PROBLEM 1. **(15 points)**

(a)

$$A \xrightarrow{k_1} B$$

is an elementary liquid-phase reaction that occurs in a 100 L CSTR at steady state. 0.25 mol/L of pure A at 320 K flows into the reactor at flow rate of 1000 L/min. The reactor is equipped with a cooling jacket.

$C_{pA} = C_{pB} = 100$ J/mol-K

$k_1 = 5$ min^{-1} at 350 K with E_1=45000 J/mol

ΔH^o_{rxn1} = -50,000 J/molA

T_{am} = 250 K

i) Given that G(T) for an exothermic reaction is shown on the curve below, write out and plot R(T) if the reactor is run adiabatically. What is T*? What is the temperature of the reactor T? **(4 points)**

$\alpha = 0$ $\boxed{+0.5}$ $T^* = \frac{T_a\alpha + T_o}{1+\alpha} = T_o = 320K$ $\boxed{+0.5}$

$R(T) = \bar{C}_{p_o}(1+\alpha)(T-T^*) = 100(T-T^*) = 100(T-320)$ $\boxed{+1}$

$T \simeq 820K$ $\boxed{+1}$

+.5 if w/in 100 K

$\boxed{\text{line } +1}$

@ T= 520

R(T) = 20000

ii) Plot the curve for R(T) if there is infinitely fast heat transfer to the surroundings. What is T*? What is the temperature of the reactor T? **(2 points)**

$\alpha = \infty$ $T^* = T_a$

$T = 250K$

$\boxed{\text{vertical line } +1}$ $\boxed{+1}$

iii) Consider the case of an endothermic reaction under the same conditions, with ΔH^o_{rxn1} = +50,000 J/molA. Does G(T) change? If so, draw the expected G(T) plot. Label T* and T for case i) and case ii) above, now for this endothermic reaction scenario. **(2 points)**

see plot

+1 correct drawing

+1 for T* & T not changing

iv) Now the cooling jacket is running with a heat transfer coefficient of UA = 25000 J/min K. Calculate T*. Plot the R(T) line. What is the reactor operating temperature if we are operating on the upper branch? **(3 points)**

$$\alpha = \frac{25000 \text{ J/min K}}{100 \frac{J}{molK}\left(1000\frac{L}{min} \times 0.25\frac{mol}{L}\right)} = 1 \quad \boxed{+0.5}$$

