Lecture #4

Difference between C$_p$ and C$_v$

In order to find this relation, we write the first law equation;

$$dE = dQ - P'\,dV$$

and the equation giving dE in terms of the properties of the system;

$$dE = C_v dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

Combining these two equations, we may write;

$$dQ - P'\,dV = C_v dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

Since we want C$_p$ in this equation, we may assume P=constant, so P'=P

$$\partial Q_p = C_V (\partial T)_P + \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right](\partial V)_P$$

Dividing both sides by $(\partial T)_P$, we obtain;

$$C_p = C_v + \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

Since each term on the right-hand side of this equation is positive, the difference between the two heat capacities is positive. This result indicates that C$_p$ > C$_v$.

The difference between the two heat capacities arises from the fact that at constant pressure system produces work in the surroundings by expanding. Whereas, at constant volume no work is produced. Therefore, the heat absorbed at constant

volume goes into the motion of the molecules. Their kinetic energy increases and this increase is reflected by a temperature increase.

In constant pressure case, the heat absorbed is divided into three portions;

- **1st Portion:** is spent to separate the molecules to larger distances against intermolecular attractive forces. The amount of this energy is;

$$\left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

- **2nd Portion:** produces work in the surroundings which is;

$$P\left(\frac{\partial V}{\partial T}\right)_P$$

- **3rd Portion:** increases the kinetic energy of the molecules and the temperature as well.

According to Joule's rule, for an ideal gas;

$$\left(\frac{\partial E}{\partial V}\right)_T = 0$$

Therefore the difference between molar heat capacities is;

$$\overline{C}_p - \overline{C}_v = P\left(\frac{\partial V}{\partial T}\right)_P = P\frac{R}{P} = R$$

Heat capacity ratio is defined as C_p / C_v and designated by γ. Since C_p is always greater than C_v, $\gamma > 1.0$.

Adiabatic Processes

In adiabatic processes, there is no heat flow. So, dQ = 0. Then, the first law equation takes the form;

$$dE = -dW = -P'dV$$

If the system produces work in the surroundings, its internal energy decreases. This is reflected by a decrease in temperature. Such processes are called **"adiabatic cooling".** Conversely, if work is destroyed in the surroundings, the system gains energy and its temperature increases.

According to the above equation, volume and internal energy change in opposite directions.

- If the system expands;

  $\Delta V > 0$ so $\Delta E < 0$ and $\Delta T < 0$

- If the system is compressed;

  $\Delta V < 0$ so $\Delta E > 0$ and $\Delta T > 0$

Adiabatic Reversible Processes for an Ideal Gas

For an ideal gas;

$$dE = C_v dT$$

Substituting this equation in the first law equation we obtain;

$$C_v dT = -P'dV$$

For a reversible process, P'=P. Therefore, the equation takes the form;

$$C_v dT = -PdV$$

By using the ideal gas law, P may be expressed in terms of V;

$$\overline{C}_v \frac{dT}{T} = -R \frac{dV}{V}$$

Integrating between the initial and final states, we obtain;

$$\int_{T_1}^{T_2} \overline{C}_v \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\overline{C}_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

For an ideal gas, $\overline{C}_p - \overline{C}_V = R$. By dividing both sides of these equations by $\overline{C}_v$ we may write ;

$$\frac{\overline{C}_p}{\overline{C}_v} - 1 = \frac{R}{\overline{C}_v} \qquad\qquad \text{or} \qquad\qquad \gamma - 1 = \frac{R}{\overline{C}_v}$$

$$\ln \frac{T_2}{T_1} = -\frac{R}{\overline{C}_v} \ln \frac{V_2}{V_1} = -(\gamma - 1) \ln \frac{V_2}{V_1}$$

By taking the antilogarithm of both sides, we obtain;

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1} \right)^{-(\gamma-1)} = \left(\frac{V_1}{V_2} \right)^{(\gamma-1)}$$

$$T_1 V_1^{(\lambda-1)} = T_2 V_2^{(\gamma-1)} \qquad\qquad \text{or} \qquad\qquad TV^{(\gamma-1)} = cons \tan t$$

By using the ideal gas law, this equation may be transformed into a form in terms of T and P;

$$\overline{V} = \frac{RT}{P}$$

$$T_1 \left(\frac{RT_1}{P_1} \right)^{(\gamma-1)} = T_2 \left(\frac{RT_2}{P_2} \right)^{(\gamma-1)}$$

$$T_1{}^\gamma P_1{}^{(1-\gamma)} = T_2{}^\gamma P_2{}^{(1-\gamma)}$$

and

$$P\overline{V} = RT \qquad\qquad T^\gamma = \frac{P^\gamma V^\gamma}{R^\gamma}$$

$$P_1{}^\gamma V_1{}^\gamma P_1{}^{(1-\gamma)} = P_2{}^\gamma V_2{}^\gamma P_2{}^{(1-\gamma)}$$

$$P_1 V_1{}^\gamma = P_2 V_2{}^\gamma$$

This may be written as;

$$PV^\gamma = cons\tan t$$