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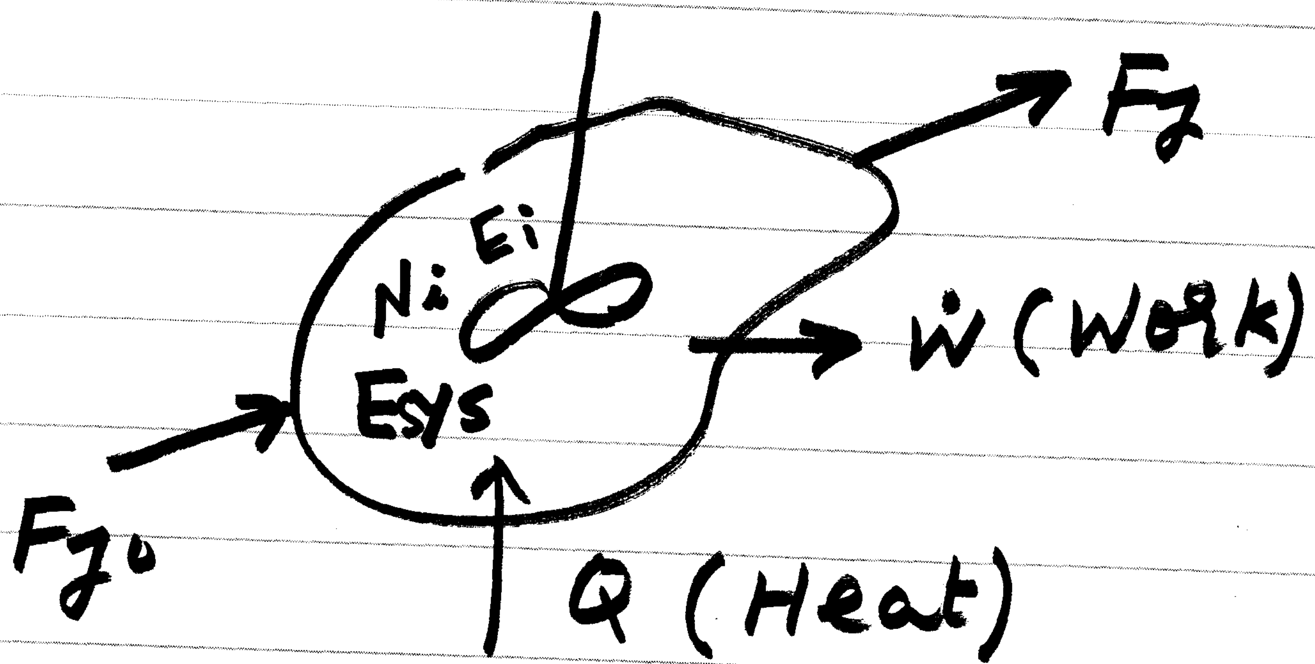
Lec-19 07/11/2012 1

Advanced Reaction Engineering

Energy Balance

Wednesday 7/NOV
10.30-11
1515-1615

ENERGY ~~ENEGY~~ BALANCE STIRRED VESSEL



Input − Output + ~~Generation~~

= Accumulation

Energy cannot be generated. So Generation is Zero

$$\frac{d}{dt}(E_{sys}) = \sum_{i=1}^{n}(E_i F_i)_{in} - \sum_{i=1}^{n}(E_i F_i)_{out} + \dot{Q} - \dot{W}$$

n: number of Species in the System

$E_i = U_i + \frac{u_i^2}{2} + g z_i$ $\quad (J/Kg \equiv m^2/s^2)$

U_i : internal energy $\quad (J/Kg \equiv m^2/s^2)$

u_i^2 : Velocity $\quad (J/Kg \equiv m^2/s^2)$

gZ_i : gravity head $\quad (J/Kg \equiv m^2/s^2)$

Flow Work

Flow work is defined as ~~em~~ energy needed to get mass into and out of the system in the absence of friction. So it is defined as

$$W_F = \sum_{i=1}^{n} (F_i P_t \omega_i)_{out} - \sum_{i=1}^{n} (F_i P_t \omega_i)_{in}$$

$$\frac{\cancel{mol}}{s} \cdot \frac{N}{\cancel{m^2}} \cdot \cancel{m^3}/\cancel{mol} = Nm/s = J/s = W$$