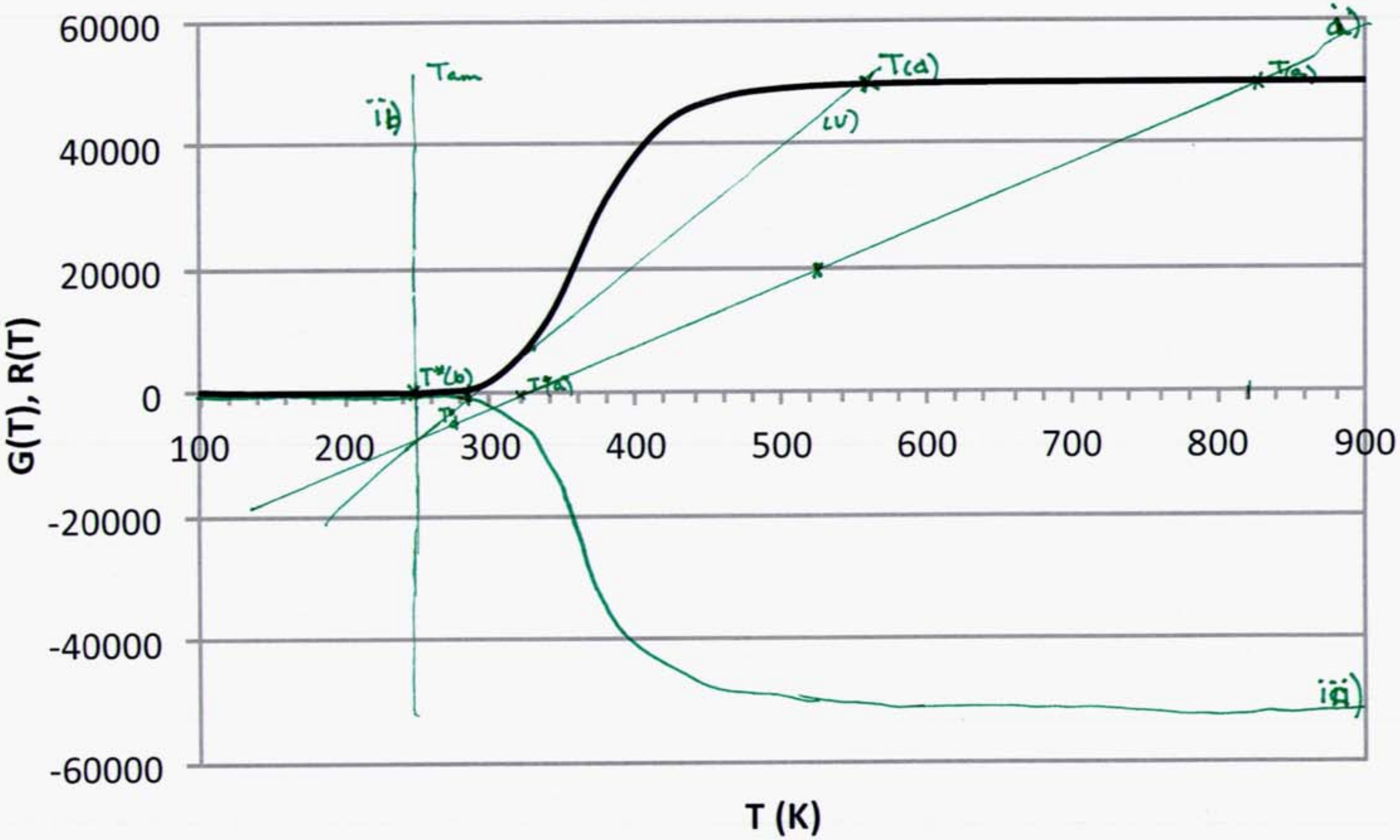
$$T^* = \frac{T_a + T_o}{2} = \frac{250K + 320K}{2} = 285K \quad \boxed{+0.5}$$

$T \simeq 540K$ $\boxed{+1}$

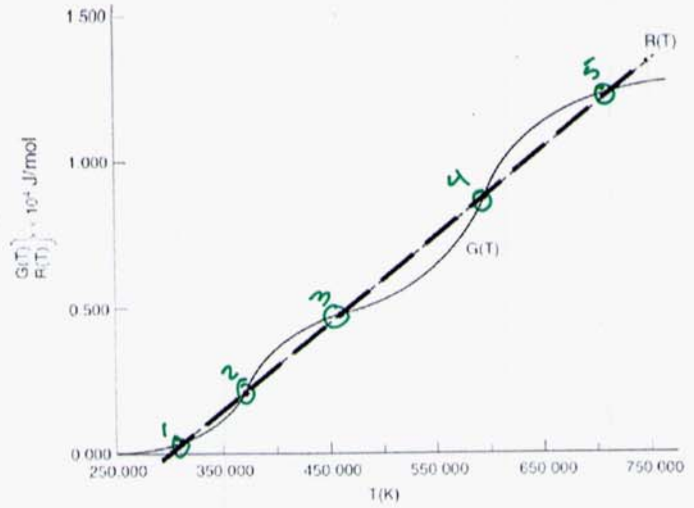
$$R(T) = 100(1+1)(T-285) = 200(T-285)$$

+0.5 if w/in 100K

$\boxed{\text{line} + 1}$


60000
40000
20000
0
-20000
-40000
-60000
G(T), R(T)
100
200
300
400
500
600
700
800
900
T (K)
i)
ii)
iii)
iv)
Tam
T*(b)
T*(a)
T_1
T(d)
T(a)

(b) Consider the G(T) and R(T) plotted below. Clearly label the steady states, and Determine and justify the stability of each steady state. Answers without justification receive no credit. **(4 points)**



