Thermodynamics: Classical to Statistical

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Lecture - 02

Concepts of Enthalpy and Heat Capacity

In the last class, we discussed about heat, work and we defined them. We discussed first law of thermodynamics. We also discussed how to calculate work done. We also discussed and proved that work done (w) is path function and internal energy (U) is a state function. Then we discussed about the work done for adiabatic reversible process.

Today we will start with what would be the work done for irreversible adiabatic processes. There can be two cases.

Case I: When there is no external pressure,

$$P_{ext} = 0$$

$$w = -P_{ext}\Delta V = 0$$

$$q = 0, \text{ as the process is adiabatic.}$$

$$\text{So, } \Delta U = 0 \text{ and } \Delta T = 0$$

Case II: when external pressure is not zero,

$$P_{ext} \neq 0$$

$$w = -P_{ext}\Delta V = P_{ext}(V_2 - V_1) = P_{ext}((nRT_2/P_2) - (nRT_1/P_1))$$

$$\Delta U = w, \text{ for adiabatic process.}$$

$$\text{So, } C_V(T_2 - T_1) = P_{ext}((RT_1/P_1) - (RT_2/P_2))$$

Comparison between isothermal and adiabatic process: We will compare the work done between isothermal and adiabatic expansion. We consider ideal gas. We consider that V_i is the initial volume, P_i is initial pressure, and V_f is the final volume, and P_{iso} is the final pressure for isothermal expansion, and P_{adia} is the final pressure for adiabatic expansion. We started with the same initial volume and same initial pressure and we reach to a same final volume for both isothermal and adiabatic processes. So pressure has to be different, so we will calculate final pressure for isothermal expansion and final pressure for adiabatic expansion. Once we get that, we can easily calculate the work done for isothermal process and work done for adiabatic process, and then we can compare between them.

Now, for isothermal process:

$$P_1V_1 = P_2V_2$$

$$P_iV_i = P_{iso}V_f$$

$$P_i/P_{iso} = V_f/V_i$$

For adiabatic process:

$$P_iV_i^{\gamma} = P_{adia}V_f^{\gamma}$$

$$P_i/P_{adia} = (V_f/V_i)^{\gamma}$$

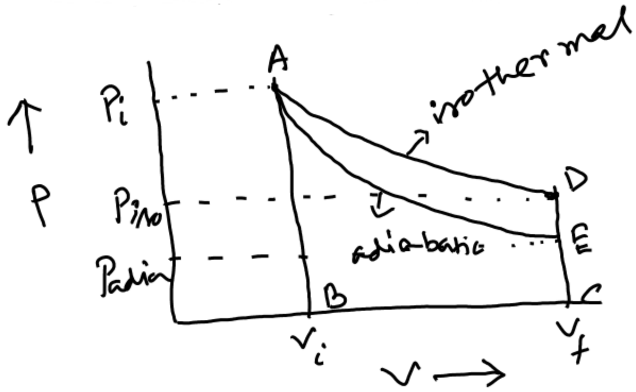
Now, we know that gamma is nothing but Cp by Cv and it is greater than 1 for most of the cases. Cp is greater than Cv for most of the cases that we know. In that case, we can write:

$$(V_f/V_i)^{\gamma} > V_f/V_i$$

$$\text{So, } P_i/P_{adia} > P_i/P_{iso}$$

$$\mathbf{P_{iso} > P_{adia}}$$

So, what we get? first we started with same initial volume for both the processes and we reached to same final volume. Initial pressure was also same for both the processes. And we obtained that for isothermal process the final pressure is higher than that adiabatic process. If we draw whatever we discussed in a simple PV diagram (Figure 1). It will look like this:



For isothermal process
work done => area
under the curve
ADCB

Figure 1

If we label them like A, B, C, D, E. So for isothermal process, workdone is nothing but area under the curve ADCB. Similarly, for adiabatic process, the work done is represented as area under the curve AECB. Since the area for isothermal process is higher than that of adiabatic process, so work done for isothermal process is greater than work done for adiabatic process. So, if we carry out our process in isothermal manner then we get more work done than the adiabatic process. We can do very similar exercise by starting with same initial volume. We can prove with similar fashion, if we started with same initial volume, same initial pressure and if we reach to same final pressure, and if we say that final volume for isothermal process (V_{iso}), and if we say V_{adia} is the final volume for adiabatic process. We will get a curve like this. So far we have compared the work done for isothermal process and work done for adiabatic process.

Now, we will discuss about enthalpy. what is enthalpy? Enthalpy we denote by H. So what do we mean by enthalpy? In enthalpy we can define it like this, it is equal to the energy transferred as heat in a constant pressure process, this is very important. Involving only P-V work. So, last part of this statement is very important. So, enthalpy can be defined as the energy transferred as heat in a constant pressure process involving only P-V work.

