines, which are hypothetical devices conceived to convert heat entirely into work. However, the second law postulates the impossibility of such a perfect conversion. In reality, no heat engine can be 100% efficient.

Carnot Engine

To understand this more clearly, consider the Carnot engine, a theoretical construct that operates between two reservoirs at constant temperatures T_1 and T_2, where $T_1 > T_2$.

- In an isothermal expansion phase, the system absorbs heat Q_1 from the reservoir at T_1 and does work on the surroundings.

- The system is then isolated and undergoes an adiabatic expansion, doing more work on the surroundings but without exchange of heat. The system cools to T_2.

- Then there is an isothermal compression phase where the system absorbs heat Q_2 from the cold reservoir at T_2.

- Finally, the system is again isolated and goes through an adiabatic compression, returning to its initial state.

Efficiency

From this cycle, we can derive the efficiency η of a Carnot engine as:

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}.$$

This tells us that all reversible engines operating between two thermal reservoirs will have the same efficiency. Furthermore, no engine operating between two reservoirs can have efficiency greater than a Carnot engine operating between the same two reservoirs. This is a statement of the second law of thermodynamics.

Another example: When an ice cube melts, it becomes more disordered as the structured lattice of the ice turns into the more random arrangement of liquid water molecules. Thus, the entropy of the water increases.

The Second Law of Thermodynamics can be stated in many ways, but all essentially have the same significance. Here are two common ways:
1. Heat cannot spontaneously flow from a colder location to a hotter location.

2. In any cyclic process, the **entropy** will either increase or remain the same. But, what is entropy?

Entropy (S) is a measure of the number of specific ways in which a thermodynamic system may be arranged, often understood as a measure of disorder.

The second law of thermodynamics can be understood mathematically using the concept of change in entropy. The formula for change in entropy, when heat is transferred into or out of a system, is:

$$\Delta S = \int \frac{dQ_{rev}}{T} = \frac{\Delta Q}{T}$$

where ΔS is the change in entropy, dQ_{rev} is a differential quantity of heat transferred reversibly, and T is the temperature at which the reversible process occurs.

Entropy

Entropy is a measure of the disorder or randomness of a system. In thermodynamics, it is often associated with the second law.

Example: For a reversible isothermal process, if 200 J of heat is added to a system at a temperature of 300 K, the change in entropy is $dS = \frac{dQ_{\text{rev}}}{T} = \frac{200\,\text{J}}{300\,\text{K}} = 0.67$ J/K.

Efficiency and the Carnot Engine

Efficiency

In the context of thermodynamics, efficiency (η) is a dimensionless measure of how effectively a system or device converts input energy into useful work. It's often expressed as a percentage, and it is calculated by dividing the useful output energy (or work) by the total input energy.

For a heat engine, efficiency is defined as the ratio of the work done by the engine (W) to the heat absorbed at high temperature (QH):

$$\eta = \frac{W}{QH} = 1 - \frac{QL}{QH}$$

where QL is the heat expelled at low temperature.

Carnot Engine

The Carnot engine, named after Sadi Carnot, is an idealized engine that operates on the reversible Carnot cycle. The significance of the Carnot engine is that it has the highest possible efficiency of any engine operating between two thermal reservoirs at constant temperatures.

The Carnot engine's operation consists of two isothermal processes – one at a high temperature (TH) where heat is absorbed, and one at a low temperature (TL) where heat is expelled – and two adiabatic processes that connect the isothermal processes.

The Carnot engine's efficiency is given by the equation:

$$\eta_{Carnot} = 1 - \frac{TL}{TH}$$

Where temperatures must be in Kelvin. This tells us that the Carnot engine's efficiency depends only on the two reservoirs' temperatures, not on the working substance or the specific processes.

Problem 3 A heat engine operates between two reservoirs at temperatures of $1000\,K$ and $400\,K$. Calculate the maximum possible efficiency of this engine.

Solution 3 The maximum possible efficiency of the engine is given by the Carnot efficiency:

$$\eta_{Carnot} = 1 - \frac{TL}{TH} = 1 - \frac{400\,K}{1000\,K} = 0.60$$

Therefore, the maximum possible efficiency of this engine is 60%.