1, 3, 5 → stable because

G(T) > R(T) to the ~~fig~~ left (↑T)

& R(T) > G(T) to the right (↓T)

$\boxed{+3}$

2, 4 → unstable because

R(T) > G(T) to the left (↓T)

G(T) > R(T) to the right (↑T)

$\boxed{+1}$

PROBLEM 2. **(15 points)**
The ideal gas-phase reaction

$$A + B \rightarrow C$$

occurs in an adiabatic nonideal flow reactor operating at steady state. A 350 K stream flows into the reactor at 40 mol/min and is comprised of 40 mol % A, 40 mol % B and the remaining inert.

$C_{pA} = C_{pB} = C_{pC} = 100$ J/mol-K
$C_{pI} = 200$ J/mol-K
$\Delta H^o_{rxn} = -10{,}000$ J/mol at 298 K

(a) If the reaction reaches X_A=0.75 at the outlet, what is the temperature of the outlet stream? (Assume no shaft work) **(7 points)**

$$\left(\frac{dE}{dt}\right)_{sys} = 0 = 0 + 0 - X_A F_{A0} \Delta H_{rxn}(T) - F_{A0} \overline{C_{p0}}(T - T_0) \quad \boxed{+2}$$

$$X_A \left[\Delta H^\circ_{rxn} + \Delta C_p (T - T_{ref})\right] \overset{\boxed{+2}}{=} \left(\frac{F_{A0}}{F_{A0}} C_{pA} + \frac{F_{B0}}{F_{A0}} C_{pB} + \frac{F_{I0}}{F_{A0}} C_{pI}\right)(T - T_0)$$

$$-0.75 \left[-10000\,J/mol + (100\,J/molK - 100\,J/molK - 100\,J/molK)(T - 298K)\right]$$

$$= (1 \times 100\,J/molK + 1 \times 100\,J/molK + 1/2 \times 200\,J/molK)(T - 350K) \quad \boxed{+2}$$

$$7500\,J/mol + (+75T) - 22350 = 300T - 105000$$

$$90150\,K = 225T$$

$$\boxed{T = 400.7K} \quad \boxed{+1}$$

if assume $\Delta C_p = 0$ -2.5

(b) Can there be multiple steady-state exit temperatures for the reactor scenario in (a) above? Explain why or why not in one sentence. **(3 points)**

$\boxed{\text{[illegible]}}$ No. By specifying a conversion, we have a specific operating temperature

↑

$\boxed{+2}$

(c) If the reactor is now being operated isothermally, calculate the rate of heat removal required for isothermal reactor operation at the same conversion as in part (a). **(5 points)**

if isothermal

$\boxed{+2}$ $\boxed{+1}$

$$\dot{Q} = +X_A F_{A0} (\Delta H_{rxn}(T)) \qquad T = T_0 = 350K$$

$$= +0.75\left(40\frac{mol}{min} \times \frac{0.4 \, mol\, A}{1 \, mol}\right)\left(-10000 \, J/mol + -100 \, J/mol\,K \, (350-298K)\right)$$

$\boxed{+1}$

$$= -182400 \, J/min = \boxed{182 kJ/min} \; \boxed{+1}$$

If assume $\Delta C_p = 0$ -1

PROBLEM 3. **(15 points)**
A set of liquid-phase parallel reactions occurs in an isothermal, isobaric batch reactor.

$$\begin{array}{ll} A \to D & r_D = k_1 C_A^m \\ A \to U & r_U = k_2 C_A^m \end{array}$$

where D is the desired product, U is the undesired product, an m is the same exponent for D and U rate expressions. You were able to monitor the concentration of A in the reactor and determine the half-life of species A for different initial concentrations of A, as shown in the table below. $t_{1/2}$ = time required for a reactant species to decrease to half its initial value and for nth order reaction kinetics, the $t_{1/2}$ can be expressed in the form:

$$t_{\frac{1}{2}} = \frac{2^{n-1}-1}{k(n-1)} C_{A0}^{1-n}$$

$t_{1/2}$ (min)	**C_{A0} (mol/L)**
10	5
15	25

For the case of C_{A0} = 5mol/L, we were also able to determine the concentration of products D and U at t = 10 minutes:

