0215

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X \xrightarrow{k_2} Y \xrightarrow{k_3} E + P$$

$$Y \xrightarrow{k_4} E_i$$

Law of mass action

$$\frac{d[S]}{dt} = -k_1[E][S] + k_{-1}[X]$$

$$\frac{d[E]}{dt} = -k_1[E][S] + k_{-1}[X] + k_3[Y]$$

$$\frac{d[X]}{dt} = \underset{+}{k_1}[E][S] - k_{-1}[X] - k_2[X]$$

$$\frac{d[Y]}{dt} = k_2[X] - k_3[Y] - k_4[Y]$$

$$\frac{d[E_i]}{dt} = k_4[Y], \quad \frac{d[P]}{dt} = k_3[Y]$$

$E(0) = e_0, \quad S(0) = S_0,$

$X(0) = Y(0) = E_i(0) = P(0) = 0$

$$\frac{d}{dt}\left\{[E] + [X] + [Y] + [E_i]\right\} = 0$$

$$\Rightarrow [E] + [X] + [Y] + [E_i] = e_0$$

$$[E] = \underline{e_0 - [X] - [Y] - [E_i]}$$ valid at all time.

eliminating $[E]$

$$\frac{d[S]}{dt} = -k_1\left(e_0 - [X] - [Y] - [E_i]\right)[S] + k_{-1}[X],$$

$$\frac{d[X]}{dt} = k_1\left(e_0 - [X] - [Y] - [E_i]\right)[S] - (k_{-1} + k_2)[X],$$

$$\frac{d[Y]}{dt} = k_2[X] - (k_3 + k_4)[Y],$$

$$\frac{d[E_i]}{dt} = k_4[Y].$$

nondimensionalization:

$$[S] = s_0 s, \quad [X] = \frac{e_0 s_0}{s_0 + K_m} x$$

$$[Y] = e_0 y, \quad [E_i] = e_0 e_i$$

$$K_m \equiv \frac{k_{-1} + k_2}{k_1}$$

fast-transient timescale

$$\tau \equiv t/t_c = t \cdot \frac{1}{\frac{1}{k_1(s_0 + K_m)}}$$

quasi-steady state timescale

$$T \equiv (1+\rho)\, t/t_s = t \cdot \varepsilon (k_{-1} + k_2)(1+\rho)$$

$$\boxed{\varepsilon \equiv \frac{e_0}{e_0 + K_m}}, \quad \rho \equiv \frac{k_{-1}}{k_2}$$

fast-transient phase:

$$\frac{ds}{d\tau} = \varepsilon\left[-s + \frac{\sigma}{1+\sigma}sx + sy + se_i + \frac{\rho}{(1+\rho)(1+\sigma)}x\right],$$

$$\frac{dx}{d\tau} = s - \frac{\sigma}{1+\sigma}sx - sy - se_i - \frac{x}{1+\sigma},$$

$$\frac{dy}{d\tau} = \frac{\sigma}{(1+\sigma)^2(1+\rho)}x - \frac{\psi}{1+\sigma}y,$$

$$\frac{de_i}{d\tau} = \frac{\phi}{1+\sigma}y,$$

$\rho, \psi, \phi \sim O(1)$

$$\sigma \equiv \frac{s_0}{K_m}, \quad \rho \equiv \frac{k_{-1}}{k_2},$$

inner Solution

$$\psi \equiv \frac{k_3+k_4}{k_{-1}+k_2}, \quad \phi = \frac{k_4}{k_{-1}+k_2}$$

initial conditions:

$\rightarrow$ $s(0)=1, \ x(0)=0, \ y(0)=0, \ e_i(0)=0$

$\Rightarrow$ the above equations give inner solution.