Therefore work ~~out~~ out a system can be set as

$$\dot{W} = W_S + W_F$$

$$W_S + \sum_{i=1}^{n} (F_i P_t w_i)_{out} - \sum_{i=1}^{n} (F_i P_t w_i)_{in}$$

W_S - shaft work, P_t total pressure

w_i - specific volume species 'i'

n - number of species

$$W_S = W - W_F$$

W_s is the measurable work since it is available on shaft to turn the motor. Not that 'W' the true work of system can be measured by measuring W_s and W_F. Not W_F can be +ve or -ve depending on system

FLOW WORK

In a $SO_2 + \frac{1}{2} O_2 = SO_3$ plant processing

3000 tm/d SO_2

$$W_F = \left(\sum_{i=1}^{n} f_i P_t w_i\right)_{out} - \left(\sum_{i=1}^{n} F_i P_t w_i\right)_{in}$$

$$\simeq - P_t v_0 (0.005)$$

$P_t = 10^5 \ N/M^2 \quad v_0 = 250 \ M^3/s$

$$W_F = -(10^5)(250)(0.005) =$$

$$-125 \ 10^3 \ J/s = -125 \ KW$$

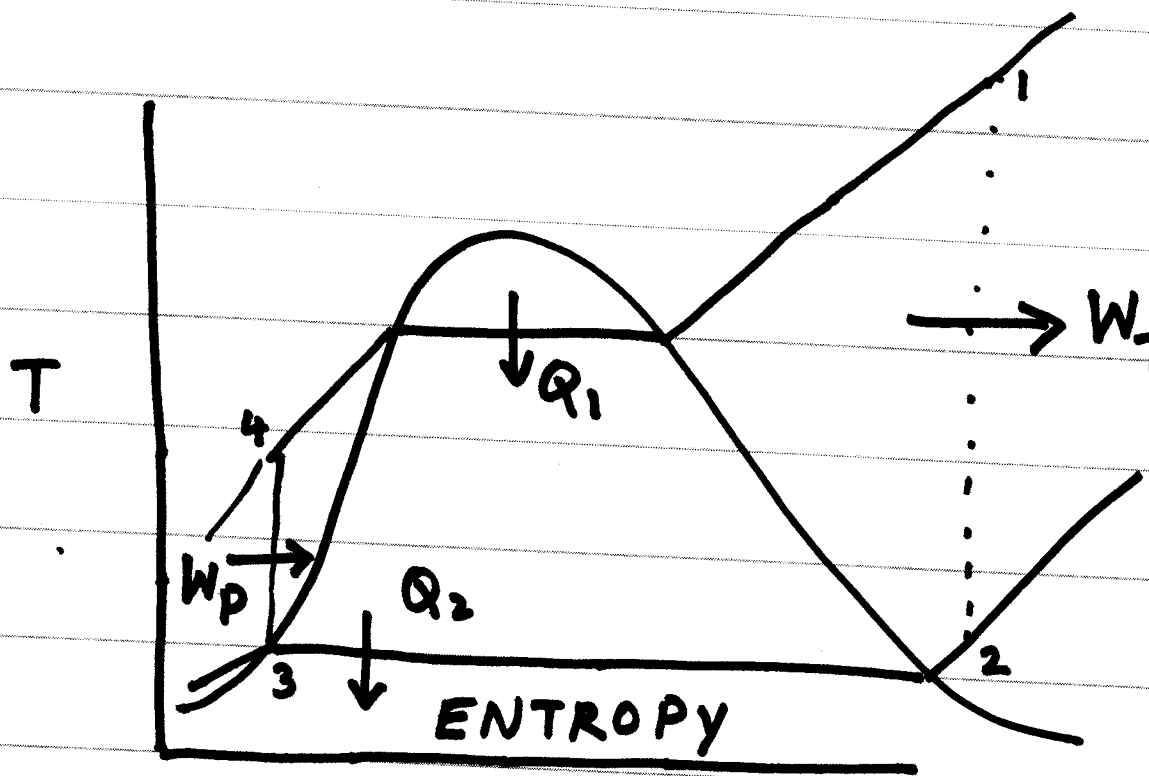
Energy to be supplied

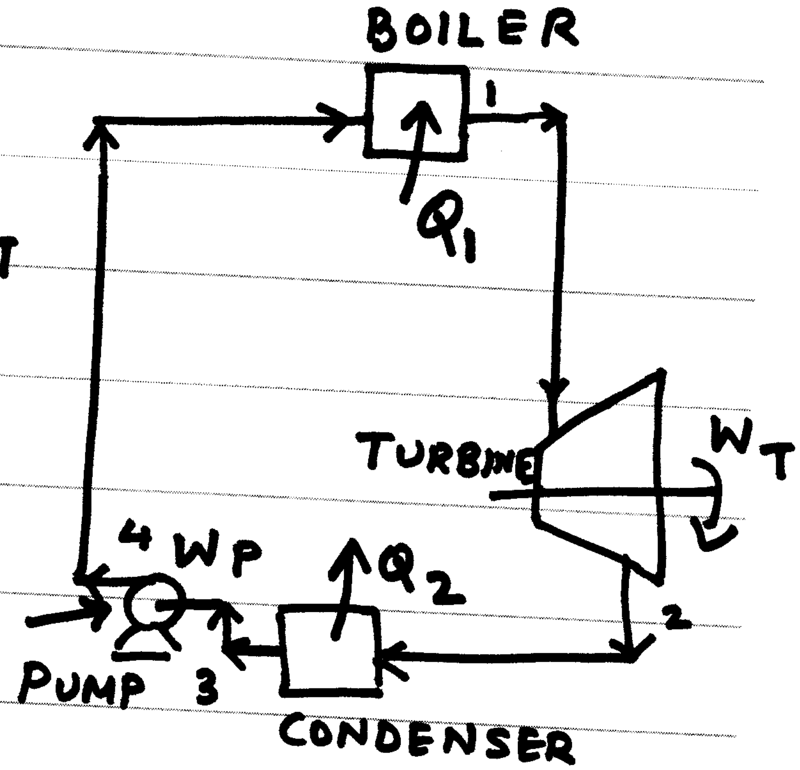
FLOW WORK

In a $SO_2 + \frac{1}{2} O_2 = SO_3$ plant blower power to pump gases through SO_3 Converter bed is 2.5 MW for a 3000 ton/d SO_2 processing plant.

Improving Catalyst Design will reduce pressures drop. But the least drop would be that of flow work -125 kW. So we cannot do better than 125 kW

FLOW WORK





	P atm	T C	H KCAL/KG	ω M³/KG
1	68	760	972	0.075
2	0.068	45	695	36.3

$$Q_1 - Q_2 = W_T + W_p$$

FLOW WORK $\quad W_F/F_i = (P_t\,\omega_i)_2 - (P_t\,\omega_i)_1$