C_D (t=10) = 3.2 mol/L
C_U (t=10) = 1.5 mol/L

(a) Determine the rate expressions, r_D and r_U. **(10 points)**

liquid phase:

$$-r_A = k_1 C_A^m + k_2 C_A^m$$

$$= \underbrace{(k_1+k_2)}_{K} C_A^m \quad (+2)$$

$K \neq k_1$ or k_2

Half life for m^{th} order kinetics: ⇒ use to solve for m and K, $K = k_1 + k_2$

solves for m

$$\frac{t_{\frac{1}{2}} @ 10}{t_{\frac{1}{2}} @ 15} = \frac{\frac{\cancel{(2^{m-1}-1)}}{\cancel{K(m-1)}} C_{AO(10)}^{(1-m)}}{\frac{\cancel{(2^{m-1}-1)}}{\cancel{K(m-1)}} C_{AO(15)}^{(1-m)}}$$

$$\frac{10}{15} = \left(\frac{5}{25}\right)^{(1-m)}$$

$$\ln\left(\frac{2}{3}\right) = (1-m)\ln\left(\frac{1}{5}\right)$$

$$\boxed{m = 0.748}$$

(+4 form)

solve for ~~K~~

$$10 = \frac{2^{m-1}-1}{K(m-1)} (5)^{1-m}$$

~~+a~~ (+1)

$$K = k_1 + k_2 = 0.095$$

we still need more information to obtain K_1, K_2.

$$\frac{r_D}{r_u} = \frac{\frac{dC_D}{dt}}{\frac{dC_U}{dt}} = \frac{K_1 \cancel{C_A^m}}{K_2 \cancel{C_A^m}}$$

(+1) $$\frac{dC_D}{dC_u} = \frac{K_1}{K_2}$$

integrate : $$\frac{C_D - C_{D0}}{C_U - C_{U0}} = \frac{K_1}{K_2}$$

(+1) $$\frac{3.2}{1.5} = \frac{K_1}{K_2}.$$

$$2.133 = \frac{K_1}{K_2}$$

w/ :

$$2.133 = \frac{K_1}{K_2}$$

$$0.095 = K_1 + K_2$$

(+1) $K_1 = 0.0647$
$K_2 = 0.0303$

$$r_D = (0.6565) C_A^{0.748}$$

$$r_U = (0.0303) C_A^{0.748}$$

(b) Assuming the activation energies E_{A1} and E_{A2} are known for both reactions above, should we run at higher or lower temperatures to have high selectivity towards D? Explain in a single sentence your reasoning and what it would be guided by. Answers without proper reasoning receive no credit. **(5 points)**

Temperature Effects:

$$S_D = \frac{r_D}{r_U} = \frac{A_D}{A_u} e^{-\left(\frac{E_D - E_u}{RT}\right)}$$ (+2)

The choice of temperature will depend on the respective activation energies – if $E_D < E_u$ a ~~higher~~ lower temperature is preferred and if $E_D > E_u$, a higher temp is preferred.

(+3)

4. $$\dot{q} - F_{A0}\frac{dT}{dV}\left(\bar{C}_{p0} + \Delta\hat{C}_p X_A\right) - F_{A0}\frac{dX_A}{dV}\left(\Delta H^{\circ}_{rxn}(T_{ref}) + \Delta\hat{C}_p(T-T_{ref})\right) = 0$$

