Auxiliary TD Functions

- Now formally introduce a set of TD properties that are *sufficient* for the development of chemical thermodynamics (and most other thermodynamic considerations)
  - T, p, v (or V) : readily measureable
  - U, S (or u, s) : less directly measureable

also have physical interpretations

- Also, can be *convenient* to use following TD properties
  - **Enthalpy** $H \equiv U + pV$ $h=u+pv$
  - **Gibbs Free Energy** (or Gibbs Function) $G \equiv H - TS$ $g=h-Ts$
  - **Helmholtz Free Energy** (or Helmholtz Function) $F \equiv U - TS$ $f=u-Ts$

Extensive *intensive*

Properties of Enthalpy

- Consider substance undergoing change of state 1→2
- From H defn. $\Delta H = H_2 - H_1 = \underbrace{U_2 - U_1}_{=\Delta U_{12}} + p_2V_2 - p_1V_1$
- For a closed system (control mass)
  - 1st Law: $\Delta U_{12} = Q_{12} + W_{12}$
    $\Rightarrow \Delta H_{12} = Q_{12} + W_{12} + p_2V_2 - p_1V_1$

a. constant p process and only $\underline{p\,dV \text{ work}}$ $W_{12} = -\int p\,dV = -p\,(V_2 - V_1)$

$\boxed{\Delta H_{12} = Q}$ *Q for isobaric CM, no other work given by ΔH*

compare to

b. constant V process and only $\underline{p\,dV \text{ work}}$ (=0)

$\boxed{\Delta U_{12} = Q}$ *Q for no work CM, given by ΔU*

c. isolated system

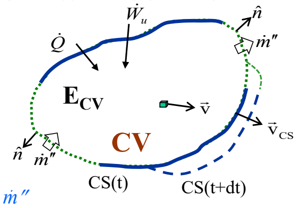
e.g., chem. rxn. in rigid, adiabatic vessel

$\Rightarrow \Delta U=0,\ \Delta V=0,\ Q=W=0$ $\boxed{\Delta H_{12} = V\underbrace{(p_2 - p_1)}_{=\Delta p_{12}}}$

enthapy not "conserved" in isolated system

Useful Work for Flowing Systems

- For flow systems, convenient to work with **control volume CV** (open system)
- For general CV (shape changing, accelerating) can write 1st Law as



e=u+mv²/2

$$\overbrace{\dot Q + \dot W_u + \dot W_{boundary} + \dot W_{body}}^{\textit{all defined as positive into CV}} = \overbrace{\frac{d}{dt}\int_{CV}\rho e\,dV}^{dE_{CV}/dt} + \int_{CS} e\overbrace{\left(\rho\vec v_{rel}\cdot\hat n\right)}^{\dot m''}dA$$

v_{rel}=vel. of mass crossing CS relative to CS

energy transfer rate into CV from $Q + W$ | **rate of change of energy inside CV** | **net rate energy flows out of CV carried by mass**

– **if** no body forces, no viscous forces, CV shape fixed

$$\dot Q + \dot W_u - \int_{CS} p\left(\vec v\cdot\hat n\right)dA = \frac{d}{dt}\int_{CV}\rho e\,dV + \int_{CS} e\left(\rho\vec v_{rel}\cdot\hat n\right)dA$$

Useful Work for Flowing Systems

$$\dot Q + \dot W_u - \underbrace{\int_{CS} p\left(\vec v\cdot\hat n\right)dA} = \frac{d}{dt}\int_{CV}\rho e\,dV + \int_{CS} e\left(\rho\vec v_{rel}\cdot\hat n\right)dA$$

Flow Work: mass entering/leaving CV has to "push" its way in/out

- Further limit consideration to stationary CV ($\Rightarrow \mathrm{v}=\mathrm{v}_{rel}$)

or reference frame is CV

$$\int_{CS} e\left(\rho\vec v_{rel}\cdot\hat n\right)dA + \int_{CS} p\left(\vec v_{rel}\cdot\hat n\right)dA = \int_{CS}\left(e+\frac{p}{\rho}\right)\left(\rho\vec v_{rel}\cdot\hat n\right)dA$$

$$= \int_{CS}\left(u+\frac{p}{\rho}+\frac{\mathrm{v}^2}{2}\right)\left(\rho\vec v_{rel}\cdot\hat n\right)dA$$

enthalpy represents internal energy + flow work of mass crossing CS

$$= \int_{CS}\left(h+\frac{\mathrm{v}^2}{2}\right)\left(\rho\vec v_{rel}\cdot\hat n\right)dA$$

$$\boxed{\dot Q + \dot W_u = \frac{d}{dt}\int_{CV}\rho e\,dV + \int_{CS}\left(h+\frac{\mathrm{v}^2}{2}\right)\left(\rho\overset{=\vec v}{\cancel{\vec v_{rel}}}\cdot\hat n\right)dA}$$

Uniform, Steady Flow System

for CV
stationary in
reference frame

$$\dot{Q}+\dot{W}_u=\frac{d}{dt}\int_{CV}\rho e\,dV+\int_{CS}\left(h+\frac{\mathrm{v}^2}{2}\right)(\rho\vec{\mathrm{v}}\cdot\hat{n})\,dA$$