$$= 0.068 \times 36.3 - 68 \times 0.075$$

$$= -2.63 \text{ Kcal/KG}$$

$$\frac{d}{dt}\left(E_{sys}\right) = \left(\sum_{i=1}^{n} F_i \cdot E_i\right)_{in} - \left(\sum_{i=1}^{n} F_i \cdot E_i\right)_{out}$$

$$+ Q - \left(W_s + \sum_{i=1}^{n}\left(F_i \cdot P_t \omega_i\right)_{out} - \sum_{i=1}^{n}\left(F_i \cdot P_t \omega_i\right)_{in}\right)$$

$$= \sum_{i=1}^{n} F_i \cdot \left(E_i + P_t \omega_i\right)_{in} - \sum F_i \left(E_i + P_t \omega_i\right)_{out} + Q - W_s$$

$$E_i = U_i + \frac{u_i^2}{2} + g z_i$$

$$\frac{d}{dt}\left[\sum_{i=1}^{N} N_i\left(U_i + \frac{u_i^2}{2} + g z_i + \right)\right]$$

$$= \left[\sum_{i=1}^{N} F_i\left(U_i + \frac{u_i^2}{2} + g z_i + P_t \omega_i\right)\right]_{in}$$

$$- \left[\sum_{i=1}^{N} F_i\left(U_i + \frac{u_i^2}{2} + g z_i + P_t w_i\right]_{out} + Q - W_s\right.$$

$$\dot{W}$$

$$= W_s + W_F$$

$h_i - P_t w_i = U_i$

$$\frac{d}{dt}\left[\sum N_i \left\{ h_i + \cancel{\frac{u_i^2}{2}} + \cancel{g z_i} \right\}\right]$$

$-P_t w_i$

$$= \left[\sum F_i \left\{ h_i + \cancel{\frac{u_i^2}{2}} + \cancel{g z_i} \right\}\right]_{in} - \left[\sum F_i \left\{ h_i + \cancel{\frac{u_i^2}{2}} + \cancel{g z_i} \right\}\right]_{out}$$

$$+ Q - W_s$$

$\therefore h_i = U_i + P_t w_i$

If $P_t w_i$ term on LHS is small in relation to h_i then we have a simplified version

$$\frac{d}{dt}\sum N_i\left\{h_i + \cancel{\frac{u_i^2}{2}} + \cancel{g z_i} \cancel{- P_T v_i}\right\}$$