(a) $\dot{q} = Ua(T_a - T)$

No reaction:

$$\dot{q} = F_{A0}\frac{dT}{dV}\cdot\bar{C}_{p0}$$

$$Ua(T_a - T) = C_{A0}\cdot v_0\,\bar{C}_{p0}\frac{dT}{dV}$$ (+5)

$$\frac{-Ua}{C_{A0}v_0\bar{C}_{p0}}\,dV = \frac{dT}{T-T_a}$$

change $dV \rightarrow d\tau$ (+1)

$$\frac{-Ua}{C_{A0}\bar{C}_{p0}}\,d\tau = \frac{dT}{T-T_a}$$

$$\int_0^{\tau} -\frac{Ua}{C_{A0}\bar{C}_{p0}}\,d\tau = \int_{T_i}^{T}\frac{dT}{T-T_a}$$ (+2)

$$-\frac{Ua\tau}{C_{A0}\bar{C}_{p0}} = \ln\frac{T-T_a}{T_i-T_a}$$

$$\frac{T-T_a}{T_i-T_a} = \exp\left(-\frac{Ua\tau}{C_{A0}\bar{C}_{p0}}\right)$$

$$\therefore\ T = (T_i - T_a)\exp\left(-\frac{Ua\tau}{C_{A0}\bar{C}_{p0}}\right) + T_a$$ (+2)

(b) $\tau = \frac{V}{v_0} = 10\ s$ (+1)

$$\therefore\ T = (400K - 300K)\exp\left(-\frac{125\times10}{10\times\underbrace{50\times2}_{\bar{C}_{p0}}}\right) + 300K$$

$$= 328.6K$$ (+2)

(c) liquid phase $A + B \rightarrow C$

(+6) $\Delta\hat{C}_p = 100 - 100 = 0 \ \text{J/(mol K)}$

$-r_A = r = k C_A C_B = k C_{A0}^2 (1 - X_A)^2$

PFR Design Equation:

$$\frac{dX_A}{dV} = \frac{-r_A}{F_{A0}} = \frac{k C_{A0}^2 (1 - X_A)^2}{v_0 C_{A0}} = \frac{k C_{A0} (1 - X_A)^2}{v_0}$$

$$k = k_{ref} \exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$

$k_{ref} = k_0 = 0.05 \ \text{L/mol·s}$, $E_a = 25{,}000 \ \text{J/mol}$, $R = 8.314$, $T_{ref} = 298\text{K}$

$v_0 = 10 \ \text{L/s}$ $C_{A0} = 10 \ \text{mol/L}$

(+5) Energy Balance: $\cdot\ \Delta\hat{C}_p = 0$

$$\dot{q} - F_{A0}\frac{dT}{dV}\cdot\bar{C}_{p0} - F_{A0}\frac{dX_A}{dV}\Delta H^\circ_{rxn}(ref) = 0$$

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + r_A \Delta H^\circ_{rxn}(ref)}{F_{A0}\bar{C}_{p0}}$$

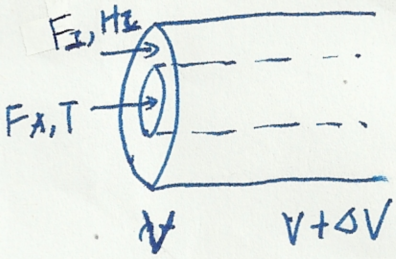
$$r_A = -k C_{A0}^2 (1 - X_A)^2$$

$$\therefore \frac{dT}{dV} = \frac{Ua(T_a - T) - k C_{A0}^2 (1 - X_A)^2 \Delta H^\circ_{rxn}(ref)}{F_{A0}\bar{C}_{p0}}$$

$Ua = 125 \ \text{J/(LSK)}$, $F_{A0} = 100 \ \text{mol/s}$, $\bar{C}_{p0} = 100 \ \text{J/(mol K)}$

$C_{A0} = 10 \ \text{mol/L}$, $\Delta H^\circ_{rxn}(ref) = -25000 \ \text{J/mol}$, k (previous expression)

