Temperature Dependence:

Heat Capacities:

The temperature dependence of Internal Energy U and Enthalpy H can be related to heat capacities Cv and Cp.

The heat capacities are defined, and experimentally determined as the energy that must be supplied from the thermal surroundings to increase the temperature of the system by 1°C, under specified conditions.

OR

Heat capacity is the heat that must be supplied to raise the temperature by 1°C.

The two common conditions are

1. Constant Volume: The symbol for heat capacity at constant volume is Cv.

2. Constant Pressure: The symbol for heat capacity at constant pressure is Cp.

Their molar quantities are represented as Cv and Cp i.e. the thermal energy that must be supplied to increase the temperature of 1 mol of sample which contains 1 mol of specified particles by 1°C.

The molar heat-capacity values for both constant volume and constant pressure are given as follow:
Heat Capacities and Internal Energy and Enthalpy;

Heat capacities are defined and measured in terms of energy supplied by the thermal surroundings.

Then measurement of heat capacity at constant volume is given as

\[ C_v = - \left( \frac{dU_{\text{therm}}}{dT} \right) \quad \text{(const V)} \]

For constant-volume processes:

\[ dU = -dU_{\text{therm}} \]

Then we can write the value of \( C_v \) is equal to derivative,

\[ C_v = \left( \frac{\partial U}{\partial T} \right)_V \]
Then measurement of heat capacity at constant pressure is given as

\[ C_p = -\left( \frac{dU_{\text{therm}}}{dT} \right) \quad \text{(const P)} \]

For constant-pressure processes:

\[ dH = -dU_{\text{therm}} \]

Then we can write the value of \( C_v \) is equal to derivative,

\[ C_p = \left( \frac{\partial H}{\partial T} \right)_P \]

Thus, the heat capacities show how the internal energy and enthalpy change with temperature when the volume or pressure of the system is suitable controlled.

**Cp -Cv for an Ideal Gas:**

Consider an ideal gas in the piston-and-cylinder device as shown in the following figure:

Refer to Fig. 3.6
If the piston position is fixed so that the volume remains constant, the energy required to raise the temperature by 1°C or 1 K is equal to \( C_v \).

Now, how much more energy is required to raise the temperature if the pressure on the gas kept constant and no the volume.

So, at constant pressure, gas expands, and volume changes.

For ideal gas

\[
PV = nRT
\]

\[
V = \frac{nRT}{P}
\]

Thus, the volume of gas changes

From \( V = \frac{nRT}{P} \)

To \( V = \frac{nR(T+1)}{P} \)

Therefore

\[
\Delta V = \left[ \frac{nR(T+1)}{P} \right] - \left[ \frac{nRT}{P} \right]
\]

\[
\Delta V = \frac{nR}{P}
\]

\[
P \Delta V = nR\]
Thus, when pressure is $P$ is kept constant, and temperature is increased by $1^\circ C$, then the gas expands and an extra amount of energy equal to $nR$ must be supplied by the thermal surroundings.

Therefore, for ideal-gas

$$C_p - C_v = nR$$

OR

$$C_p - C_v = R$$

**Temperature Dependence of Heat Capacities:**

Heat capacities at constant pressure $C_p$ will be used more than heat capacities at constant volume $C_v$.

Molar heat capacities at constant pressure are measured over a range of temperature and following two empirical equations have been arrived at.

$$C_p = a' + b'T + c'T^2 + \ldots$$

And

$$C_p = a + bT + c/T^2 + \ldots$$

The second equation of these two forms is more satisfactory. The values of coefficients $a$, $b$, $c$ are given in following table.
Problem 1:

When 10-g lead slug is taken from a beaker of boiling water and dropped into a beaker containing 100g of ice-temperature water, the temperature of this 0°C water rises by 0.310°C. What does this study tell us about the molar heat capacity of lead? Specific heat capacity of water = 4.184 J g⁻¹°C.

Energy gained by water = \(\Delta U_{\text{therm}} = c \times m \times \Delta T\)

Where \(c\) = specific heat capacity for water, \(m\) = mass, \(\Delta T\) = difference in temperature.

\[
= (4.184 \text{ J g}^{-1}\text{C}) (100 \text{ g}) (0.310\text{C})
\]

\[
= 130 \text{ J}
\]

Energy lost by Lead = \(n_{\text{pb}} \times C_{\text{p}} \times \Delta T\)

For 10g lead slug

\[
n_{\text{pb}} = \frac{10 \text{ g}}{(207.2 \text{ g mol}^{-1})} = 0.048 \text{ mol of lead atoms}
\]

\(\Delta T\) (for lead) = 99.7°C
By equating the energy gained by water with that of energy lost by hot lead

We have,

\[ 130 \, \text{J} = n_{\text{pb}} \times \text{C}_p \times \Delta T \]

\[ 130 \, \text{J} = 0.048 \, \text{mol} \times \text{C}_p \times 99.7^\circ \text{C} \]

\[ \text{C}_p = 27 \, \text{J} \, ^\circ \text{C}^{-1} \, \text{mol}^{-1} \]

Problem 2:

Calculate the value of \( \text{C}_p \) at 0, 50, and 100\(^\circ\)C. \( a = 22.13, \, b = 11.72 \times 10^3, \, c = 0.96 \times 10^{-5} \).

\[ \text{C}_p, \, \text{J} \, \text{K}^{-1} \, \text{mol}^{-1} = a + bT + c / T^2 \]

\[ = 22.13 + 11.72 \times 10^3 \times T + 0.96 \times 10^{-5} / T^2 \]

At 0\(^\circ\)C (273 K)
\[ \text{C}_p = 22.13 + 3.20 + 1.29 = 26.62 \]

At 50\(^\circ\)C (323 K)
\[ \text{C}_p = 22.13 + 3.79 + 0.92 = 26.84 \]

At 100\(^\circ\)C (373 K)
\[ \text{C}_p = 22.13 + 4.37 + 0.69 = 27.19 \]