Thermal efficiency is the ratio of work output to heat input. A Carnot engine is a hypothetical engine that operates on the Carnot cycle, which is the most efficient cycle possible.

$$\eta = 1 - \frac{Q_c}{Q_h} \tag{1}$$

A Carnot engine with a hot reservoir at 500 K and a cold reservoir at 300 K has a thermal efficiency of $\eta = 1 - \frac{300\,K}{500\,K} = 0.4$ or 40%.

Problem 4 Consider a Carnot engine operating between a hot reservoir at $600\,K$ and a cold reservoir at $300\,K$. If $1200\,J$ of heat is taken from the hot reservoir in each cycle, find the increase in entropy of the cold reservoir.

Solution 4 From the Carnot efficiency $\eta_{Carnot} = 1 - \frac{TL}{TH}$, we can calculate the work done by the Carnot engine:

$$W = QH \times \eta_{Carnot} = QH\left(1 - \frac{TL}{TH}\right) = 1200\,J \times \left(1 - \frac{300\,K}{600\,K}\right) = 600\,J$$

So, the heat expelled to the cold reservoir, QL, is the heat absorbed from the hot reservoir minus the work done, which is $1200\,J - 600\,J = 600\,J$.

The increase in entropy of the cold reservoir is given by $\Delta S = \frac{QL}{TL} = \frac{600\,J}{300\,K} = 2\,J/K$.

More Examples:

1 A system receives 800 J of heat and does 700 J of work. What is the change in internal energy of the system?

Solution Using the first law of thermodynamics, $\Delta U = Q - W$, we find that the change in internal energy is $\Delta U = 800\,J - 700\,J = 100\,J$.

2 A Carnot engine operates between two reservoirs at temperatures of 600 K and 300 K. What is the efficiency of the engine?

Solution   The efficiency of a Carnot engine is given by $\eta = 1 - \frac{T_c}{T_h}$. Substituting the given values, we find that $\eta = 1 - \frac{300\,\text{K}}{600\,\text{K}} = 0.5$ or 50%.

3   During a reversible isothermal expansion, a gas absorbs 500 J of heat at a temperature of 350 K. What is the change in entropy of the gas?

Solution   The change in entropy for a reversible isothermal process is given by $dS = \frac{dQ_{\text{rev}}}{T}$. Substituting the given values, we find that $dS = \frac{500\,\text{J}}{350\,\text{K}} \approx 1.43\,\text{J/K}$.

Third Law of Thermodynamics

The third law of thermodynamics, sometimes called Nernst's Theorem, states that as a system approaches absolute zero – the lowest possible temperature at 0 Kelvin or -273.15 degrees Celsius – all processes cease and the entropy of the system approaches a minimum value.

This law has two important implications:

Unattainability of Absolute Zero

Absolute zero cannot be reached through any finite number of processes. Even though cooling techniques can bring a system extremely close to absolute zero, it is impossible to actually reach this temperature. This is sometimes referred to as the unattainability principle.

Entropy at Absolute Zero

For a perfect crystalline substance, the entropy is zero at absolute zero. A perfect crystal is one where the internal structure of the substance is uniform and there are no defects or dislocations.

Mathematically, the third law of thermodynamics is often stated as:

$$\lim_{T \to 0} S(T) = S_0 \tag{2}$$

where $S(T)$ is the entropy of the system at temperature T, and S_0 is a constant, which is zero for a perfect crystal.

This implies that at absolute zero, the system is in its ground state, where entropy is at its minimum. This ground state refers to the lowest energy state of the system, where all the particles are perfectly ordered, and thus the entropy is zero for a perfect crystal.

The third law of thermodynamics states that as the temperature of a system approaches absolute zero, the entropy of the system approaches a minimum value or zero for perfect crystalline substances. This is significant because it

provides a basis for the concept of absolute zero, where all molecular motion ceases.

Example: Suppose we have a perfect crystalline substance at $0\,K$. According to the third law of thermodynamics, the entropy of this system is zero. Now, let's increase the temperature of this system to $T\,K$ reversibly and isothermally. What would be the entropy change of the system?

Solution: We know from the definition of entropy that $dS = \frac{dQ_{\text{rev}}}{T}$, where dQ_{rev} is the heat absorbed reversibly and T is the absolute temperature.