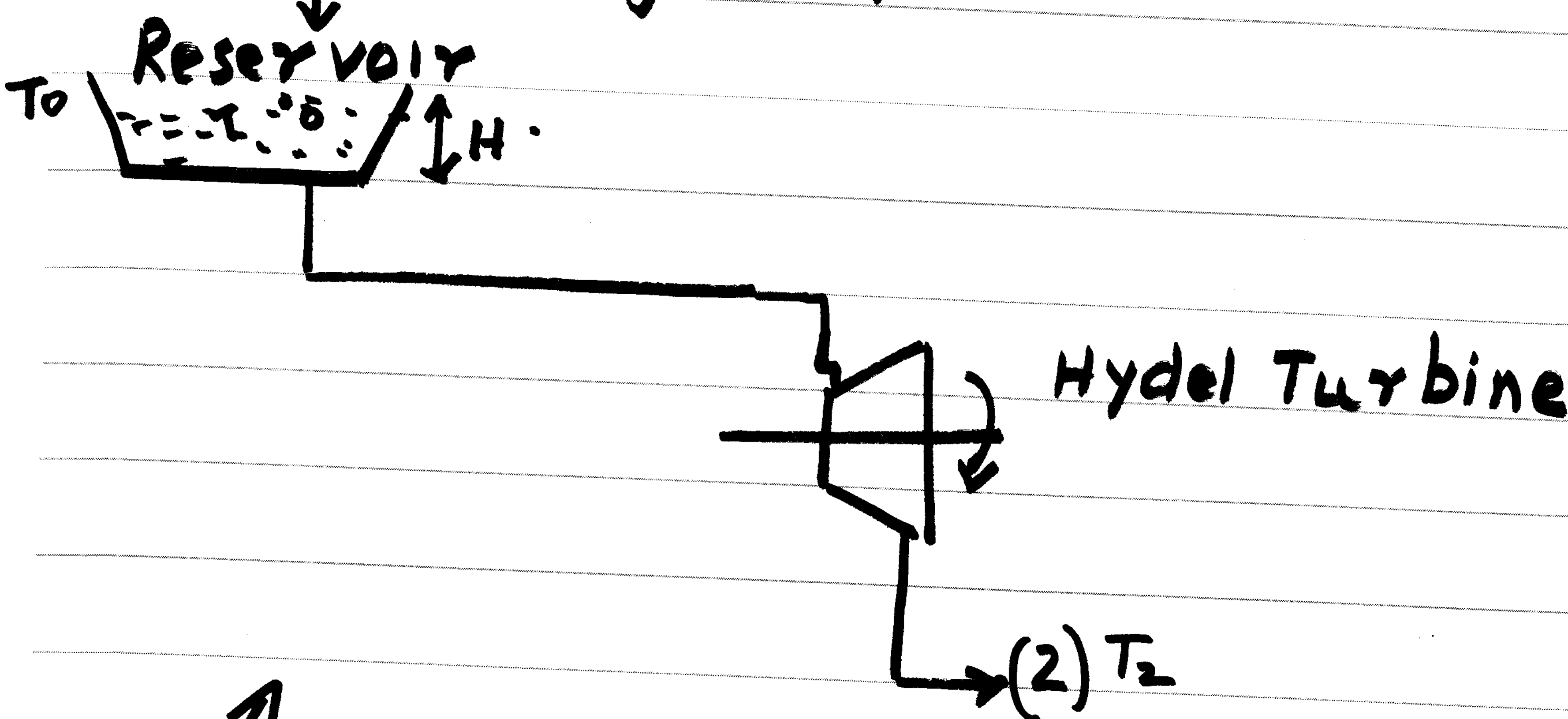
$$= \left[\sum F_i\left\{h_i + \cancel{\frac{u_i^2}{2}} + \cancel{g z_i}\right\}\right]_{in}$$

$$- \left[\sum F_i\left\{h_i + \cancel{\frac{u_i^2}{2}} + \cancel{g z_i}\right\}\right]_{out} + Q - W_s$$

if $u_i^2/2$ and $g z_i$ terms are small which is so in chemical Rxn equipment we then have

$$\frac{d}{dt}\left[\sum_{i=1}^{n} N_i h_i\right] = \sum_{i=1}^{n}(F_i h_i)_{in} - \sum_{i=1}^{n}(h_i F_i)_{out} + Q - W_s$$

Application to hydel power station



$$\frac{d}{dt}\left[\cancel{\ \ }\right] = \left(\cancel{\frac{p_0}{\rho}} + C_v(T_0 - \cancel{T_R}) + \cancel{\frac{u_0^2}{2}} + g z_0\right)F$$

$$- F\left(\cancel{\frac{p_2}{\rho}} + C_v(T_2 - \cancel{T_R}) + \cancel{\frac{u_2^2}{2}} + g z_2\right) + \cancel{Q} - W_s$$

Reservoir holds huge quantity of water

So Rate of change may be taken as small.