⑭ For Co-Current flow, $C_{p_I} = 100 J/(mol K)$



Energy Balance

$$F_I H_I|_V - F_I H_I|_{V+\Delta V} + Ua(T-T_a)\Delta V = 0$$

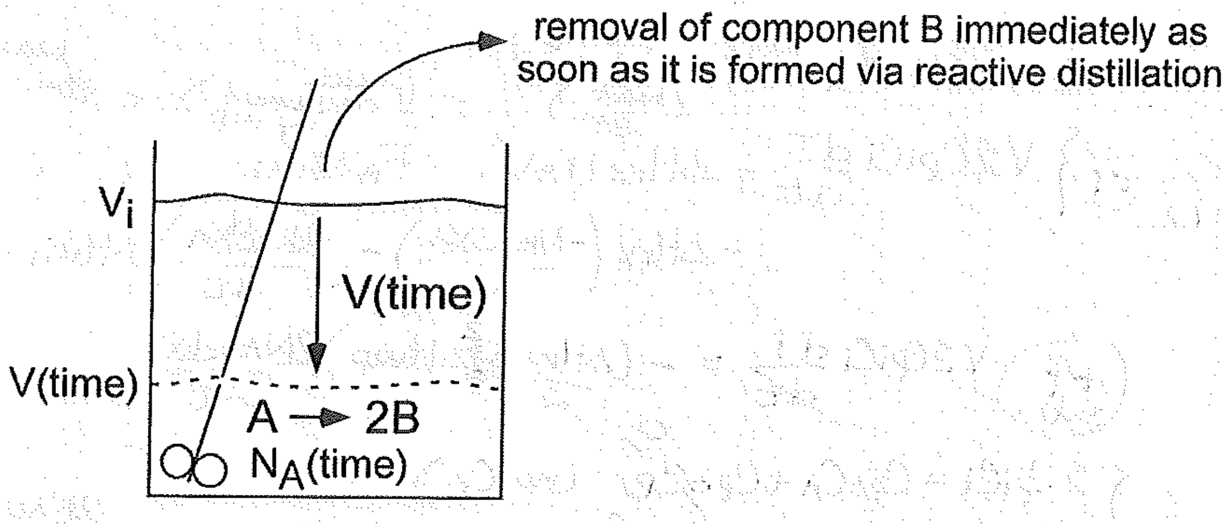
$$-F_I \frac{dH_I}{dV} + Ua(T-T_a) = 0$$

$$\frac{dH_c}{dV} = C_{p_I} \cdot \frac{dT_a}{dV}$$

$$\therefore \frac{dT_a}{dV} = \frac{Ua(T-T_a)}{F_I C_{p_I}} = \frac{\overset{\overset{Ua = 125 J/L\cdot s\cdot K}{\uparrow}}{Ua}(T-T_a)}{\underbrace{C_{p_I}}_{\overset{\downarrow}{100 J/mol\cdot K}} \cdot \frac{\dot{m}_I}{MW_I}}$$

PROBLEM 5. **(27 points)**

A well-stirred tank reactor initially charged with a volume V_i of pure liquid A at temperature T_i undergoes the elementary reaction A → 2B starting at t = 0. This reaction has a standard enthalpy of reaction equal to ΔH^0_{rxn} (kJ/mol), an activation energy E_{act} (kJ/mol), and a preexponential factor A (1/s). All of species B is removed from the reactor via evaporation as soon as it is formed, and has a temperature-independent heat of vaporization equal to ΔH_{vap}. The walls of the reactor are adiabatic – meaning no heat exchange through the walls. All species have the same molar heat capacity of Cp (kJ/(mol °C)) and density (kg/m³), both of which can be assumed to be temperature independent. The molecular weight of A (MW_A) and B ($MW_B = MW_A/2$) are known.



$N_A(\text{time } t = 0) = N_{ao}$

$V(\text{time } t = 0) = V_i$

$T(\text{time } t = 0) = T_i$

Write the reactor volume V explicitly as a function of the reactor temperature T and other known quantities. Show all work. Answers without rigorous justification and reasoning receive zero credit.

We want $V = f(T)$ only.

- mole balance A:

(+2)
$$\frac{dN_A}{dt} = r_A V = -kN_A = -N_{Ao}\frac{dX_A}{dt}$$

- mole balance on B

(+3)
$$\frac{dN_B}{dt} = -2r_AV - F_B = 0$$

F_B = molar flow rate of B out.

