Lecture 5, Sep 19, 2022

Enthalpy

- Consider a hot water tank
  - To do work with it, we can transfer heat to expand a gas, doing work
    * The amount of work depends on the internal energy
  - We can also use the water's pressure
    * If we open the bottom of the tank, we can get more work than if we open the top of the tank
    * The amount of work depends on the pressure
- The ability to do work by a system depends on its pressure and internal energy
- Consider a bit of water coming out of the tank with volume V, mass m, pressure P, area A, moving by a distance L
  - The force exerted by the system to push the liquid out is $F = PA$, so work done is PLA
  - This is called the *flow work* $W_{flow} = pV$
  - The flow work per unit mass is $w_{flow} = \frac{W_{flow}}{m} = \frac{PV}{m} = Pv$ where v is the specific volume
  - The flow carries $u + pv$ where u is the internal energy per unit mass of the water

Definition

Enthalpy $H = U + PV$, is a measure of the potential to do work

- Enthalpy is an extensive property with units of Joules
- Define the specific enthalpy $h = \frac{H}{m}$, an intensive property
- For an ideal gas u is a function of T only, so in this case $h = u + Pv = u + RT$ is a function of T only
- Consider rate of mass $\dot{m}_1$ entering the system and $\dot{m}_2$ exiting the system
  - Rate of energy entering the system is $\dot{m}_1(u_1 + P_1v_1)$
  - Rate of energy exiting the system is $\dot{m}_2(u_2 + P_2v_2)$
- Consider an isovolumetric process; add heat δQ to a system resulting in $\mathrm{d}U$
  - Since this is a constant volume process $\delta w = 0$, so $\delta Q = \mathrm{d}U$, the heat added is directly added to internal energy
- Consider an isobaric process; add heat δQ
  - The system is allowed to expand, so it does work $\delta W = -P\,\mathrm{d}V$
  - Part of the energy put in becomes work
  - $\delta Q + \delta W = \mathrm{d}U \implies \delta Q = \mathrm{d}U + P\,\mathrm{d}V$
  - Note $H = U + PV \implies \mathrm{d}H = \mathrm{d}U + P\,\mathrm{d}V + V\,\mathrm{d}P = \mathrm{d}U + P\,\mathrm{d}V$ for a constant pressure process
  - For an isobaric process the heat added is equal to the change in enthalpy

Specific Heats

- Add heat Q to a mass m, resulting in ΔT, then the specific heat $c_{avg} = \frac{Q}{m\Delta T} = \frac{q}{\Delta T}$
- The relationship between q and ΔT is not necessarily linear, so $c(T)$ is a function of temperature

Definition

The specific heat $c(t) = \frac{\delta q}{\mathrm{d}T}$

- Consider heating a system at constant volume ($\delta q = \mathrm{d}u$)
  - Define the specific heat at constant volume $c_v = \left(\frac{\partial u}{\partial T}\right)_V$
- Define the specific heat at constant pressure $c_p = \left(\frac{\partial h}{\partial T}\right)_P$

- For an ideal gas, we can write these as total derivatives since h and u are functions of T only
- Note $h = u + RT \implies \frac{\mathrm{d}h}{\mathrm{d}T} = \frac{\mathrm{d}u}{\mathrm{d}T} + R \implies c_p = c_v + R$

Important

For an ideal gas, $c_p = c_v + R$

Definition

The specific heat ratio $\gamma = \frac{c_p}{c_v}$

- Assume c_p, c_v are constants, then $\Delta u = c_v \Delta T, \Delta h = c_p \Delta T$
  - Use T_{avg} to look up values of c_p, c_v
  - If we don't know T_2, we can guess T_2, calculate T_{avg} then iterate guess for T_2
- Liquids and solids are incompressible, so $c_p = c_v = c = \frac{\mathrm{d}u}{\mathrm{d}T}$
  - In this case $\mathrm{d}h = \mathrm{d}u + v\,\mathrm{d}P$
  - $\mathrm{d}u = c\,\mathrm{d}T$
  - $\Delta h = \int_{T_1}^{T_2} c\,\mathrm{d}T + \int_{P_1}^{P_2} v\,\mathrm{d}P$, where c and v are both constants
- For incompressible substances enthalpy can be increased by adding heat or increasing the pressure
- If the process is neither isobaric nor isovolumetric:
  - $\Delta u = c_v(T_2 - T_1)$
  - $\Delta h = c_p(T_2 - T_1)$
  - u and h are properties that are path independent, so even if the process is neither isobaric nor isovolumetric, we can equate it to them