Fundamentals of Physics in Engineering I

Unit 5.- THERMODYNAMICS

• Work

Work is a transfer of energy between a system and its surroundings due to movement of part of the surroundings. The work done by a liquid on its surroundings is given by:

\[ W = \int_{V_1}^{V_2} p\,dV \]

The work done by a system is positive when energy is transferred from the system to the surroundings.

**Work in gas systems (reversible processes):**

(a) Isochoric process (constant volume, \( dV = 0 \)): \( W = 0 \).

(b) Isobaric process (constant pressure, \( dp = 0 \)):

\[ W = \int_{V_1}^{V_2} p\,dV = p(V_2 - V_1) = p\Delta V \]

(c) Isothermal process (constant temperature, \( dT = 0 \)), for an ideal gas \( pV = nRT \) and if \( T \) is constant \( pV_1 = pV_2 \):

\[ W = \int_{V_1}^{V_2} p\,dV = \int_{V_1}^{V_2} nRT = nRT \ln \frac{V_2}{V_1} \]

\[ = pV_1 \ln \frac{V_2}{V_1} = pV_2 \ln \frac{V_2}{V_1} = pV_1 \ln \frac{V_1}{p} \]

(d) Adiabatic process (\( Q = 0 \)), for an ideal gas \( pV = cte \):

\[ \gamma = \frac{C_p}{C_v} \]

\[ pV = pV_1^{\gamma} \Rightarrow p = \frac{pV_1^{\gamma}}{V^{\gamma}} \]

\[ W = \int_{V_1}^{V_2} p\,dV = \int_{V_1}^{V_2} \frac{pV_1^{\gamma}}{V^{\gamma}} \,dV = \frac{pV_1}{\gamma - 1} \left[ \frac{V_2^{\gamma}}{V_1^{\gamma - 1}} \right] \]

• State functions and equations of state

The state variables \( p, V, T \) and \( n \) of a substance are interrelated by a mathematical equation called an equation of state. For example, for an ideal gas:

\[ pV = nRT \]

where \( R = 8.31 \text{ J mol}^{-1} \text{K}^{-1} = 2 \text{ cal mol}^{-1} \text{K}^{-1} \) is the universal gas constant. A system's state of equilibrium may be represented by a point on the \( p-V \) diagram. *Quasistatic* processes are those in which the system goes through a series of equilibrium states, and may be represented by curves on a \( p-V \) diagram.

• First law of thermodynamics. Internal energy

The relationship between the energy transferred between a system and its surroundings and change in internal energy \( U \) of the system is given by:

\[ \Delta U = Q - W \]

The heat \( Q \) ceded to the system and the work \( W \) done by the system depends on each particular process. However, internal energy is a function of state: the change in internal energy \( \Delta U = U_f - U_i \) depends solely on the initial \( (i) \) and final \( (f) \) states, and not on the process carried out to go from one to the other. In the equation describing the first law of thermodynamics, the sign convention is as follows: \( Q > 0 \) if heat is ceded to the system from its surroundings and \( W > 0 \) if the system does work on its surroundings.

• Some applications of the first law of thermodynamics

(a) Isochoric process (\( V = cte \)): The work done is zero \( (W = 0) \) and applying the first law:

\[ \Delta U = Q - W = Q \]

(b) Isobaric process \( (p = cte) \): Both types of energy, heat \( Q \) and work \( W \), may be transferred between the system and its surroundings.

(c) Adiabatic process \( (Q = 0) \): \( \Delta U = Q - W = -W \)

(d) Isothermal process \( (T = cte) \): An example of an isothermal process is a phase change.

(i) Free expansion of an ideal gas: Take a container with two compartments, one of which holds an ideal gas and the other a vacuum. The two compartments are separated from each other and the container is isolated from the surroundings. When the stopcock between the two compartments is opened the gas expands freely until the pressure in the two compartments is the same. In the case of free expansion there is no change in temperature of the gas and therefore \( Q = 0 \). The system does not do any work on its surroundings \( W = 0 \), so the internal energy does not change either \( \Delta U = 0 \). Since the pressure and volume of the gas changed, \( U \) is not a function of either \( p \) or \( V \), but since the temperature remains constant it may be deduced that the internal energy of an ideal gas depends only on the temperature, \( U(T) \). Since at constant volume \( dU = dQ = nC_vdT \) and \( U \) only depends on \( T \). At constant pressure it will be also \( dU = nC_vdT \).

(f) Cyclic process: Initial and final states coincide. Since \( U \) is a function of state, in a cycle \( \Delta U = 0 \).

• Heat capacity of gases

Heat capacity of an ideal monatomic gas:

\[ C_V = \frac{3}{2} R \]

\[ C_p = C_V + R = \frac{5}{2} R \]

Heat capacity of an ideal diatomic gas:

\[ C_V = \frac{5}{2} R \]

\[ C_p = C_V + R = \frac{7}{2} R \]

The equation:

\[ C_p - C_V = R \]

is known as *Meyer's relation*. An ideal gas that undergoes a quasistatic adiabatic process experiences changes in pressure and volume given by the equation:

\[ pV^\gamma = cte \]

with \( \gamma = C_p/C_v \). For ideal monatomic gases \( \gamma = 5/3 = 1.67 \), and for ideal diatomic gases \( \gamma = 7/5 = 1.40 \).

• Heat engines and the second law of thermodynamics

According to the *Kelvin-Planck* statement of the second law of thermodynamics, no cycle is possible in which heat is absorbed from a reservoir at a fixed temperature and completely converted into work. Any device that transforms heat partly into work or mechanical energy is called a heat engine. A refrigerator is a heat engine operating in reverse.