So LHS = 0.

RHS: $P_0 = P_2$ = atm. No change in density.

$U_0 = U_2$ since we ~~do~~ ~~not~~ design ~~expect~~ ~~to~~ for no ~~allow~~ velocity ~~to~~ change. Q - heat/Energy Loss = 0.

$$0 = g(Z_0 - Z_2) + C_v(T_0 - T_2) + \cancel{Q} - W_s/F$$

$$\left(\frac{W_S}{F}\right) = g(Z_0 - Z_2) + C_v(T_0 - T_2)$$

a) if $T_0 = T_2$ and $F = 4000\ kg/s$; $Z_0 - Z_2 = 50M$

$$W_S = \overset{g}{(10)}\,\underset{m}{(\overset{H}{50})}\,\underset{kg/s}{4000}\ (m/s^2)(m)(kg/s) = \cancel{2MW}\ \underline{\underline{2\ MW}}$$

b) if $T_2 - T_0 = \underline{0.05C}$ (due to friction)

$$W_S = \left[(10)50\ \cancel{(4000)} - \overbrace{(4180)(0.05)}^{210}\right]4000.$$

$$= (210)(4000) = \underline{\underline{0.81}}\ MW$$

Frictional Loss can be serious.

Steam Turbine

$$\frac{d}{dt}\cancel{\left[\;\;\right]} = \left[\sum F_i (h_i)\right]_{in} - \left[\sum F_i h_i\right]_{out} + \dot{Q} - \dot{W}_s$$

LHS can be taken as zero since accumulations are not relevant at steady state.

Q can be important since heat losses are significant.

Energy Balance Chemical Reactions Stirred Vessel

species

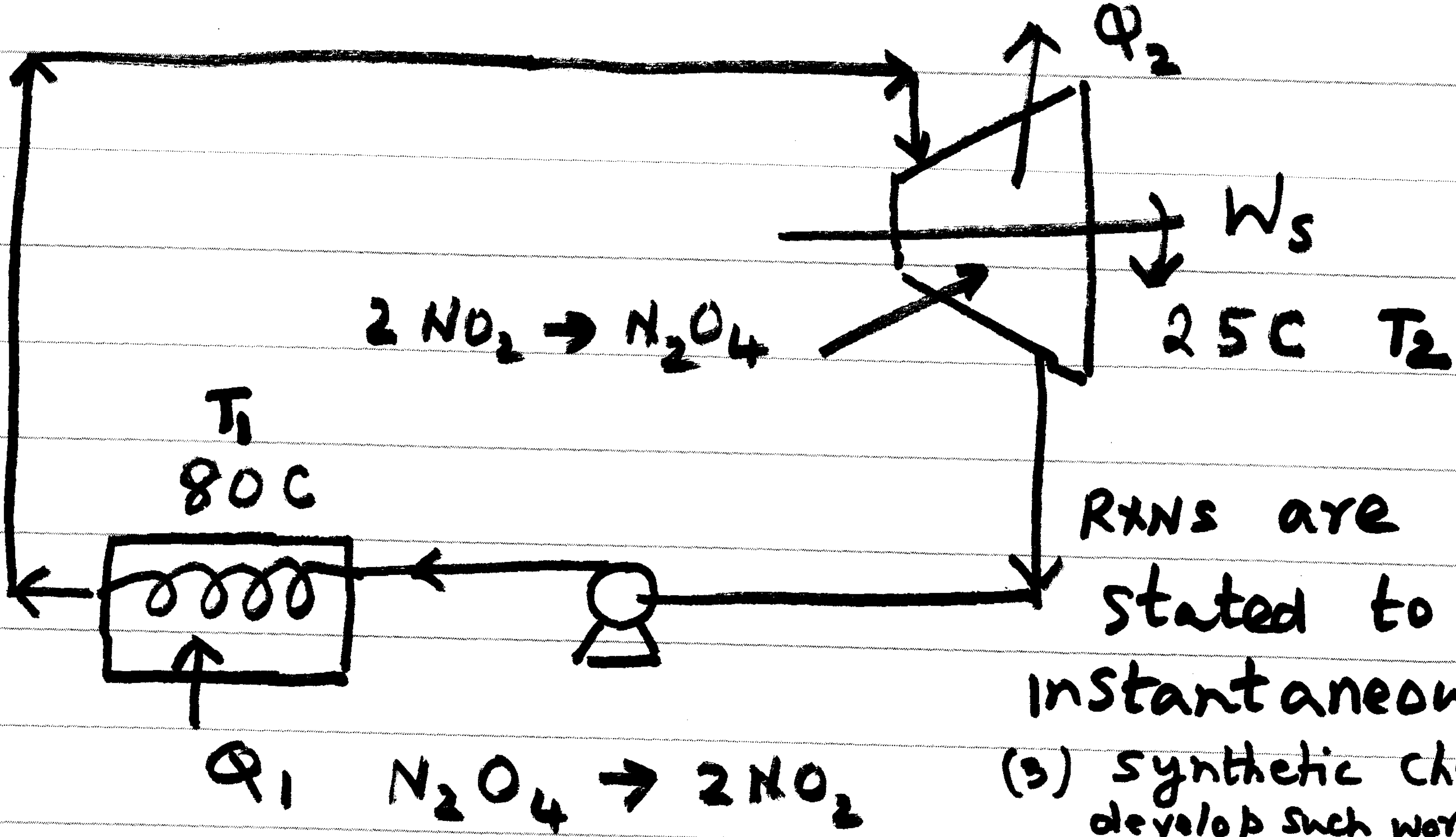
$$\frac{d}{dt}\left[\sum_{i=1}^{n}(N_i H_i)_{sys}\right] = \left(\sum_{i=1}^{n} F_i H_i\right)_{in} - \left(\sum_{i=1}^{n} F_i H_i\right)_{out} + Q - W_s \qquad (1)$$