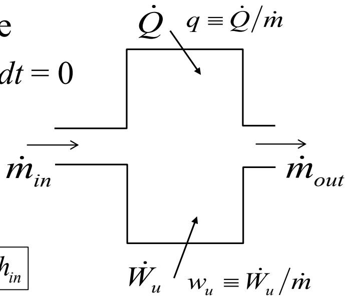
- Example for system where mass inflows/outflows are uniform and CV is in steady-state
  - steady: $\dot{m}_{in}=\dot{m}_{out}\equiv\dot{m}$, and $dE_{CV}/dt=0$

$$\dot{Q}+\dot{W}_u=\dot{m}\left(h_{out}+\frac{\mathrm{v}_{\mathrm{out}}^2}{2}\right)-\dot{m}\left(h_{in}+\frac{\mathrm{v}_{\mathrm{in}}^2}{2}\right)$$

  - assuming negligible KE change

$$\dot{Q}+\dot{W}_u=\dot{m}(h_{out}-h_{in})\Rightarrow\boxed{q+w_u=h_{out}-h_{in}}$$

  - for example if this was an adiabatic valve, q and $w_u=0$ $\Rightarrow h_{out}=h_{in}$, **isenthalpic** process



Second Law for CV

- In similar fashion, can write 2nd Law for CV

$$\boxed{\dot{\mathcal{P}}_s+\int_{CS}\frac{\dot{Q}''}{T}dA=\frac{d}{dt}\int_{CV}\rho s\,dV+\int_{CS}s(\rho\vec{\mathrm{v}}_{rel}\cdot\hat{n})\,dA}$$

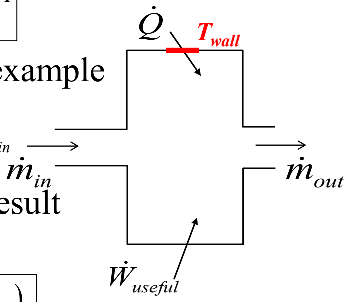
- For simple, steady flow system example

$$\dot{\mathcal{P}}_s+\frac{\dot{Q}}{T_{wall}}=\dot{m}(s_{out}-s_{in})\Rightarrow\frac{\dot{\mathcal{P}}_s}{\dot{m}}+\frac{q}{T_{wall}}=s_{out}-s_{in}$$

- Combine with previous energy result

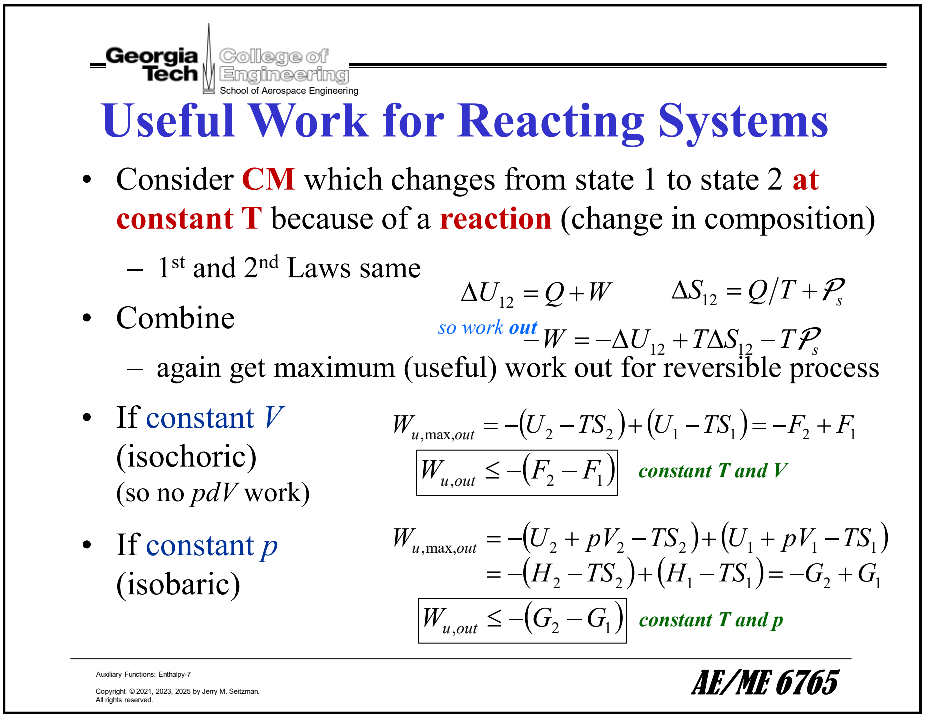
$$w_u=(h_{out}-h_{in})-T_{wall}\left\{(s_{out}-s_{in})-\dot{\mathcal{P}}_s/\dot{m}\right\}$$

$$\dot{\mathcal{P}}_s\geq 0\Rightarrow\boxed{\begin{aligned}w_{u,\min in}&=(h_{out}-h_{in})-T_{wall}(s_{out}-s_{in})\\ w_{u,\max out}&=(h_{in}-h_{out})-T_{wall}(s_{in}-s_{out})\end{aligned}}$$



