

Thermodynamics
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Lecture - 32
Specific heats at constant pressure and constant volume

Let's look at the definitions of specific heat at constant pressure (C_p) and specific heat at constant volume (C_v). C_p is the amount of heat needed for a unit value rise in temperature of a unit mass of a substance at constant pressure. Similarly, C_v is the amount heat needed for a unit value rise in temperature of a unit mass of a substance at constant volume.

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The slide contains the following derivations:

- Constant Pressure ($p=c$):**

$$C_p = \frac{1}{m} \frac{\delta Q}{dT} \Rightarrow \delta Q = m C_p dT$$
- Constant Volume ($v=c$):**

$$C_v = \frac{1}{m} \frac{\delta Q}{dT} \Rightarrow \delta Q = m C_v dT$$
- First Law of Thermodynamics:**

$$dE = \delta Q - \delta W$$
- Internal Energy Change:**

$$\Delta U = \Delta E = Q - W$$
- Enthalpy Change:**

$$H = U + pV$$

$$dH = dU + p dV + V dp$$
- Relationship between C_p and C_v :**

$$C_p - C_v = \frac{1}{m} \frac{dH}{dT} \Big|_{p=c} - \frac{1}{m} \frac{dU}{dT} \Big|_{v=c}$$

Mathematically, $C_p = \frac{1}{m} \frac{Q}{\Delta T}$ and $C_v = \frac{1}{m} \frac{Q}{\Delta T}$, where m is the mass of the substance, Q is the amount of heat transferred and ΔT is the quantity by which the temperature is raised.

Let's look at C_v in detail.

Consider a stationary rigid container which contains some gas. Transfer some amount of heat Q to the container. There is no work interaction here (there is no electrical work, magnetic work, surface tension work, etc.). The first law in the integrated form is

$\Delta E = Q - W$. The system is not moving or getting lifted. Hence, changes in kinetic and potential energy are zero. Thus, $\Delta U = Q$ which can also be written as $m\Delta u = Q$, where m is the mass of the system content and u is the specific internal energy. We know that $Q = mC_v\Delta T$. Hence, $\Delta u = C_v\Delta T$ which implies $C_v = \frac{\Delta u}{\Delta T} = \frac{1}{m} \frac{\Delta U}{\Delta T}$. In the differential form, $C_v = \frac{du}{dT} = \frac{1}{m} \frac{dU}{dT}$ at $V = \text{constant}$.

Let's look at C_p in detail.

Consider a frictionless piston-cylinder arrangement (which is the system under consideration). Heat Q is transferred to the system. The system undergoes a constant pressure process and the piston moves. Hence, there is work interaction. The first law in the integrated form for this system is $\Delta U = Q - W$ (there are no changes in kinetic and potential energy). Now, $m\Delta u = Q - W$. In the differential form, $mdu = \delta Q - \delta W = \delta Q - pdV = mC_p dT - mpdv$ ($V = mv$ and m is constant, it can be taken out). Cancelling out m , $C_p dT = \delta q = du + pdv = du + pdv + vdp$ (adding dp doesn't change anything as $dp=0$ as it is a constant pressure process). Now, $C_p dT = \delta q = du + d(pv) = d(u + pv) = dh$, where h is specific enthalpy. Hence, $C_p = \frac{dh}{dT} = \frac{1}{m} \frac{dH}{dT}$. We had defined earlier that $C_p = \frac{1}{m} \frac{Q}{\Delta T}$. For a constant pressure process as in the case of the frictionless piston-cylinder system above, $Q = \Delta H$. Hence, $C_p = \frac{1}{m} \frac{\Delta H}{\Delta T}$.