In a well stirred system $(H_i)_{sys} = (H_i)_{out} = H_i$ (say)

$$\frac{d}{dt}\left[\cancel{H_i}\sum N_i H_i\right] = \left(\sum (F_i H_i)_0\right) - \left(\sum H_i F_i\right) + Q - W_s \qquad (2)$$

'o' denotes input

Chemically Reacting Fluid in a Turbine.



RXNs are stated to be instantaneous

(3) synthetic chemistry to develop such working fluids

1) suitable choice of T_1 and T_2 is required to get power output desired.

2) Q_2 can be used for space heating.

$$\sum N_i \frac{dH_i}{dt} + \sum H_i \frac{dN_i}{dt} = \sum F_{i0} H_{i0} - \sum F_i H_i + Q - W_s \quad - (3)$$

Take single reaction

$$\alpha_{11} A_1 + \alpha_{12} A_2 + \alpha_{13} A_3 + \dots \alpha_{1n} A_n = 0$$

$$\frac{r_{A1}}{\alpha_{11}} = \frac{r_{A2}}{\alpha_{12}} = \frac{r_{An}}{\alpha_{1n}} = r_1$$

Material Balance for Stirred Vessel

$$F_{i0} - F_i + r_1 \alpha_{1i} V = \frac{d}{dt} N_i \quad \dots \quad (4)$$

Multiply by H_i and sum over all species

$$\sum_{i=1}^{n} H_i F_{io} - \sum_{i=1}^{n} H_i F_i + \sum_{i=1}^{n} r_1 \underbrace{\alpha_{1i} H_i}\, V = \sum_{i=1}^{n} H_i \frac{dN_i}{dt} \qquad -(4)$$

Essentially Eq (4) implies that we have written 'n' eqn one for each species. Multiplied each equation by the enthalpy H_j for the species for which material balance has been written. Then we have added all these eqns to get Eqn (4)

Substituting for $\sum H_i \frac{dN_i}{dt}$ in ~~Eq~~ (3)

$$\sum N_i \frac{dH_i}{dt} + \sum H_i F_{i0} - \cancel{\sum H_i F_i} + \sum r_1 \alpha_{1i} H_i V$$

$$= \sum F_{i0} H_{i0} - \cancel{\sum F_i H_i} + Q - W_s + Q - W_s$$

Notice that term

$$\sum r_1 \alpha_{1i} H_i V = r_1 \left[\underbrace{\alpha_{11} H_1 + \alpha_{12} H_2 + \ldots \alpha_{1n} H_n}_{\Delta H_1^*} \right] V$$

which is ΔH_1^* - the enthalpy change fr rxn

$$\sum N_i \frac{dH_i}{dt} = \sum F_{io}(H_{io} - H_i) + r_1 V(-\Delta H_1^*) + Q - W_s$$

