Phys 427 - HW10

1) $F_L = g_0(T) + \frac{1}{2}\alpha(T-T_c)\xi^2 + \frac{1}{4}g_4(T)\xi^4 + \frac{1}{6}g_6(T)\xi^6$

find extrema: $\left.\frac{\partial F_L}{\partial \xi}\right|_T = \alpha(T-T_c)\xi + g_4\xi^3 + g_6\xi^5 = 0$

$\Rightarrow \xi_{eq} = 0$ or $\xi_{eq}^2 = \dfrac{-g_4 \pm \sqrt{g_4^2 - 4g_6\alpha(T-T_c)}}{2g_6}$

use ξ_{eq} where $T \geq T_c$, expand ξ_{eq}^2 about T_c

$\hookrightarrow \xi_{eq}^2 \approx \dfrac{-g_4 \pm g_4\left(1-(4)(\frac{1}{2})\frac{g_6\alpha(T-T_c)}{g_4^2}\right)}{2g_6} = \dfrac{g_4}{2g_6}\left[-1 \pm \left(1 - \dfrac{2g_6\alpha(T-T_c)}{g_4^2}\right)\right]$

looking @ the positive root

$\hookrightarrow \xi_{eq}^2 = \dfrac{g_4}{2g_6}\left[\dfrac{-2g_6\alpha(T-T_c)}{g_4^2}\right] = \dfrac{\alpha(T_c-T)}{g_4}$

negative root

$\hookrightarrow \xi_{eq}^2 = \dfrac{g_4}{2g_6}\left[-2 + \dfrac{2g_6(T-T_c)}{g_4^2}\right] = -\dfrac{g_4}{g_6} + \dfrac{\alpha(T-T_c)}{g_4}$

$\Rightarrow$ since $g_4, g_6 \geq 0$, this is a complex root ← not physical

$$\boxed{\therefore \xi = \begin{cases} 0, & T \geq T_c \\ A(T_c-T)^{1/2} \text{ w/ } A = \sqrt{\alpha/g_4}, & T < T_c \end{cases}}$$

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2) $E+S \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} ES \xrightarrow[k_{+2}]{} E+P$

a) $\frac{d[E]}{dt} = k_1^- [ES] - k_1^+[E][S] + k_2^+ [ES]$

$\frac{d[ES]}{dt} = -k_1^-[ES] + k_1^+[E][S] - k_2^+[ES] = -\frac{d[E]}{dt}$

$\frac{d[S]}{dt} = -k_1^+[E][S] - k_1^-[ES]$; $\frac{d[P]}{dt} = k_2^+[ES]$

Since $\frac{d[E]}{dt} = -\frac{d[ES]}{dt}$, $\frac{d[E]_{total}}{dt} = \frac{d[E]}{dt} + \frac{d[ES]}{dt} = 0$

$\int$

$\Rightarrow \boxed{[E]_{total} = \text{constant}}$

b) $v = \frac{d[P]}{dt}$, $[ES]$ in SS means $\frac{d[ES]}{dt} = 0 = -\frac{d[E]}{dt}$