• Thermal efficiency of heat engines and coefficient of performance of refrigerators

If a heat engine extracts heat, \( Q_C \), from a hot reservoir, performs work, \( W \), and cedes heat, \( Q_F \), to a cold reservoir, its thermal efficiency, \( \eta \), is:

\[ \eta = \frac{W}{Q_C} = \frac{Q_C - Q_F}{Q_C} = \frac{Q_C - |Q_F|}{Q_C} = 1 - \frac{|Q_F|}{Q_C} \]
A refrigerator extracts heat, $Q_C$, from a cold reservoir, and cedes heat, $Q_F$, to a hot reservoir. The refrigerator requires a net input of mechanical work, $W$. The coefficient of performance of a refrigerator, $e$, is given by:

$$ e = \frac{Q_F}{W} $$

According to the Clausius statement of the second law, no process is possible in which the sole result is the transfer of heat from a body of lower temperature to a body of higher temperature.

- **The Carnot cycle**

A reversible process is one which may be reversed by means of infinitesimal changes in the surroundings of the system. Any process that is not reversible is irreversible. A Carnot machine is a reversible machine working between two reservoirs at temperatures $T_C$ and $T_F$, following a cycle made up of:
- 1. A quasistatic isothermal expansion that absorbs heat ($Q_C$) from the hot reservoir at temperature $T_C$.
- 2. A quasistatic adiabatic expansion to a lower temperature $T_F$.
- 3. A quasistatic isothermal compression ceding heat ($Q_F$) to a cold reservoir at temperature $T_C$.
- 4. A quasistatic adiabatic compression to the initial state (temperature $T_C$).

The efficiency of the Carnot cycle is given by:

$$ \eta = 1 - \frac{|Q_F|}{Q_C} = 1 - \frac{T_F}{T_C} $$

and it is the upper limit on efficiency of real heat engines operating between these two temperatures. According to *Carnot's theorem*, all reversible engines operating between two temperatures, $T_C$ and $T_F$, are equally efficient and no engine operating between these temperatures can be more efficient than a Carnot engine operating between the same temperatures.

- **Thermodynamic temperature**

The quotient between the absolute temperatures of two reservoirs is defined by the quotient between the heat ceded and absorbed by the reservoirs when it is shown that an engine undergoes a Carnot cycle between the two reservoirs:

$$ \frac{T_F}{T_C} = \frac{|Q_F|}{Q_C} $$

The thermodynamic temperature $T$ of a system is defined as:

$$ T = 273.16 \frac{|Q|}{|Q_1|} K $$

where $Q$ and $Q_1$ are the exchanges of heat that take place in a Carnot cycle operating between the system and water at its triple point.

- **Entropy**

Entropy ($S$) is a state variable. The infinitesimal entropy change $dS$ during an infinitesimal reversible process at absolute temperature $T$ is given by:

$$ dS = \frac{dQ_{rev}}{T} $$

where $dQ_{rev}$ is the heat ceded to the system in a reversible process connecting these states. The variation in entropy of a system may be positive or negative. The difference in entropy between two states of a system is given by:

$$ \Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \frac{dQ_{rev}}{T} $$

where the integral is valid for any reversible process connecting the two states. Entropy is a measure of the disorder in a system.

- **Calculation of variations in entropy in various processes**

When a system undergoes a process, the change in entropy depends solely on the initial and final states, since it is a function of state. Thus, in a real process, reversible or irreversible, a reversible process connecting the initial and final states is used to calculate the entropy, bearing in mind that this reversible process is used only for the purpose of the calculation.

(i) *Phase change:* For example, when a solid such as ice melts, the process is irreversible; however, we imagine a reversible process that consists in using a reservoir whose temperature is insignificantly higher than that of the solid and the heat is ceded reversibly at the melting point of ice. The heat absorbed by the ice is $Q_f = mL_f$, and since the temperature does not change:

$$ \Delta S = S_{\text{liq}} - S_{\text{sol}} = \int_{T_i}^{T_f} \frac{dQ_{rev}}{T} = \frac{mL_f}{T_f} $$

(ii) *Change in temperature:* For example, if water is heated at constant pressure, a reversible process is considered with reservoirs at temperatures insignificantly higher than that of the water:

$$ \Delta S = \int_{T_i}^{T_f} \frac{dQ_{rev}}{T} = \frac{mc_p \Delta T}{T_f} = mc_p \ln \frac{T_f}{T_i} $$

(iii) *Change in volume:* For example, in the case of free expansion (an irreversible process) of an ideal gas ($Q = 0$, $W = 0$, $\Delta U = 0$, $\Delta T = 0$), we imagine an isothermal reversible process between two states ($V_i$, $T$) and ($V_f$, $T$). According to the first law:

$$ dQ = dU + pdV = 0 + pdV = pdV $$

and since $pV = nRT$,

$$ \int_{V_i}^{V_f} \frac{dQ_{rev}}{T} = \int_{V_i}^{V_f} \frac{nRdT}{V} = \int_{V_i}^{V_f} \frac{nRdV}{V} = nR \ln \frac{V_f}{V_i} $$

- **Entropy and the second law**

The change in entropy of the universe is equal to the sum of the changes in entropy of a system and its surroundings. According to the expression of entropy found in the second law, in all processes the entropy of the universe either increases (if the process is irreversible) or remains constant (if the process is reversible).

The increase in entropy of an isolated system in an irreversible process is related to a lost opportunity to do work ($W_{\text{lost}} = T \Delta S$). Irreversible processes go from more ordered to less ordered states. Entropy is related to probability: a highly ordered system has low probability and low entropy.