With T as the time scale

$$\frac{ds}{dT} = -s\left[(\sigma+1) - \sigma x - (\sigma+1)y - (\sigma+1)e_i\right] + \frac{\rho}{1+\rho}x$$

$$\varepsilon\frac{dx}{dT} = s\left[(\sigma+1) - \sigma x - (\sigma+1)y - (\sigma+1)e_i\right] - x$$

$$\varepsilon\frac{dy}{dT} = \frac{\sigma}{(1+\sigma)(1+\rho)}x - \psi y$$

$$\varepsilon\frac{de_i}{dT} = \phi y$$

$\Rightarrow$ outer solution

Look at inner solution first:

$$s(\tau) = s^{(0)}(\tau) + \varepsilon s^{(1)}(\tau) + \varepsilon^2 s^{(2)}(\tau) + \cdots$$

$$x(\tau) = x^{(0)}(\tau) + \varepsilon x^{(1)}(\tau) + \varepsilon^2 x^{(2)}(\tau) + \cdots$$

$$y(\tau) = y^{(0)}(\tau) + \varepsilon y^{(1)}(\tau) + \varepsilon^2 y^{(2)}(\tau) + \cdots$$

$$e^{i}(\tau) = e^{i(0)}(\tau) + \varepsilon e^{i(1)}(\tau) + \varepsilon^2 e^{i(2)}(\tau) + \cdots$$

$O(\varepsilon^0)$: $$\frac{d s^{(0)}}{d\tau} = 0 \Rightarrow \boxed{s^{(0)}(\tau) = 1}$$

note that we assume $0 < \varepsilon \ll 1$

$$\varepsilon \equiv \frac{e_0}{e_r + K_m}, \quad e_0 \sim O(1), \quad K_m \gg 1$$

$$\Rightarrow \sigma \equiv \frac{s_0}{K_m} \ll 1$$

$$\frac{dy^{(0)}}{d\tau} = -\frac{\psi}{1+\sigma} y^{(0)}$$

$$y^{(0)}(0) = 0 \Rightarrow \boxed{y^{(0)}(\tau) = 0}$$

$$\frac{d e^{i(0)}(\tau)}{d\tau} = -\frac{\phi}{1+\sigma} y^{(0)} = 0$$

$$\boxed{e^{i(0)}(\tau) = 0}$$

$$\frac{dx^{(0)}}{d\tau} = s^{(0)} - s^{(0)} y^{(0)} - s^{(0)} e^{i(0)} - \frac{x^{(0)}}{1+\sigma}$$

$$- \frac{\sigma s^{(0)} x^{(0)}}{1+\sigma}$$

$$\boxed{\frac{dx^{(0)}}{d\tau} = 1 - x^{(0)}} \Rightarrow \boxed{x^{(0)}(\tau) = 1 - e^{-\tau}}$$

For nontrivial y & e^i, we need to proceed to $O(\varepsilon)$ as follows:

$$\boxed{\varepsilon = \frac{e_0}{S_0}\frac{\sigma}{1+\sigma}}$$

$$(1+\sigma)\varepsilon = \frac{e_0}{S_0}\sigma$$

$$\left(\varepsilon - \frac{e_0}{S_0}\right)\sigma = -\varepsilon$$

$$\boxed{\sigma = \frac{\varepsilon}{\frac{e_0}{S_0} - \varepsilon} = \frac{S_0}{e_0}\frac{\varepsilon}{1 - \frac{S_0}{e_0}\varepsilon}}$$

$$\sim \frac{S_0}{e_0}\varepsilon\left(1 + \frac{S_0}{e_0}\varepsilon\right)$$

$$\boxed{\sigma \sim \frac{S_0}{e_0}\varepsilon + O(\varepsilon^2)}$$

$$\Rightarrow \sigma \simeq \varepsilon P \quad P \sim O(1)$$

$$\frac{dy^{(1)}}{d\tau} = \frac{P}{1+\rho} x^{(0)} - \psi y^{(1)}$$

$$x^{(0)} = 1 - e^{-\tau}$$

$$\left[\frac{dy^{(1)}}{d\tau} + \psi y^{(1)} = \frac{P}{1+\rho}\left(1 - e^{-\tau}\right)\right] e^{\psi\tau}$$