previous CM result
$w_{u,\max\,out}=(u_{in}-u_{out})-T_o(s_{in}-s_{out})$

Δh replaces Δu for flowing system



Useful Work for Reacting Systems

- Consider **CM** which changes from state 1 to state 2 **at constant T** because of a **reaction** (change in composition)
  - 1st and 2nd Laws same $\Delta U_{12} = Q + W \qquad \Delta S_{12} = Q/T + \mathcal{P}_s$
- Combine *so work* ***out*** $-W = -\Delta U_{12} + T\Delta S_{12} - T\mathcal{P}_s$
  - again get maximum (useful) work out for reversible process
- If constant V (isochoric) (so no pdV work)

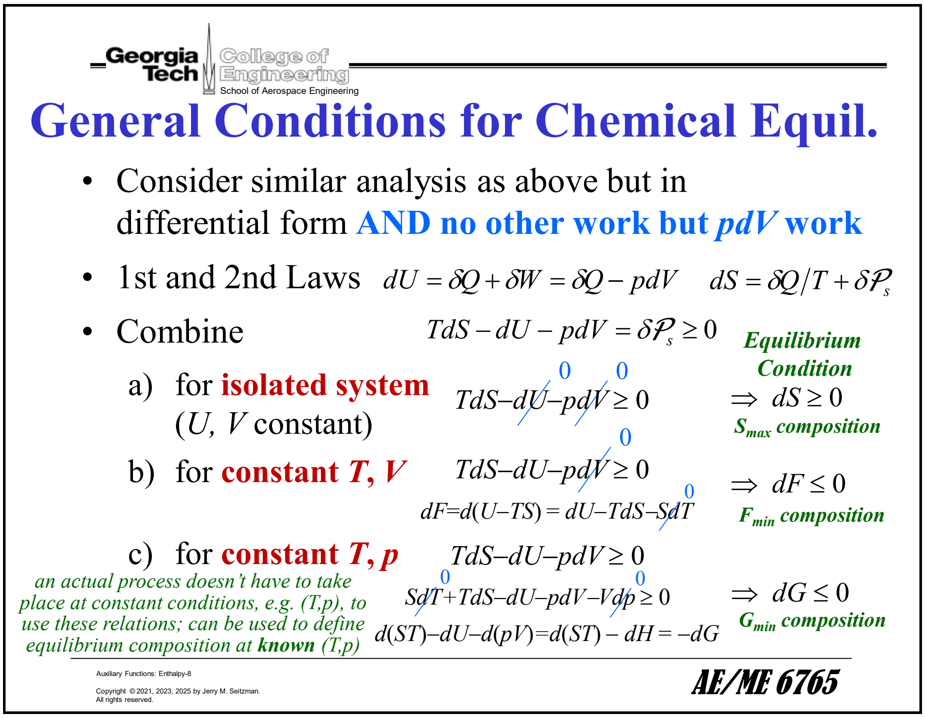
$$W_{u,\max,out} = -(U_2 - TS_2) + (U_1 - TS_1) = -F_2 + F_1$$

$$\boxed{W_{u,out} \le -(F_2 - F_1)}$$ ***constant T and V***

- If constant p (isobaric)

$$W_{u,\max,out} = -(U_2 + pV_2 - TS_2) + (U_1 + pV_1 - TS_1)$$
$$= -(H_2 - TS_2) + (H_1 - TS_1) = -G_2 + G_1$$

$$\boxed{W_{u,out} \le -(G_2 - G_1)}$$ ***constant T and p***



General Conditions for Chemical Equil.

- Consider similar analysis as above but in differential form **AND no other work but *pdV* work**
- 1st and 2nd Laws $dU = \delta Q + \delta W = \delta Q - pdV \qquad dS = \delta Q/T + \delta\mathcal{P}_s$
- Combine $TdS - dU - pdV = \delta\mathcal{P}_s \ge 0$

Equilibrium Condition

a) for **isolated system** (U, V constant)

$$TdS - \overset{0}{\cancel{dU}} - p\overset{0}{\cancel{dV}} \ge 0 \quad \Rightarrow \quad dS \ge 0$$

S_{max} composition

b) for **constant *T, V***

$$TdS - dU - p\overset{0}{\cancel{dV}} \ge 0 \quad \Rightarrow \quad dF \le 0$$

$$dF = d(U - TS) = dU - TdS - S\overset{0}{\cancel{dT}}$$

F_{min} composition

c) for **constant *T, p***

$$TdS - dU - pdV \ge 0$$

$$S\overset{0}{\cancel{dT}} + TdS - dU - pdV - V\overset{0}{\cancel{dp}} \ge 0 \quad \Rightarrow \quad dG \le 0$$

$$d(ST) - dU - d(pV) = d(ST) - dH = -dG$$

G_{min} composition

an actual process doesn't have to take place at constant conditions, e.g. (T,p), to use these relations; can be used to define equilibrium composition at ***known*** *(T,p)*