Internal energy and enthalpy

The total energy of a system is conserved. (First law)

Total energy = internal energy + mechanical energy

$$= \quad U \quad + \tfrac{1}{2} m v^2 + m g z$$

In a stationary system $E_{kin} = 0$ and $E_{pot} = \text{const.}$

$\Rightarrow$ Internal energy is conserved

Fundamental thermodynamic relation

$$dU = T\,dS - p\,dV$$

U = internal energy $\left[\frac{ML^2}{T^2}\right]$ ie, Joule

S = entropy $\left[\frac{ML^2}{T^2\Theta}\right]$

naturally $U = U(S,V)$

$\Rightarrow$ simple to consider isochoric ($dV = 0$) or isenthalpic ($dS = 0$) processes

In an incompressible system $dV = 0$

$$dU_v = T\,dS$$

If $S = S(T,p)$: $dS = \frac{\partial S}{\partial T}\Big|_p dT + \frac{\partial S}{\partial p}\Big|_T dp$

$$dU_v = T\frac{\partial S}{\partial T}\Big|_p dT + T\frac{\partial S}{\partial p}\Big|_T dp$$

- Introduce material properties:

  Heat capacity at const. pressure: $C_p = T\frac{\partial S}{\partial T}\Big|_p$

  Coefficient of thermal expansion: $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\Big|_p$

- Maxwell relation: $\frac{\partial S}{\partial p}\Big|_T = -\frac{\partial V}{\partial T}\Big|_p \Rightarrow \frac{\partial S}{\partial p}\Big|_T = -\alpha V$

$$\Rightarrow \boxed{dU_v = C_p\,dT - \alpha V T\,dp}$$

Change in internal energy with p and T at const. volume

If p is held constant in adition to V.

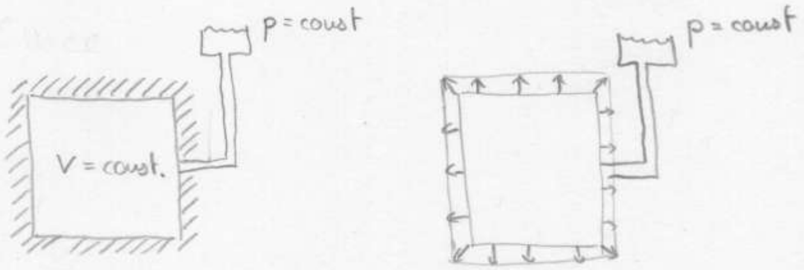
$$\boxed{dU_{V,p} = C_p \, dT}$$

This is identical to the change in Enthalpy at const. p.

$H = U - pV$ Internal energy plus pressure-volume work

$dH = dU - Vdp - pdV = TdS + Vdp$

if $dp = 0$ $\boxed{dH_p = dU_{V,p} = C_p \, dT}$



$dU = C_p \, dT$ $dH = C_p \, dT$

The justification for $C_p dT$ comes from conservation of internal energy of a incompressible material at const. pressure. Typically $C_p dT$ is interpreted as an isobaric enthalpy/heat change.

Since we are interested in melting/freezing which is discussed in enthalpy chanes (latent heat) we discuss energy conservation in terms of enthalpy below.