↑ = 0 because no accumulation of B.

$$\Rightarrow F_B = -2r_AV = 2N_{Ao}\frac{dX_A}{dt}$$

- mass balance on system:

(+2) $$\frac{d(\rho V)}{dt} = -MW_B \cdot \underbrace{F_B}_{\substack{2r_AV \\ +2kN_A}}$$ (B leaving)

ρ = constant

$$\frac{dV}{\cancel{dt}} = -\frac{MW_B}{\rho} \cdot \left(2N_{A0}\frac{dX_A}{\cancel{dt}}\right)$$

(+2 sub) $$-\left(\frac{\rho}{MW_B}\right)dV = 2N_{A0}\,dX_A$$

[we now have
$V = f(X_A)$.
need $T = f(X_A)$]

- energy balance on system:

For an unsteady state CSTR:

adiabatic: $Q = 0$

(+4) $$V\sum C_{pi}C_i\frac{dT}{dt} = \overset{\text{(heat gen)}}{\Delta H_{rx}(r_AV)} - \overset{\text{(heat consumed by vap)}}{F_B\Delta H_{vap}} + \overset{\text{heat in \& ou}\ \cancel{\text{flowrates}}}{\phi}$$

$$= \Delta H_{rx}\left(-\frac{N_{A0}dX_A}{dt}\right) - \left(\frac{2N_{A0}dX_A}{dt}\right)\Delta H_{vap}$$

(+4 sub) $$V\sum C_{pi}C_i\frac{dT}{\cancel{dt}} = -(\Delta H_{rx} + 2\Delta H_{vap})\frac{N_{A0}dX_A}{\cancel{dt}}$$

(+2) $$\sum C_{pi}C_i = C_{pA}C_A + C_{pB}\overset{0}{\cancel{C_B}} \quad (\text{no } C_B)$$

$\hookrightarrow C_A = \frac{\rho}{MW_A}$ (ρ constant) C_A is constant.

$N_{A0}dX_A$ ‖ (from mass bal)

$$V\left(C_{pA}\cdot\cancel{\frac{\rho}{MW_A}}\right)dT = -(\Delta H_{rx} + 2\Delta H_{vap})\left[\frac{\cancel{1}-\cancel{\rho}}{2MW_B}dV\right]$$

(+3) $$\frac{2C_{pA}\frac{MW_B}{MW_A}dT}{\Delta H_{rx} + 2\Delta H_{vap}} = \frac{dV}{V}$$

$$\Delta H_{rx} = \Delta H^{0}_{RX} + \Delta C_p(T - T_{ref})$$

$$\Delta C_p = 2(C_p) - 1(C_p)$$ from stoich

(+2) $$= +C_p.$$

$$\Delta H_{rx} = \Delta H^{0}_{RX} + C_p(T - T_{ref})$$

$$\Delta H_{rx} + \Delta H_{vap} = \underbrace{\Delta H^{0}_{Rx} + 2\Delta H_{vap}}_{\Delta H_T} + C_p(T - T_{ref})$$

$$\frac{2MW_B}{MW_A} = \frac{2MW_A \frac{1}{2}}{MW_A} = 1$$

+1 So $$\int_{T_0}^{T} \frac{C_{pA}\, dT}{\Delta H_T + C_p(T-T_{ref})} = \int_{V_0}^{V} \frac{dV}{V}$$

solve

+2.

$$\cancel{C_{pA}} \cdot \cancel{\frac{1}{C_p}} \cdot \ln\left[\Delta H_T + C_p(T-T_{ref})\right]\Big|_{T_0}^{T} = \ln V \Big|_{V_0}^{V}$$

$$\ln\left[\frac{\Delta H_T + C_p(T-T_{ref})}{\Delta H_T + C_p(T_0-T_{ref})}\right] = \ln\left(\frac{V}{V_i}\right)$$

$$\boxed{V = V_i \cdot \left[\frac{\Delta H_T + C_p(T-T_{ref})}{\Delta H_T + C_p(T_0-T_{ref})}\right]}$$

$$V = f(T)$$