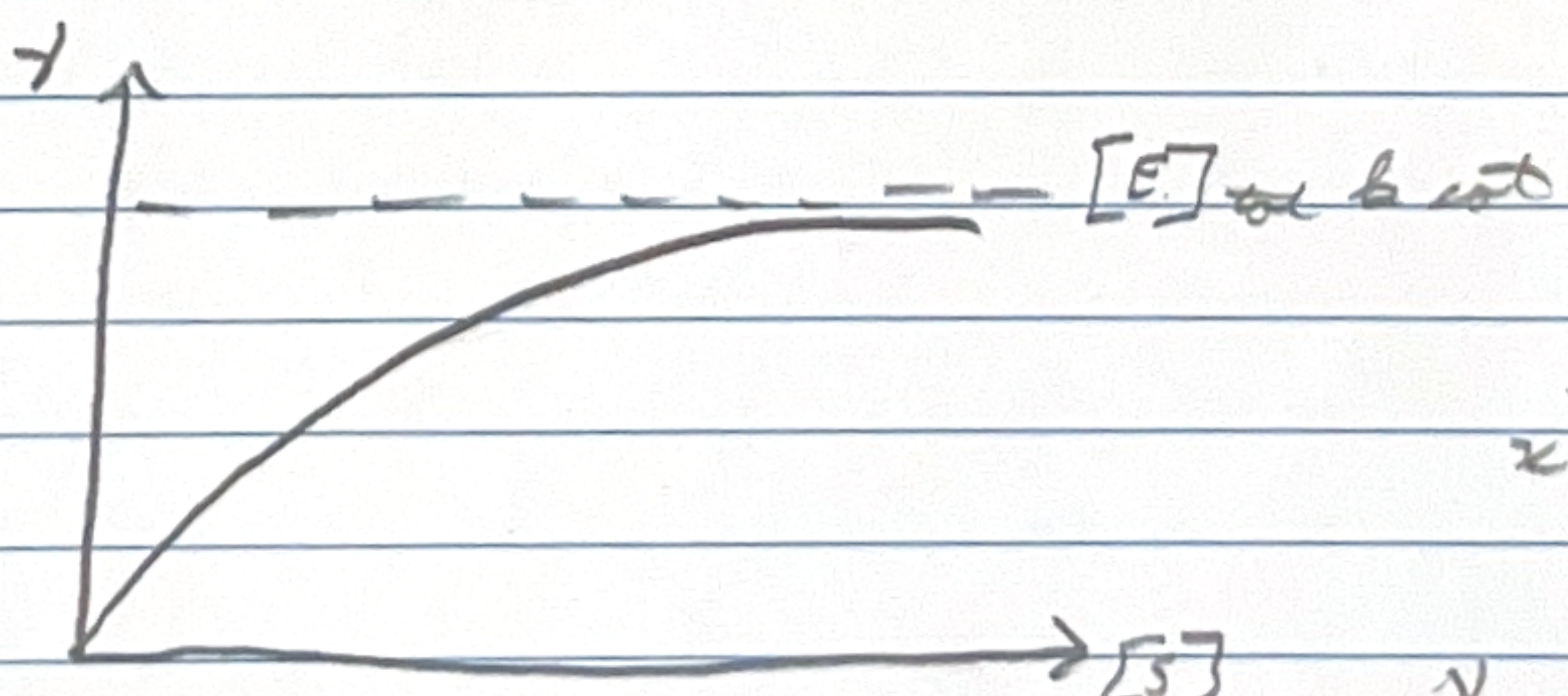
use master Eq

$\Rightarrow k_1^+[E][S] = (k_1^- + k_2^+)[ES] \Rightarrow [ES] = \frac{k_1^+}{k_1^- + k_2^+}[E][S]$

w/ $[E]+[ES] = [E]_{tot}$, $[ES] = k[S]([E]_{tot} - [ES])$ w/ $k = \frac{k_1^+}{k_1^- + k_2^+}$

$\Rightarrow [ES] = \frac{[S][E]_{tot}}{\frac{1}{k} + [S]}$ $\Rightarrow$ into master Eq for $[P]$

$$\boxed{v = \frac{k_2^+ k_1^+ [E]_{tot}[S]}{k_1^- + k_2^+ + [S]} = \frac{k_{cat}[E]_{tot}[S]}{K_M + [S]}, \quad k_{cat} = k_2^+ k_1^+, \; K_M = k_1^- + k_2^+}$$



$\lim_{x\to\infty} A\frac{x}{x+C} = A$, so

$v \to [E]_{tot}\, k_{cat}$

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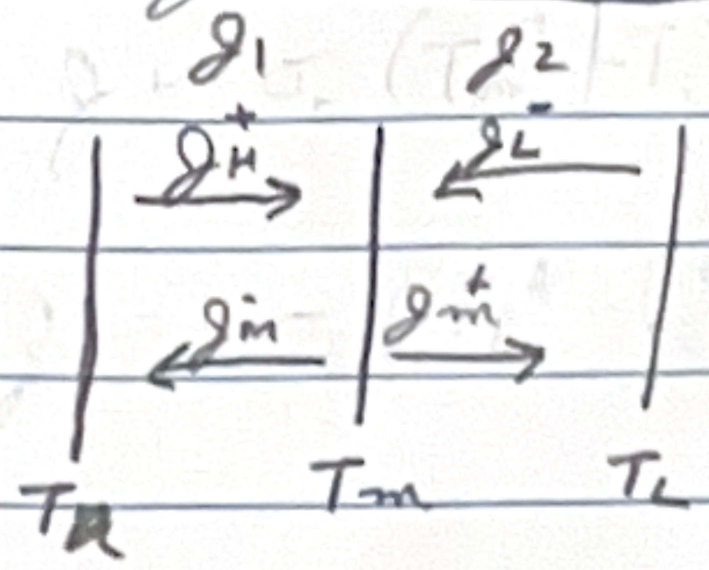
3 a)