Integrating from the initial state $(S_i = 0,\ T_i = 0\,K)$ to the final state $(S_f = S,\ T_f = T\,K)$, we get:

$$S - 0 = \int_0^T \frac{dQ_{\text{rev}}}{T}$$

Assuming the heat capacity C of the system is independent of temperature (which is a rough approximation as it can depend on temperature), we can write $dQ_{\text{rev}} = CdT$. Then, the above equation becomes:

$$S = \int_0^T \frac{C\,dT}{T}$$

On integrating, we get:

$$S = C\ln(T) - C\ln(0)$$

Since $\ln(0)$ is undefined, we might seem to have a problem. However, in real systems, the heat capacity C goes to zero as temperature goes to zero faster than T goes to zero, which makes the integral finite. The details of this are beyond the scope of this course.

Conclusion

In this course, we have explored the fundamental principles of thermodynamics, which is the study of energy and its transformations. Thermodynamics provides a macroscopic description of how physical systems interact with one another and how changes in energy, pressure, volume, and temperature occur.

Starting with the zeroth law, we've seen how thermal equilibrium allows us to establish a temperature scale. The first law of thermodynamics has demonstrated that energy is conserved, showing the interplay between internal energy, heat, and work. The second law introduces us to the concept of spontaneous processes and entropy, where it states that total entropy of an isolated system can never decrease over time. We've also touched upon the third law of thermodynamics, which deals with the absolute zero of temperature and the unattainability of this absolute zero.

Furthermore, we've delved into the properties of an ideal gas, learning about the ideal gas law, kinetic theory of gases, and the different thermodynamic processes. Through examples and exercises, we've seen these laws and principles in action, providing a concrete basis for these abstract concepts.

However, the study of thermodynamics does not end here. These concepts and laws serve as a foundation for a multitude of fields within physics and engineering such as statistical mechanics, quantum mechanics, and chemical engineering.

Finally, always remember that the laws of thermodynamics govern the universe in which we live, from the smallest particles to the largest galaxies, from the coldest corners of space to the hottest stars.

Problems and Solutions

1. Explain the Zeroth Law of Thermodynamics in your own words and provide a real-world example of it.

2. What is the difference between an isochoric process and an isobaric process? Give an example of each.

3. Describe how heat transfer occurs and give examples of the three modes of heat transfer: conduction, convection, and radiation.

4. What does the Second Law of Thermodynamics state about the direction of heat flow?

5. In your own words, explain what an adiabatic process is. Provide an example.

6. What is the difference between a state function and a path function in thermodynamics? Give an example of each.

7. Explain what degrees of freedom are in the context of the kinetic theory of gases.

8. What is the significance of Avogadro's law in thermodynamics?

9. A gas at pressure $P_1 = 3$ atm, volume $V_1 = 5$ L is compressed isothermally to a volume $V_2 = 2$ L. Calculate the work done on the gas. Assume the gas to be ideal.

10. Consider an ideal gas which absorbs 500 J of heat in an isochoric process, causing its internal energy to increase by 500 J. What is the work done during the process?

11. A Carnot engine operates between two reservoirs at temperatures T_1 and T_2 ($T_1 > T_2$). If the efficiency of the engine is 30%, what is the ratio T_2/T_1?

12. Calculate the change in entropy of an ideal gas that expands isothermally from an initial volume V_1 to a final volume $V_2 = 2V_1$.

13. An ideal gas undergoes a process defined by the equation $PV^3 = constant$. What kind of process is this, and what is its corresponding adiabatic exponent?

14. A monoatomic ideal gas expands adiabatically from an initial state (P_1, V_1) to a final state (P_2, V_2). Given that $P_1 V_1^\gamma = P_2 V_2^\gamma$ (where $\gamma = 5/3$ is the adiabatic constant for monoatomic ideal gas), find an expression for P_2 as a function of P_1, V_1, and V_2.

15. An engine absorbs 500 J of heat from a hot reservoir and expels 300 J to a cold reservoir during each operating cycle. What is the efficiency of the engine and what is the work done in each cycle?

16. A gas expands according to the law $PV^n = constant$ where n is a constant. If $n > \gamma$, where γ is the adiabatic index, what type of process is this and what is the value of n for an isothermal process?

