



Constant-Volume Process

for closed system, constant volume

$$\Delta U^1 = Q + W \qquad \text{1st law}$$

$$d(nU) = dQ + dW$$

since volume is constant, $dW = 0$

$$dQ = d(nU)$$

$$Q = n\Delta U$$

given heat \Rightarrow increase in *internal energy*

Thus for a mechanically reversible, constant-volume, closed-system process, the heat transferred is equal to the internal-energy change of the system.

for 1-component, 1-phase system

degree of freedom, $F = 2 - 1 + 1 = 2$

$$U = f^n(T, V) \quad \text{or} \quad U = U(T, V)$$

Thus,

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

C_V 0, for const V



Constant-Pressure Process

for closed system, constant pressure

$$\Delta U^t = Q + W \quad \text{1st law}$$

$$d(nU) = dQ + dW$$

since pressure is constant, $dW = - PdV^t = - Pd(nV)$

$$dQ = d(nU) + Pd(nV)$$

$$Q = n\Delta H$$

given heat \Rightarrow increase in *enthalpy*

the appearance of (U +PV) group suggests as a new thermodynamic property define enthalpy .Thus for a mechanically reversible, constant-pressure, closed-system process, the heat transferred equals the enthalpy change of the system.

for 1-component, 1-phase system

degree of freedom, $F = 2 - 1 + 1 = 2$

$$H = f^n(T,P) \quad \text{or} \quad H = H(T,P)$$

Thus,

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

C_P 0, for const P



ENTHALPY

Enthalpy is explicitly defined for any system by mathematical expression

$$H \equiv U + PV$$

It appears in energy balances for flow processes as applied to heat exchangers, evaporators, distillation columns, pumps, compressors, turbines, engines, etc., for calculation of heat and work. All terms of enthalpy equation must be expressed in the same units. The product $P V$ has units of energy per mole or per unit mass, as does U ; therefore H also has units of energy per mole or per unit mass. In the SI system the basic unit of pressure is the Pascal or N m^{-2} and, for molar volume, $\text{m}^3 \text{mol}^{-1}$.

Since U , P , and V are all state functions, H as defined by equation is also a state function. The differential form

$$dH = dU + d(PV)$$

Integration gives :

$$\Delta H = \Delta U + \Delta(PV)$$

The above equation may be written for any amount of material, though they are often applied to unit of mass or to a mole.

Example

Calculate ΔU and ΔH for 1Kg water vaporized at constant temperature and pressure (100°C , 101.33 KPa) the specific volumes of liquid and vapor water at these conditions are 0.00104 and $1.673 \text{ m}^3 \text{ kg}^{-1}$, for this change, heat in the amount of $2,256.9 \text{ kJ}$ is added to water.

$$W = P\Delta V = 101.33 \text{ kPa} \times (1.673 - 0.001) \text{ m}^3 = 169.4 \text{ kJ}$$

$$\Delta U = Q - W$$

$$2,256.9 - 169.4 = 2,087.5 \text{ kJ}$$

$$\text{With } P \text{ constant: } \Delta H = \Delta U + P\Delta V$$

$$\text{But } P\Delta V = W$$

$$\Delta H = \Delta U + W = Q = 2,2256.9 \text{ kJ}$$

HEAT CAPACITY

This is the origin of the idea that a body has a capacity for heat, in other words

Heat Capacity connects heat with temperature

$$C = \frac{dQ}{dT}$$



Heat Capacity at Constant Volume

The constant-volume heat capacity is defined as:

$$C_v \equiv \left(\frac{dU}{dT} \right)_v$$

This definition accommodates both the molar heat capacity and the specific heat capacity (usually called specific heat), depending on whether U is the molar or specific internal energy. Although this definition makes no reference to any process, it relates in an especially simple way to a constant-volume process in a closed system

$$dU = \int_{T_1}^{T_2} C_v dT \quad \text{constant volume}$$

Integration yields: $\Delta U = \int_{T_1}^{T_2} C_v dT$

For constant volume process $Q = n \Delta U$

$$\therefore Q = n \int_{T_1}^{T_2} C_v dT$$

Heat Capacity at Constant Pressure

The constant-volume heat capacity is defined as:

$$C_p \equiv \left(\frac{dU}{dT} \right)_p$$

This heat capacity relates in an especially simple way to a constant-pressure, closed-system process, $dH = C_p dT$

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

For a mechanically reversible, constant-pressure process, $Q = n \Delta H$

$$\therefore Q = n \int_{T_1}^{T_2} C_p dT$$