$$\frac{d}{d\tau}\left(e^{\psi\tau} y^{(1)}\right) = \frac{P}{1+\rho}\left(1 - e^{-\tau}\right) e^{\psi\tau}$$

$$e^{\psi\tau} y^{(1)} \Big|_0^{\tau} = \frac{P}{1+\rho}\frac{1}{\psi} e^{\psi\tau}\Big| - \frac{P}{1+\rho}\frac{1}{\psi-1} e^{(\psi-1)\tau}\Big|$$

$$y^{(1)} = \frac{P}{(1+\rho)}\left(\frac{1-e^{-\psi\tau}}{\psi} + \frac{e^{-\psi\tau}-e^{-\tau}}{\psi-1}\right)$$

$$\varepsilon \frac{dy}{dT} = \frac{\sigma}{(1+\sigma)(1+\rho)} x - \psi y \quad \text{—— (3)}$$

$$\varepsilon \frac{de_i}{dT} = \phi y \quad \text{—— (4)}$$

$$S(T) = S_{(0)}(T) + S_{(1)}(T)\varepsilon + S_{(2)}(T)\varepsilon^2 + \cdots$$

recall that $\sigma = \varepsilon p$ with $p \sim \mathcal{O}(1)$

From (2)

$\mathcal{O}(1)$ terms in Eq. (1)

$$\boxed{S_{(0)} - S_{(0)} y_{(0)} - X_{(0)} - S_{(0)} e_{i(0)} = 0}$$

$$\frac{de_i^{(1)}}{d\tau} = \frac{\phi}{1+\varepsilon\rho}\,\frac{\rho}{1+\rho}\left(\frac{1-e^{-\psi\tau}}{\psi} + \frac{e^{-\psi\tau}-e^{-\tau}}{\psi-1}\right)$$

$$e_i^{(1)} = \frac{\phi\rho}{1+\rho}\left(\frac{\tau}{\psi} + \frac{e^{-\tau}-1}{\psi-1} + \frac{1-e^{-\psi\tau}}{\psi^2(\psi-1)}\right)$$

Similarly

$$S^{(1)} = -\frac{\tau}{1+\rho} + \frac{\rho}{1+\rho}\left(e^{-\tau}-1\right)$$

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quasi-steady dynamics

$$\frac{dS}{dT} = -S\Big[(\sigma+1) - \sigma x - (\sigma+1)y - (\sigma+1)e_i\Big] + \frac{\rho}{1+\rho}x \quad \text{— ①}$$

$$\Rightarrow \underline{\underline{\varepsilon\frac{dx}{dT}}} = S\Big[(\sigma+1) - \sigma x - (\sigma+1)y - (\sigma+1)e_i\Big] - x \quad \text{— ②}$$

$$\varepsilon \frac{de_i}{dT} = \phi y \rightarrow \boxed{y_{(0)} = 0}$$

$$\Rightarrow \boxed{x_{(0)} = S_{(0)}(1 - e_{i(0)})}$$

$$y_{(1)} = \frac{P}{\psi(1+\rho)} x_{(0)} \quad \text{from ③}$$

$$\frac{P}{1+\rho} x_{(0)} - \psi y_{(1)} = 0$$

$$\boxed{y_{(1)} = \frac{P}{(1+\rho)\psi} x_{(0)}}$$

$\boxed{\text{Case I}}$ $\rho \sim \mathcal{O}(1)$

$\psi \sim \mathcal{O}(1)$

$\phi \sim \mathcal{O}(1)$

From ①

$$\frac{dS_{(0)}}{dT} = -\frac{1}{1+\rho}\, S_{(0)}\left(1-e_{i(0)}\right)$$

$$\frac{de_{i(0)}}{dT} = \frac{\phi\rho}{\psi(1+\rho)}\, S_{(0)}\left(1-e_{i(0)}\right)$$

$$\frac{de_{i(0)}}{dS_{(0)}} = \frac{\phi\rho}{\psi}$$

$$\int_{B}^{S_{(0)}(T)} \frac{\phi\rho}{\psi}\, dS_{(0)} = \frac{\phi\rho}{\psi}\left(S_0(T) - B\right)$$