Answers

1. The Zeroth Law of Thermodynamics states that if two systems are each in thermal equilibrium with a third system, they are in thermal equilibrium with each other. This implies the transitive property in thermodynamics and establishes a fundamental basis for temperature measurement. For example, if we have three bodies A, B, and C and if A is in thermal equilibrium with B and B is in equilibrium with C, then A and C are also in thermal equilibrium.

2. An isochoric process is a thermodynamic process in which the volume remains constant. If you heat a gas in a rigid, sealed container, the volume will stay the same, but the pressure and temperature may change. On the other hand, an isobaric process is a process in which the pressure remains constant. An example of an isobaric process could be boiling water at sea level, where the pressure remains constant (1 atm) and the water (the system) changes phase from liquid to gas.

3. Heat transfer occurs when there is a temperature difference between two systems or a system and its surroundings. The three modes of heat transfer are: conduction (heat transfer due to molecular collisions, such as when you touch a hot pan), convection (heat transfer due to the motion of a fluid, such as boiling water), and radiation (heat transfer due to electromagnetic waves, such as the heat from the sun).

4. The Second Law of Thermodynamics states that heat flow will spontaneously occur from a region of higher temperature to a region of lower temperature, but not the other way around. In other words, it is the natural direction of heat flow.

5. An adiabatic process is a process in which no heat enters or leaves the system. In such a process, any change in the internal energy of the system is due to work done on or by the system. An example could be the rapid compression or expansion of a gas within an insulated container.

6. State functions depend only on the state of the system and not on the path taken to reach that state. Examples include internal energy, temperature, and pressure. Path functions, on the other hand, depend on the path taken to change the state of the system. Work and heat are examples of path functions.

7. Degrees of freedom in the kinetic theory of gases refer to the number of independent ways that the molecules of a gas can store kinetic energy. For monatomic gases, the molecules have three degrees of freedom (one each

for motion in the x, y, and z directions). For diatomic gases, there are five degrees of freedom (three translational and two rotational).

8. Avogadro's law states that equal volumes of all gases, at the same temperature and pressure, contain an equal number of molecules. This is significant in thermodynamics as it provides a link between the macroscopic properties of gases (which we can measure, like pressure and volume) and their microscopic properties (which we can't directly measure, like the number of molecules).

9. For an isothermal process for an ideal gas, $P_1V_1 = P_2V_2$. We can find the work done during the isothermal compression of the gas using the formula $W = P_1V_1 \ln(V_2/V_1)$. Substituting the given values, we find $W = 3 \times 5\ln(2/5) = -7.64$ L.atm. To convert this to Joules, we use the conversion factor 101.3 J/L.atm, giving $W = -7.64 \times 101.3 = -774$ J. The work done on the gas is positive, so the work done by the gas is $-W = 774$ J.

10. For an isochoric process, the volume of the gas remains constant. Therefore, no work is done because work is given by $W = P\Delta V$, and $\Delta V = 0$.

11. The efficiency η of a Carnot engine operating between two reservoirs at temperatures T_1 and T_2 is given by $\eta = 1 - \frac{T_2}{T_1}$. If the efficiency is 30%, then $0.30 = 1 - \frac{T_2}{T_1}$. Therefore, $\frac{T_2}{T_1} = 0.70$.

12. The change in entropy ΔS for an ideal gas expanding isothermally is given by $\Delta S = nR\ln(V_2/V_1) = R\ln(V_2/V_1)$, since we can consider $n = 1$ for simplicity. Substituting $V_2 = 2V_1$ gives $\Delta S = R\ln 2$.

13. The process is defined by the equation $PV^3 = constant$. This is similar to the polytropic process, which is defined by the equation $PV^n = constant$, where n is the polytropic index. Therefore, for this process, the polytropic index is 3. For an adiabatic process, the adiabatic exponent γ is the polytropic index, and $\gamma = 5/3$ for monoatomic ideal gases, so this process is not adiabatic.

14. Using the equation $P_1V_1^{\gamma} = P_2V_2^{\gamma}$, we find $P_2 = P_1(V_1/V_2)^{\gamma}$.

15. The efficiency of the engine is given by $\eta = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{300\,\text{J}}{500\,\text{J}} = 0.4$ or 40%. The work done in each cycle is the net energy transfer, which is the heat absorbed from the hot reservoir minus the heat expelled to the cold reservoir: $W = Q_{in} - Q_{out} = 500\,\text{J} - 300\,\text{J} = 200\,\text{J}$.

