
Lecture #3**Internal Energy in terms of Properties**

Internal energy is a state function. A change in the state of the system causes a change in its properties. So, we express the change in internal energy in terms of the changes in its properties.

Internal energy is a function of temperature and volume of the system.

$$E = E(T, V)$$

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

This equation indicates that if the temperature of the system increases by an amount dT and the volume increases by an amount dV then the total increase in energy is the sum of two contributions.

- $\left(\frac{\partial E}{\partial T}\right)_V$: rate of increase in E with temperature at constant volume
- $\left(\frac{\partial E}{\partial V}\right)_T$: rate of increase in E with volume at constant temperature

In order to calculate dE we must express these partial derivatives in terms of measurable quantities.

Constant Volume Processes

By using the first law equation, it may be written;

$$dQ - P' dV = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

At constant volume $dV=0$

$$dQ_v = \left(\frac{\partial E}{\partial T}\right)_v dT$$

$$\left(\frac{\partial E}{\partial T}\right)_v = \frac{dQ_v}{dT}$$

Heat absorbed per degree rise in temperature is the constant volume heat capacity C_v . C_v is defined as the change in internal energy with temperature at constant volume.

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v$$

Using the definition of C_v we can write;

$$dE = C_v dT$$

or integrating we have

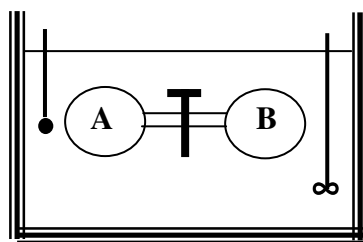
$$\Delta E = \int_{T_1}^{T_2} C_v dT$$

Internal energy is an extensive property, so C_v is also an extensive property. Generally, molar heat capacity \bar{C}_v is used. If C_v is constant in the temperature range investigated, the change in internal energy can be calculated as;

$$\Delta E = C_v \Delta T$$

Joule's Rule

The identification of the second partial derivative is not so easily managed. For



$$T_1 = T_2$$

gases it can be done by an experiment devised by Joule. In this experiment, two containers are connected through a stopcock. In the initial state, A is filled with a gas while B is evacuated. The apparatus is immersed in a water bath and is allowed to equilibrate with water at T . The water is continuously stirred. The initial temperature is read on the thermometer. Then, the stopcock is opened and the gas expands to fill B. After allowing time for the system to come to thermal equilibrium, the temperature is read again. It was observed that there is no temperature change.

In this experiment, no work is produced in the surroundings. Since B is evacuated $P' = 0$. There is no opposing force against the expanding gas. This is called "**free-expansion**". First law equation takes the form;

$$dE = dQ$$

Since the temperature does not change $dQ = 0$, then $dE = 0$.

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

In the experiment $dV \neq 0$, so;

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

The energy is independent of the volume. **Joule's rule** states that the internal energy of an ideal gas is a function only of temperature.

Joule's rule is not correct for real gases. For real gases, it is greater than zero. For liquids and solids, the volume change is very small. Even though the value of the

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

derivative is very large, the value of ΔV is so small that the product is very nearly zero. Therefore, the internal energy of all substances is considered to be a function only of T.

Constant Pressure Processes

Most of the experiments are carried out in the laboratory at constant pressure. At equilibrium, the external pressure is equal to the pressure of the system. For constant pressure processes, the first law equation may be written as;

$$dE = dQ_p - PdV$$

Since P is constant, the integration gives;

$$\int_1^2 dE = \int_1^2 dQ_p - \int_1^2 PdV$$

$$E_2 - E_1 = Q_p - P(V_2 - V_1)$$

Rearranging, we obtain;

$$(E_2 + PV_2) - (E_1 + PV_1) = Q_p$$

P and V are properties of the system. E is a state function. So, the function (E + PV) is itself a state function. It depends upon the state of the system. This function is called "**enthalpy**" and designated by **H**. Enthalpy is defined as;

$$H = E + PV$$

Enthalpy is an extensive property. By using the definition of enthalpy, we can rewrite Q_p as;

$$H_2 - H_1 = Q_p \quad \text{or} \quad \Delta H = Q_p$$

This equation indicates that in constant pressure processes heat absorbed by the system is equal to the increase in its enthalpy.

For an infinitesimal change;

$$dH = dQ_p$$

Since H is a state function, dH is an exact differential. H is a function of T and P.