Note $r_1(-\Delta H_1^*) = r_1 \alpha_{1k} \dfrac{(-\Delta H_1^*)}{\alpha_{1k}}$

$r_1 \alpha_{1K}$ - is rate of formation of 'k'

$\left(\dfrac{-\Delta H_i^*}{\alpha_{1k}}\right)$ = is heat of reaction expressed w.r.t component 'k'

Expressing enthalpy in terms of T and C_p.

$$H_i(T) = H_i^0(T_R) + \int_{T_R}^{T_s} c_{psi}\,dT + \Delta H_s + \int_{T_s}^{T_B} c_{pli}\,dT + \Delta H_{vi} + \int_{T_s}^{T} c_{pig}\,dT$$

if ~~So~~ no phase change

$$H_i(T) = H_i(T_R) + \int_{T_R}^{T} c_p\,dT$$

$$H_i(T) = H_i^0(T_R) + \hat{c}_{pi}\,(T - T_R)$$

$$H_i(T_0) = H_i(T_R) + \hat{c}_{pi}\,(T_0 - T_R)$$

substituting

$$\sum_{i=1}^{n} \underset{N_i}{\overset{V C_i}{\cancel{N_i}}} \hat{C}_{pi} \frac{dT}{dt} = \sum_{i=1}^{n} F_{i0} \hat{c}_{pi} (T_0 - T) + r_1 V (-\Delta H_1^*) + Q - W_s$$

Let $\sum C_i \hat{c}_{pi} = \hat{C}_p \quad (\text{cal}/L\ {}^\circ K)$

$$\sum C_{i0} \hat{c}_{pi} = \tilde{C}_p \quad (\text{cal}/L\ {}^\circ K)$$

$$\sum_{i=1}^{n} V C_i \hat{C}_{pi} \frac{dT}{dt} = \sum_{i=1}^{n} C_{i0} c_{pi} (T_0 - T) v_0 + r_1 V (-\Delta H_1^*) + Q - W_s$$

$$V \hat{C}_p \frac{dT}{dt} = v_0 \tilde{C}_p (T_0 - T) + r_1 V (-\Delta H_1^*) + Q - \cancel{W_s}$$

Energy Balance for multiple Reactions

$$\sum N_i \frac{dH_i}{dt} + \sum H_i \frac{dN_i}{dt} = \sum F_{i0} H_{i0} - \sum F_i H_i + Q - W_s \quad -(1)$$

Consider

$$\alpha_{11} A_1 + \alpha_{12} A_2 + \alpha_{13} A_3 + \cdots \alpha_{1n} A_n = 0$$

$$\alpha_{21} A_1 + \alpha_{22} A_2 + \alpha_{23} A_3 + \cdots \alpha_{2n} A_n = 0$$

$$\alpha_{p1} A_1 + \alpha_{p2} A_2 + \alpha_{p3} A_3 + \cdots \alpha_{pn} A_n = 0$$

Material Balance for spieces 'i'

$$F_{i0} - F_i + (r_1 \alpha_{1i} + r_2 \alpha_{2i} + \cdots r_p \alpha_{pi}) V = \frac{d}{dt} N_i \quad -(2)$$

Note all p rate processes occur in the energy balance

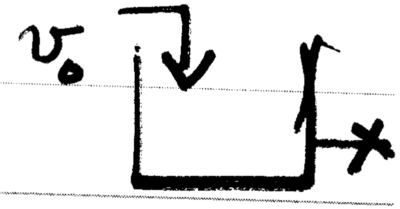
Multiply by H_i and sum over all species in Eqn (2)

$$\sum F_{io} H_i - \sum F_i H_i + \sum (r_1 \alpha_{1i} H_i + r_2 \alpha_{2i} H_i + \cdots r_p \alpha_{pi} H_i) V = \cancel{\frac{d}{dt}} \cancel{N_i H_i} \sum H_i \frac{dN_i}{dt} \quad - (3)$$

Substituting for $\sum H_i \frac{dN_i}{dt}$ in Eq (1)

$$\sum N_i \frac{dH_i}{dt} + \sum F_{i0} H_i - \sum \cancel{F_i H_i} + \sum r_1 \alpha_{1i} H_i + \cdots \sum r_p \alpha_{pi} H_i$$