16. The process is polytropic, as it is defined by the equation $PV^n = constant$. The value of n is greater than γ, which is the adiabatic index. For an isothermal process, $n = 1$.

Problem Set - 5

Conceptual Questions

1. Explain the Zeroth Law of Thermodynamics and how it relates to the concept of temperature.

2. What is the significance of the First Law of Thermodynamics in energy conservation?

3. What does the Second Law of Thermodynamics say about the direction of heat transfer and the increase of entropy in the universe?

4. Why does a Carnot engine have the highest efficiency among all heat engines working between the same temperature reservoirs?

5. What is the difference between a reversible process and an irreversible process in thermodynamics?

6. Explain how entropy is related to the disorder or randomness of a system.

7. How does an increase in temperature generally affect the entropy of a system?

8. Explain the term "entropy" and how it relates to the Second Law of Thermodynamics.

9. How does a refrigerator utilize the principles of thermodynamics to cool a space?

10. Explain why the efficiency of a heat engine cannot be 100% according to the Second Law of Thermodynamics.

Mathematical Problems

1. Calculate the work done on a gas when it expands from volume V_1 to V_2 under the pressure law $P = \alpha V$, where α is a constant.

2. A monoatomic ideal gas expands according to the law $PV^2 = $ constant. Calculate the amount of heat absorbed by the gas during this process.

3. Determine the change in entropy of one kilogram of water at $100°C$ when it is converted into steam at $100°C$. Given that the latent heat of vaporization of water is $2.26 \times 10^6 \ J/kg$.

4. A heat engine operates between two heat reservoirs at temperatures $600 \ K$ and $300 \ K$. Determine the efficiency of this heat engine.

5. For an adiabatic process of an ideal gas, derive the relation $PV^\gamma = $ constant, where γ is the ratio of specific heats.

6. Determine the increase in entropy of a system when $200\,J$ of heat is transferred reversibly to it at a constant temperature of $50\,K$.

7. A Carnot engine operates between two heat reservoirs at temperatures $500\,K$ and $400\,K$. The engine absorbs $500\,J$ of heat from the hotter reservoir in each cycle. Calculate the work done per cycle.

8. Given the heat capacity at constant volume, C_V, for a monatomic ideal gas is $3/2R$, where R is the ideal gas constant, derive the heat capacity at constant pressure, C_P.

9. An ideal gas undergoes an isothermal expansion at a temperature of $300\,K$. If the initial and final volumes are $0.1\,m^3$ and $0.2\,m^3$ respectively, and the pressure at the start of the expansion is $10^5\,Pa$, calculate the work done by the gas during this expansion.

10. Derive the formula for the efficiency of a Carnot engine, $\eta_{Carnot} = 1 - \frac{TL}{TH}$, starting from the definitions of heat, work, and the Carnot cycle.

11. Derive an expression for the work done in an isobaric process. Use the first law of thermodynamics to find an equation for the change in internal energy.

12. A monoatomic ideal gas undergoes an adiabatic expansion. Given that the initial pressure and volume are P_1, V_1 and the final pressure and volume are P_2, V_2, find an expression relating P_1, V_1, P_2, V_2.

13. The coefficient of performance for a refrigerator is given by the ratio of the heat extracted from the cold reservoir to the work done on the system. Derive an expression for this ratio in terms of the temperatures of the hot and cold reservoirs.

14. Consider an ideal gas that expands isothermally from a volume V_1 to a volume V_2. Compute the work done by the gas.

15. A gas is contained in a cylinder with a movable piston. The gas undergoes a quasi-static isochoric process. Sketch the P-V diagram and calculate the work done by the gas.

16. A Carnot engine operates between two reservoirs at temperatures T_H and T_C. Using the second law of thermodynamics, derive an expression for the efficiency of the engine.

17. An ideal gas is compressed adiabatically. Show that the quantity PV^γ is a constant, where γ is the ratio of specific heats.

18. Show that the entropy change of an ideal gas undergoing an isothermal expansion is given by $nR\ln\left(\frac{V_f}{V_i}\right)$, where n is the number of moles, R is the ideal gas constant, and V_i, V_f are the initial and final volumes.