From the 1st law of thermodynamics,

$$\Delta U = q + w$$

If the process is carried out at constant volume, means there is no change in volume for a process. Then we can write, delta U is nothing but q_v. The subscript V stands for constant volume process. So constant volume means V_1 equals to V_2 (there is no volume change in that process). So we can calculate internal energy change for a process by measuring the heat change provided the process is carried out at constant volume.

$$\Delta U = q_v \text{ (as } V_1 = V_2\text{)}$$

For constant pressure process

$$q_p = \Delta U + P\Delta V = \Delta H$$

So, by definition this q_p is nothing but enthalpy change for that process.

So,

$$\Delta H = \Delta U + P\Delta V = \Delta U + \Delta n_g RT$$

Δn_g = change in the number of moles of gaseous product minus number of moles of gaseous reactants.

For example,

$$1.\ N_2(g) + 3H_2(g) = 2NH_3(g)$$

$$\Delta n_g = 2 - (1 + 3) = -2$$

$$2.\ 2H_2(g) + O_2(g) = 2H_2O(l)$$

$$\Delta n_g = -3$$

Molar volume of liquids are much much smaller than the molar volume of gases and we ignore this. So this is how one can calculate Δn_g.

Next we move to heat capacity. What do we mean by heat capacity? Heat capacity is defined as, the amount of heat required to raise or to increase the temperature of a substance by 1 degree or 1 kelvin. Heat capacity, in general we term as C, so C is nothing but dU/dT. Now, whether it is an extensive property or it is an intensive property. So heat capacity depends or the amount of heat required to raise the temperature of the substance by 1 degree, it depends on the amount of substance. So heat capacity is an extensive property. But heat capacity per mole or molar heat capacity is an intensive property. Now the next question is whether heat capacity is a path function or is a state function. Heat capacity in general is a path function. Because we get different heat capacity value if process is carried out in constant volume process or in constant pressure. So heat capacity in general is a path function but, heat capacity at constant pressure or volume, C_P or C_V are state function. How do you define heat capacity at constant volume?

$$C_V = (\delta U/\delta T)_V = \Delta U/\Delta T = q_V/\Delta T$$

Heat capacity at constant pressure,

$$C_P = (\delta H/\delta T)_P = \Delta H/\Delta T = q_P/\Delta T$$

We know C_p is always greater than (in most of the cases) greater than C_V. So what is the relationship between C_P and C_V? A very simple derivation we can carry out.

We know,

$$U = U(P,T)$$

$$dU = (\delta U/\delta P)_T\, dP + (\delta U/\delta T)_P\, dT \text{ ----------(1)}$$

Similarly,

$U = U(V,T)$

$dU = (\delta U/\delta V)_T\, dV + (\delta U/\delta T)_V\, dT$ ----------(2)

Again,

$V = V(P,T)$

$dV = (\delta V/\delta P)_T\, dP + (\delta V/\delta T)_P\, dT$ ----------(3)

Substituting the value of dV from equation (3) to equation (2),

$dU = (\delta U/\delta V)_T\, [(\delta V/\delta P)_T\, dP + (\delta V/\delta T)_P\, dT] + (\delta U/\delta T)_V\, dT$

$dU = (\delta U/\delta V)_T\, (\delta V/\delta P)_T\, dP + [(\delta U/\delta V)_T\, (\delta V/\delta T)_P + (\delta U/\delta T)_V]\, dT$ ---(4)

Now, if we compare equation 1 and equation 4 we obtain,

$(\delta U/\delta P)_T = (\delta U/\delta V)_T\ (\delta V/\delta P)_T$ ----------(5)

And, $(\delta U/\delta T)_P = (\delta U/\delta V)_T\, (\delta V/\delta T)_P + (\delta U/\delta T)_V$ -------(6)

Now, $H = U + PV \Rightarrow U = H – PV$

$(\delta U/\delta T)_P = (\delta H/\delta T)_P – P(\delta V/\delta T)_P$ ----------(7)

So from equation 6 and 7,

$(\delta H/\delta T)_P – P(\delta V/\delta T)_P = (\delta U/\delta V)_T\, (\delta V/\delta T)_P + (\delta U/\delta T)_V$

Now, $(\delta H/\delta T)_P = C_P$ and $(\delta U/\delta T)_V = C_V$

So, $C_P – C_V = [P + (\delta U/\delta V)_T]\, (\delta V/\delta T)_P$ -------------(8)

This expression is general expression.

Ideal gas case is special case. For ideal gas,

$(\delta U/\delta V)_T = 0$ and $(\delta V/\delta T)_P = nR/P$ (as, $V = nRT/P$)

$C_P – C_V = nR$

$$\mathbf{\bar{C}_P - \bar{C}_V = R}$$