$$= \sum F_{i0} H_{i0} - \sum \cancel{F_i H_i} + Q - W_s$$



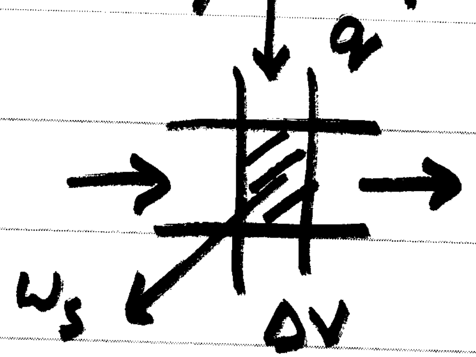
$$\sum N_i \frac{dH_i}{dt} = \sum F_{i0} (H_{10} - H_i) + r_1 V(-\Delta H_1^*) + \cdots r_p V(-\Delta H_p^*)$$
$$+ Q - W_s$$

$$\rightarrow \sum V C_i \frac{dH_i}{dt} = \sum v_0 C_{10} (H_{10} - H_i) + r_1 V (-\Delta H_1^*) + \cdots r_p V(-\Delta H_p^*)$$
$$+ Q - W_s$$

$$\rightarrow V \hat{C}_p \frac{dT}{dt} = v_0 \tilde{C}_p (T_0 - T) + \sum_{j=1}^{p} r_j (-\Delta H_j^*) V + Q - W_s \quad \cdots (4)$$

Energy Balance for plug Flow Vessel

We Set up eqns for steady state Case



Neglecting heat of Mixing

$$\sum (F_i H_i)_V - \sum (F_i H_i)_{V+\Delta V} + q \Delta V - W_s \Delta V = 0 \; [SS]$$

$$-\frac{d}{dV}\left(\sum F_i H_i\right) + q - W_s = 0$$

$$\boxed{\frac{d}{dV}\left(\sum F_i H_i\right) = q - W_s} \quad \dots \quad (1)$$

Material Balance for species 'i'

$$\frac{dF_i}{dV} = r_1 \alpha_{1i} + r_2 \alpha_{2i} + \cdots r_p \alpha_{pi} \quad \cdots \quad (2)$$

Multiply by H_i and sum over all species

$$\sum H_i \frac{dF_i}{dV} = \sum r_1 \alpha_{1i} H_i + \sum r_2 \alpha_{2i} H_i + \cdots \sum r_p \alpha_{pi} H_i \quad - (3)$$

From (1 & 3) we get

$$\sum F_i \frac{dH_i}{dV} + \sum H_i \frac{dF_i}{dV} = q - W_s \quad (4)$$

substituting for $\sum H_i \frac{dF_i}{dV}$ from (3) into (4)

$$\sum F_i \frac{dH_i}{dV} + \sum r_1 \alpha_{11} H_i + \sum r_2 \alpha_{2i} H_1 + \cdots \sum r_p \alpha_{pi} H_i$$

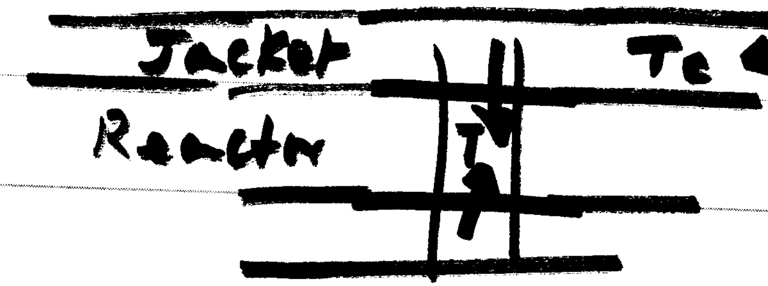
$$= q - W_s$$

$$\sum \nu C_i C_{pi} \frac{dT}{dV} + (r_1 \Delta H_1^*) + r_2 (\Delta H_2^*) + \cdots r_p (\Delta H_p^*)$$

$$= q - W_s$$

$$\nu \hat{C}_p \frac{dT}{dV} = \sum_{j=1}^{p} r_j (-\Delta H_j^*) + q - W_s$$

$$v \hat{C}_p \frac{dT}{dV} = \sum_{j=1}^{p} r_j \left(-\Delta H_j^*\right) + q - W_s \quad \text{— (5)}$$



Cooling or heating

h : heat tranfer Coeff

ΔV

a_H - heat transfer area/vol.

$$q = h\left(a_H\right)\left(T_c - T\right)$$

(a_H) for a pipe = $\pi D L \Big/ \frac{\pi}{4} D^2 L = \left(\frac{4}{D}\right)$

Similarly for other geometries

substituting for q for pipe

$$v C_p \left(\frac{dT}{dV}\right) = \sum_{j=1}^{p} r_j \left(-\Delta H_j^*\right) + \frac{4h}{D}\left(T_c - T\right) - \cancel{W_s} \quad \text{— (6)}$$

ve   -ve