University of Mosul

College of Science

Department of Physics

Second Stage

Heat and Thermodynamic

2024 – 2025

Lecture 9: Heat capacity (C_p & C_v)

Preparation

Lec. Enas Mohammed Yonis

Heat capacity C

Heat: It is energy in transit or transmission, and the word heat ceases to be used whenever the thermal energy transit or transmission stops

Heat capacity C : The heat capacity of a system is defined as the amount of heat that the system absorbs To raise its temperature by one degree. Since the heat capacity changes with the change of temperature, it is advisable to define it differently

$$\mathbf{C = \frac{d\acute{Q}}{dT} \dots\dots\dots\dots\dots..(1)}$$

dQ' : The amount of heat transferred to the system

dT : the rise in temperature

Since the temperature is not a function of the state, the amount of heat transferred dQ' to a system in a thermodynamic process depends on the path of the process, and accordingly, the heat capacity of a system depends on the course of the process, and since the number of possible paths is not specified, which loses its importance, so we must define the method in which it is done. By the transfer of heat to the system, the easiest and most common way is to make the volume of the system or the pressure exerted on it constant and thus we have determined the heat capacity.

Heat capacity at a constant volume is given by the equation

$$\mathbf{C_V = \left(\frac{\partial Q}{\partial T}\right)_V \dots\dots\dots..(2)}$$

The heat capacity of a system under constant pressure is given by the equation

$$\mathbf{C_P = \left(\frac{\partial Q}{\partial T}\right)_P \dots\dots\dots..(3)}$$

The difference between C_P ,C_V (V, T, independent variables):

that the internal energy of any entity is a characteristic that depends on the state of the entity only, and for gas, its state can be fully defined using any two of the following properties: pressure P, volume V, temperature T) If we choose the two properties V , T as an independent property then U can be considered as a function of V, T i.e. that

U= f(T,V)………………(4)

From this equation it is possible to calculate the amount of change in the internal energy dU when the values of V and T change in magnitudes respectively by differentiating equation 4

$$\mathbf{dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \ldots\ldots\ldots\ldots.(5)}$$

If an amount of heat is prepared for the gas and its volume increases by the amount under constant pressure P, according to the first law of thermodynamics, it is produced.

$$\mathbf{dQ = dU + PdV \ldots\ldots\ldots\ldots(6)}$$

Substituting dU into equation (6) we get

$$\mathbf{dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV \ldots\ldots\ldots\ldots(7)}$$

Dividing eq. (7) by dT at constant pressure we get

$$\mathbf{\left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \ldots\ldots\ldots\ldots(8)}$$

At constant V from 1st law of thermodynamic we have

dQ =dU +PdV (V constant, dV = 0

dQ =dU

OR $\left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V \ldots\ldots\ldots\ldots..(9)$

We have $\left(\frac{\partial Q}{\partial T}\right)_p = C_P \ldots\ldots\ldots\ldots\ldots(10)$

Sub. Eq.9 and 10 in eq. 8 we get

$$C_P = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

Equation 11 indicates that Cp is greater than C_V, because the heat capacity under a fixed volume is equal to the amount of heat Q required to raise the temperature of the gas under a fixed volume, so its pressure increases accordingly. As for the heat capacity under constant pressure, it is equal to the amount of heat needed to raise the temperature of the gas by one degree.

When this gas is heated under constant pressure, its volume increases accordingly, which leads to the completion of mechanical work on the surroundings. That is, the gas in this case needs heat to raise its temperature, a thermal oasis, in addition to additional energy to extend its limits so that its pressure remains constant.

$C_P > C_V$

Now it is useful to give the physical significance of Equation 11

1. The limit $P\left(\frac{\partial V}{\partial T}\right)_P$ represents the amount of work produced when the volume of a gas expands as a result of increasing its temperature by one degree under pressure.
2. The limit $\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$ represents the amount of work done against the attractive or repulsive partial forces between the gas molecules.

3. By comparing the limits $\mathbf{P}\left(\frac{\partial V}{\partial T}\right)_P$, $\left(\frac{\partial U}{\partial V}\right)_T$ $\left(\frac{\partial V}{\partial T}\right)_P$ we notice that P bears the pressure of the resulting gas due to the collision of gas molecules with the walls of the vessel, while $\left(\frac{\partial U}{\partial V}\right)_T$ it represents the internal pressure of the resulting gas due to the attraction of the particles with each other.