Total differential of H may be written as;

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

For a constant pressure process $dP = 0$ and $dH = dQ_p$;

$$dQ_p = \left(\frac{\partial H}{\partial T} \right)_P dT$$

dQ_p/dT is the amount of heat absorbed per degree rise in temperature. It is the constant pressure heat capacity C_p . So, the definition of C_p may be written as;

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

Therefore the total differential of H takes the form;

$$dH = C_p dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

For constant pressure processes;

$$dH = C_p dT$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

If C_p is constant in the temperature range;

$$\Delta H = C_p \Delta T$$

Enthalpy Change with Pressure

Definition of H is;

$$H = E + PV$$

Differentiating we obtain;

$$dH = dE + PdV + VdP$$

We can write dH and dE in terms of the properties of the system;

$$dH = C_p dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

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

Substituting these equations in dH equation we obtain;

$$C_p dT + \left(\frac{\partial H}{\partial P} \right)_T dP = C_v dT + \left(\frac{\partial E}{\partial V} \right)_T dV + PdV + VdP$$

We are calculating the change in enthalpy with pressure at constant temperature. So, $dT = 0$.

$$\left(\frac{\partial H}{\partial P} \right)_T dP = \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] dV + VdP$$

Dividing both sides by dP we obtain;

$$\left(\frac{\partial H}{\partial P}\right)_T dP = \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial P}\right)_T + V$$

Since **solids and liquids** are incompressible phases, their volume does not change much with pressure. Therefore, the first term in the above expression is negligible.

$$\left(\frac{\partial H}{\partial P}\right)_T = V$$

Moreover, molar volume of solids and liquids is very small. If the pressure change is not too large, the change in enthalpy with pressure can be ignored.

For **ideal gases**,

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

Substituting this equation into the definition of enthalpy we obtain;

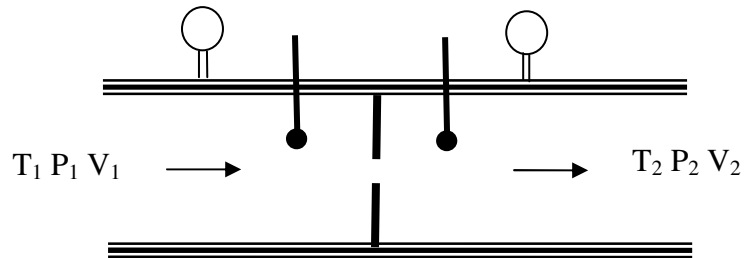
$$\bar{H} = \bar{E} + P\bar{V} = \bar{E} + RT$$

Since the internal energy is a function only of temperature, H for an ideal gas is also a function only of temperature.

For a **real gas**, enthalpy is a function of both temperature and pressure.

Joule-Thomson Experiment

For a real gas, $(\partial H / \partial P)_T$ can be measured by Joule-Thomson experiment. In this experiment, an insulated pipe is used. There is an obstruction in the middle of the pipe with a hole on it. Gas flows in the direction of the arrows. Gauges and thermometers are placed in the pipe to measure the changes in T and P.



Due to the presence of the obstruction, the pressure of the gas decreases in passing from left to right. If one mole of gas passes from left to right, the gas in the left-hand side produces work equal to $P_1\bar{V}_1$ while the gas in the right-hand side gains energy equal to $P_2\bar{V}_2$. The mole of gas is pushed by the gas behind in the left side, while it pushes the gas ahead in the right side. Since the pipe is insulated $Q = 0$.

$$W = -P_1\bar{V}_1 + P_2\bar{V}_2$$

$$\Delta E = P_1\bar{V}_1 - P_2\bar{V}_2$$

$$\bar{E}_2 - \bar{E}_1 = P_1\bar{V}_1 - P_2\bar{V}_2$$

$$\bar{E}_2 + P_2\bar{V}_2 = \bar{E}_1 + P_1\bar{V}_1$$

$$\bar{H}_2 = \bar{H}_1$$

In Joule-Thomson experiment, enthalpy remains constant, so $dH = 0$.

$$0 = C_p dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

$$\frac{dT}{dP} = \left(\frac{\Delta T}{\Delta P} \right)_H$$

The limit of this ratio is known as "**Joule-Thomson Coefficient**" and designated by μ .

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H$$

Substituting into the above equation we obtain;

$$\left(\frac{\partial H}{\partial P} \right)_T = -C_p \mu_{JT}$$

μ_{JT} changes sign at Joule-Thomson inversion temperature. Above this temperature $\mu_{JT} < 0$, below it is positive. For all gases except H_2 and He, T_{JT} is above room temperature. Gas pressure and gas temperature change in the same direction. So, if the pressure of the gas is decreased, its temperature also decreases.