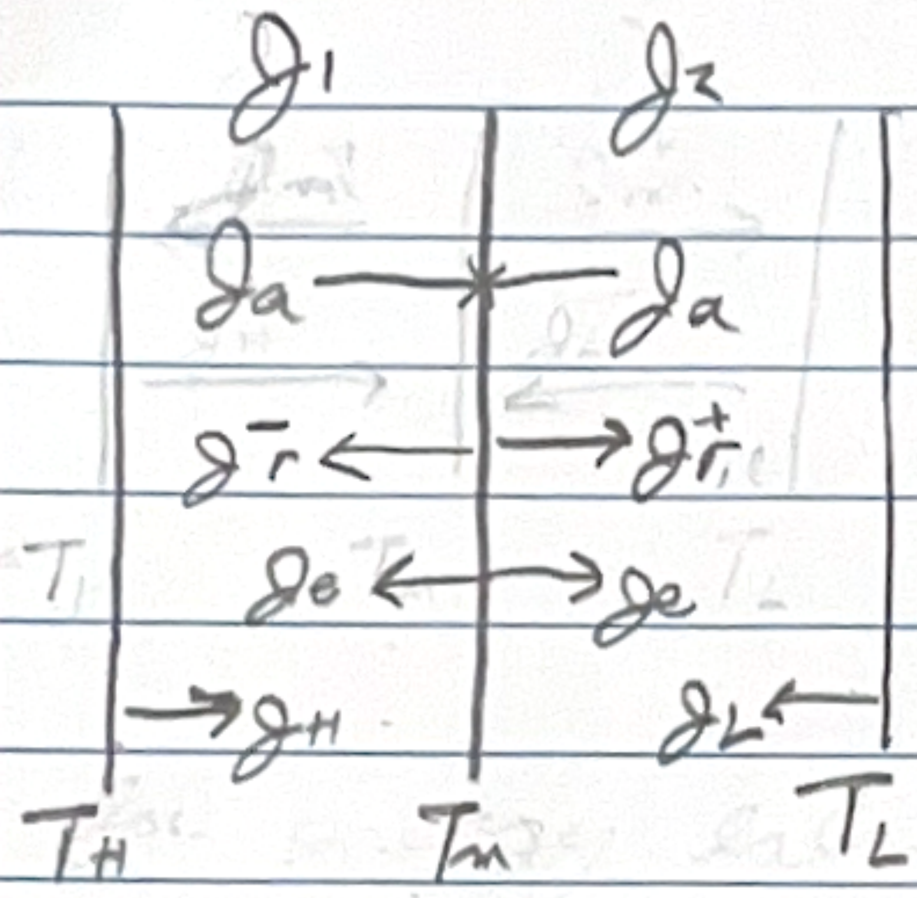


$$\Rightarrow \begin{aligned} J_1 &= J_a^+ + J_m^- = \sigma(T_a^4 - T_m^4) \\ J_2 &= J_m^+ + J_L^- = \sigma(T_m^4 - T_L^4) \end{aligned}$$

Know $J_1 = J_2 \Rightarrow \sigma(T_a^4 - T_m^4) = \sigma(T_m^4 - T_L^4) \Rightarrow 2T_m^4 = T_a^4 + T_L^4 \Rightarrow T_m^4 = \frac{T_a^4 + T_L^4}{2}$

$$\therefore J_1 = \sigma(T_a^4 - T_m^4) = \sigma\left(T_a^4 - \frac{T_a^4 + T_L^4}{2}\right) = \frac{\sigma}{2}(T_a^4 - T_L^4)$$

b)



$$\begin{aligned} J_1 &= J_a - J_e - J_r^- \\ &= \sigma T_a^4 - \epsilon\sigma T_m^4 - r\sigma T_h^4 \\ &= \sigma(1-r)T_a^4 - (1-r)\sigma T_m^4 \end{aligned}$$

$$\begin{aligned} J_2 &= -J_l + J_e + J_r^+ \\ &= -\sigma T_l^4 + e\sigma T_m^4 + r\sigma T_l^4 \\ &= -\sigma(1-r)T_l^4 + (1-r)\sigma T_m^4 \end{aligned}$$

Know $J_1 = J_2$ $\therefore T_m^4 = \frac{1}{2}(T_h^4 + T_l^4)$ like in part a)

$\Rightarrow$ have $J_1 = \sigma(1-r)T_a^4 - (1-r)\sigma\left(\frac{1}{2}(T_h^4 + T_l^4)\right)$

$$\boxed{J_1 = J_2 = \frac{1-r}{2}\sigma(T_a^4 - T_l^4)}$$