The internal pressure $\left(\frac{\partial U}{\partial V}\right)_T$ of the gas means the change in the internal energy with the volume when the temperature is constant. The internal pressure of the real gas is very small compared to the pressure of the gas P.

As for the ideal gas, the internal pressure is zero, as there are no attractive forces between its molecules.

Note: the internal pressure of liquid solids is usually large due to the large holding forces between molecules compared to the molecular forces in gases.

Difference between C_P, C_V for ideal gas (V, T are independent variables):

From Equation 11

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Since the ideal gas equation for one mole

PV=RT

We differentiate the equation of the ideal gas with respect to T at constant pressure

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \ldots\ldots\ldots\ldots\ldots . (12)$$

After substituting it into equation 11 it results

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\frac{R}{P} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

Since the internal energy of an ideal gas is not dependent on its volume, therefore

$$\left(\frac{\partial U}{\partial V}\right)_T = Zero$$

$$C_P - C_V = [P + Zero]\frac{R}{P}$$

$$\therefore C_P - C_V = R \ldots\ldots\ldots\ldots\ldots.(14)$$

The difference between C_P, C_V (P, T, independent variables):

the enthalpy of any pure substance is a property of that substance, so it depends on the state of the entity only. For gas, its state can be determined completely using any two of the following properties: pressure P, volume V, temperature T) If we choose the two properties P and T as independent properties, then H can be considered as a function of P, T i.e.

H= F(T,P)………………(15)

The difference in enthalpy dH between two contiguous states of an entity can be obtained by differentiating equation 15, resulting in

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \ldots\ldots\ldots\ldots\ldots\ldots.(16)$$

From the definition of enthalpy, we have H

H=U+PV……………..(17)

From the differential of equation 17, we get

dH = dU+ PdV + VdP……………..(18)

If we provide the entity with a quantity of heat Q under constant pressure and in a reverse process by applying the first law of thermodynamics

dQ =dU+ PdV………(19)

We substitute the equation 19 into equation 18 to yield

dH =dQ+ VdP…………….(20) OR

dQ =dH - VdP…………….(21)

at constant P we get

dQ = dH or

$$\left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P = C_P \dots\dots\dots.(22)$$

we have $\left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V \dots\dots\dots\dots\dots(23)$

After substituting equation 16 in eq. 21 we get

$$dQ = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP - VdP \dots\dots\dots\dots\dots\dots.(24)$$

$$dQ = \left(\frac{\partial H}{\partial T}\right)_P dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] dP \dots\dots\dots\dots\dots\dots.(25)$$

Dividing both sides of the equation (under a constant volume) on dT is obtained

$$\left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial H}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V - V\left(\frac{\partial P}{\partial T}\right)_V \dots\dots\dots\dots\dots\dots.(26)$$

After substituting equations 22 and 23 in eq. 26 we get

$$C_V = C_P + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\left(\frac{\partial P}{\partial T}\right)_V \dots\dots\dots\dots\dots(27)$$

$$C_P - C_V = -\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\left(\frac{\partial P}{\partial T}\right)_V \dots\dots\dots\dots\dots(28)$$

The ratio between C_P, C_V

The ratio between heat capacity under constant pressure and heat capacity under constant volume is denoted by **ɣ**

$$\gamma = \frac{C_P}{C_V} \ldots\ldots\ldots\ldots\ldots (29)$$

This ratio is of great importance, and the experimental results indicated

1. The value of **ɣ** depends on the number of atoms in a single molecule,

2. In practice, **ɣ** was found that for all gases that contain (their molecules the same number of atoms) approximately the same value.For example,

for monatomic gases theoretical value of **ɣ** = 1.67

for diatomic gases, the theoretical value of **ɣ** = 1.4,

for triple atom gases the theoretical value of **ɣ** = 1.33

There are practically many ways to find value ɣ

1. Clement and Desorems Method
2. Partington method
3. Ruchhardt method
4. Voice method