$$\frac{1}{\beta}$$

$$e_{i(0)} = \boxed{\frac{\phi\rho}{\psi}}\left(B - S_{(0)}(T)\right)$$

B is $S_{(0)}(T)$ when $T \to 0$

$$S_0(T) \to 1$$

$$e_{i0}(T) \to 0$$

$$X_0(T) \to 1$$

$$y_0(T) \to 0 \qquad \text{as } T \to 0$$

$$\therefore \quad \boxed{e_{i(0)}(T) = \frac{1}{\beta}\left(1 - S_{(0)}(T)\right)}$$

$$\frac{dS_{(0)}}{dT} = -\frac{1}{1+\rho} S_{(0)} \left(1 - e_{i(0)}\right)$$

$$= -\frac{(\beta-1)}{\beta(1+\rho)} S_{(0)} \left[1 - \frac{S_{(0)}}{1-\beta}\right]$$

$$\boxed{S_{(0)}(T) = \frac{1-\beta}{1-\beta e^{T(1-1/\beta)/(1+\rho)}}}$$

Case II $\quad \rho \sim O(1)$

$$\psi \sim O(1)$$

$$\phi \equiv \frac{k_4}{k_{-1}+k_2} \sim O(\varepsilon)$$

$$\varepsilon \frac{dy}{dT} = \frac{\sigma}{(1+\sigma)(1+\rho)} X - \psi y$$

$$\frac{dy_{(0)}}{dT} = 0, \quad \boxed{y_{(0)}(T) = 0}$$

$$\varepsilon \frac{de_{i(0)}}{dT} = \phi y_{(0)} = 0, \quad \boxed{e_{i(0)} = 0}$$

$$\frac{dS_{(0)}}{dT} = -S_{(0)} + \frac{\rho}{1+\rho} X_{(0)}$$

$$\boxed{X_{(0)} = S_{(0)}\left(1 - e_{i(0)}\right) = S_{(0)}}$$

$$\frac{dS_{(0)}}{d\tau} = \frac{-1}{1+\rho} S_{(0)}$$

$$\boxed{S_{(0)} = e^{-\tau/(1+\rho)}}$$ because $S_0(T \to 0) = 1$

$$\varepsilon^2 \frac{de_{i(1)}}{dT} = \phi \varepsilon y_{(1)} = \phi \varepsilon \cdot \frac{\rho}{\psi(1+\rho)} X_{(0)}$$

$$\varepsilon^2 \frac{de_{i(1)}}{dT} = \phi \varepsilon \frac{\rho}{\psi(1+\rho)} S_{(0)}$$

$$\varepsilon \frac{de_{i(1)}}{dT} = \frac{1}{\beta(1+\rho)} e^{-T/(1+\rho)}$$

$$\boxed{\varepsilon e_{i(1)}(T) = \frac{1}{\beta}\left(1 - e^{-\tau/(1+\rho)}\right)}$$

Matching between inner & outer solutions :

Construct the composite solution

$$S_{comp} = S(\tau) + S(T) - \text{common part}$$

common part = inner solution as $\tau \to \infty$

= outer solution as $T \to 0$

Case 2 : $S_{(0)}(\tau) = 1$

$$S_0(T) = e^{-T/(1+\rho)}$$

common part = 1

composite solution for $S_{(0)}$

$$\Rightarrow S_{(0)\,comp} = 1 + e^{-T/(1+\rho)} - 1$$

$$= e^{-T/(1+\rho)}$$

$$= e^{-t/t_s} = \underline{\underline{e^{-\varepsilon(k_{-1}+k_2)t}}}$$

$$e_{i(0)\,comp} = 0$$

$$\varepsilon e_{i(1)\,comp} = \frac{1 - S_{(0)\,comp}}{\beta}$$

$$X_{(0)\,comp} = S_{(0)}(T) + (1 - e^{-\tau})$$

$$- \text{common part}$$

$$= S_{(0)\,comp} - e^{-t/t_c}$$