

First Law of Thermodynamics

4. Laws of Thermodynamics

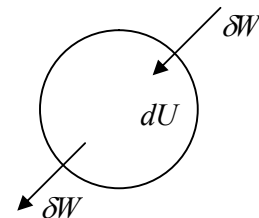
Zerth Law of Thermodynamics: If two systems 1 and 2 are separately in thermal equilibrium with third 3 they must be in thermal equilibrium with one another.

First Law of Thermodynamics: Energy is conserved when heat is taken into account.

Mathematically If δQ amount of heated to the system and if system will do δW amount of work then change in internal energy is dU given by

$$dU = \delta Q - \delta W$$

obviously heat exchange and work is dependent on path and internal energy is state function.



U is a mathematical abstraction that keeps account of the exchange of energy that be fall the system.

The term δQ means the amount of that amount of energy added to or remove by conduction of heat or by thermal radiation.

δW is amount of energy gained or lost as result of work.

Work Done during Different Process.

Work done when process is occur to between A to B

$$W = \int_A^B PdV$$

work done is area under the PV diagram.

If work is done by the system it has positive sign, and if work is done on the system it has negative sign.

Specific Heat: Heat capacity of a body is numerically equal to quantity of heat required to raise its temperature by 1 unit.

$$C = \frac{\Delta\theta}{\Delta T}$$

The specific heat of a material is numerically equal to quantity of heat required to raise the temperature of unit mass of that materials through 1unit

$$C = \frac{d\theta}{mdT}$$

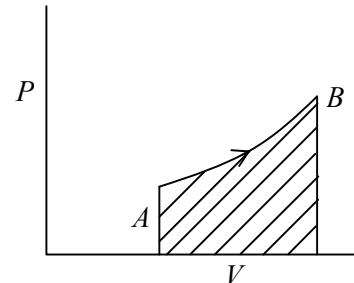
Heat Capacity of Ideal Gas: if f is degree of freedom of Ideal gas then from equipartition of energy total sum of energy is equivalent to sum of kinetic energy associated with each degree of freedom

Molar Heat Capacity: heat capacity defined as the energy required to raise the temperature of one mole of Ideal gas by one Kelvin at constant volume.

$$U = \frac{f}{2} N_A K T \text{ where } N_A \text{ is Avogadro number}$$

$$\frac{dU}{dT} = \frac{f}{2} N_A K = \frac{fR}{2}$$

$$C_V = \frac{Rf}{2}, \quad \text{for Ideal gas}$$



$$C_p = C_v + R = R\left(\frac{f}{2} + 1\right)$$

γ is defined as ratio of heat capacity at constant pressure to constant volume.

$$\gamma = \frac{C_p}{C_v} = \left(1 + \frac{2}{f}\right)$$

Coefficient of Volume Expansion: (α) or expansivity $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

Isothermal Elasticity: $E_T = -V\left(\frac{\partial P}{\partial V}\right)_T$ and **Isothermal compressibility** $\beta_T = \frac{1}{E_T}$

Example: Find the isothermal compressibility α of a Van der Waals gas as a function of volume V at temperature T .

Note: By definition, $\alpha = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$.

Solution: We know bulk modulus of a gas is given by

$$\text{Van der Waals equation: } \left(P + \frac{a}{V^2}\right)(V - b) = RT \quad (i)$$

If process is isothermal: $T = \text{constant}$

$$\left(dP + \frac{-a}{V^3}dV\right)(V - b) + \left(P + \frac{a}{V^2}\right)(dV) = 0$$

$$\left(\frac{dP}{dV} - \frac{a}{V^3}\right)(V - b) + \left(P + \frac{a}{V^2}\right) = 0$$

$$\frac{dP}{dV} = -\frac{\left(P + \frac{a}{V^2}\right)}{(V - b)} + \frac{a}{V^3} = \frac{-\left(PV^3 + aV\right) + a(V - b)}{V^3(V - b)}$$

$$\alpha = -\frac{1}{V}\left[\frac{V^3(V - b)}{\left(-PV^3 + aV\right) + a(V - b)}\right] = \frac{V^2(V - b)}{\left[\left(PV^3 - aV\right) + a(b - V)\right]} \quad (ii)$$

Put values of P from (i) in (ii)

$$\alpha = \frac{V^2(V - b)}{\left[RTV^3 - 2a(V - b)^2\right]}$$