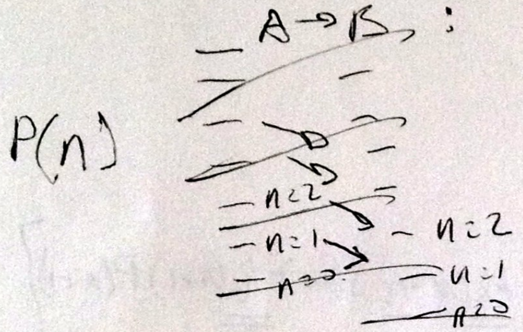
July 21, 2012

$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$ Stochastic Chem ME

<u>States</u>: Total $n_A + n_B = N$

$n \equiv n_A$

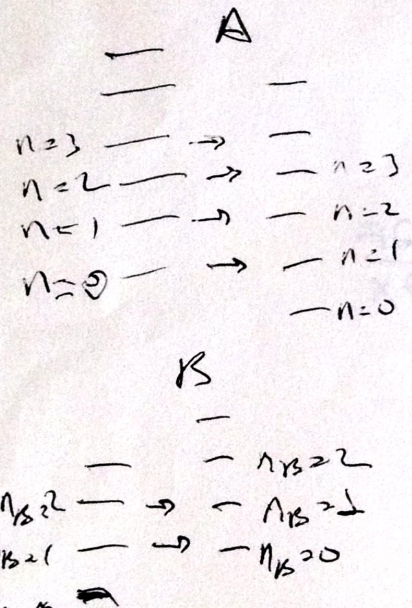
$A \to B$:



$$\frac{dP(n)}{dt} = k_f(n+1)\,P(n+1) - k_f\, n\, P(n)$$

$+$

$B \to A$



$$\frac{dP(n)}{dt} = k_b(N-n+1)\,P(n-1) - k_b(N-n)\,P(n)$$

$$\frac{dP(n)}{dt} = k_b(N-n+1)\,P(n-1) - [k_f n + k_b(N-n)]\,P(n) + k_f(n+1)\,P(n+1)$$

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again

$$\frac{dP(n)}{dt} = k_b(N-n+1)\,P(n-1) - \{k_f n + k_b(N-n)\}\,P(n) + k_f(n+1)\,P(n+1)$$

$n_B = N - n_A = N - n$

for n & $N-n$
$B \to A$
$n+1$ $N-n-1$

or

for $n-1$ & $N-n+1$
n $N-n$

<u>B.C.</u> $t=0 \Rightarrow n = N$

Generating F-n Soln:

$$F(x) = \sum_{n=0}^{N} P(n)\, x^n$$

$$\frac{dF}{dx} = \sum_{n=1}^{N} n P(n) x^{n-1} = \frac{1}{x}\sum_{n=1}^{N} n P(n) x^n = \frac{1}{x}\sum_{n=0}^{N} n P(n) x^n$$

$$x\frac{dF}{dx} = \sum_{n=0}^{N} n P(n) x^n$$

$$x^n \sum_n \left\{ \frac{dP(n)}{dt} = k_b(N - \underset{4}{\underline{n}} + 1) P(n-1) - \left[\underset{1}{\underline{k_f n}} + \underset{2}{\underline{k_b}}(N - \underset{1}{\underline{n}})\right] P_n + \underset{3}{\underline{k_f}}(n+1) P(n+1) \right]$$

$$\frac{\partial F(x,t)}{\partial t} = \cdots \underbrace{- \sum_{n=0}^{\infty} k_f n P(n) x^n \cdots}$$

1) $-k_f x \dfrac{\partial F}{\partial x}$

and $+k_b x \dfrac{\partial F}{\partial x}$

$$\Big\}\; -(k_f - k_b)\frac{\partial F}{\partial x}$$

2) $-k_b N \sum P(n) x^n = -k_b N F(x)$

3) $+k_f \displaystyle\sum_{n=0}^{\infty} (n+1) P(n+1) x^n \to +\frac{k_f}{x}\sum_{n=0}^{\infty} (n+1) P(n+1) x^{n+1}$

$m = n+1$

$$\to +\frac{k_f}{x}\sum_{m=1}^{\infty} m P(m) x^m \to +\frac{k_f}{x}\sum_{m=0}^{\infty} m P(m) x^m \cancel{+P(0)}$$

$$\to +\frac{k_f}{x}\, x\, \frac{\partial F}{\partial x} = +k_f \frac{\partial F}{\partial x}$$

4) $-k_b \sum_{n=} (n-1) P(n-1) x^n \frac{x}{x} = -k_b x \sum_{n=1} (n-1) P(n-1) x^{n-1} \overset{m=n-1}{=}$

summation lower limit?

$- k_b x \sum_{m=0} m P(m) x^{m} = -k_b x \frac{\partial F}{\partial x}$

Eqn for $n=0$

$$\frac{dP(0)}{dt} = -k_b (N-m) P(0) + k_f P(1)$$

(but $\sum_{n=0}^{\infty} n P(n) = \sum_{n=1}^{\infty} n P(n)$)

1 is missing
2 is present
3 is present
4 is missing

$n=1$

$$\frac{dP(1)}{dt} = \underset{\substack{B \to A \\ n_A=0 \quad n_A=1}}{k_b N P(0)} - [k_f + k_b (N-1)] P(1) + k_f (2) P(2)$$

$\dots$

Note: $N-n+1 = N-(n-1)$

4') $k_b N \sum_{n=1} P(n-1) x^{n} \frac{x}{x} = k_b N x \sum_{n=1} P(n-1) x^{n-1}$

$$\xrightarrow{m=n-1} k_b N x \sum_{m} P(m) x^{m} = k_b N F x$$

Putting together:

$$\frac{\partial F}{\partial t} = -(k_f - k_b) \frac{\partial F}{\partial x} x - k_b N F + k_f \frac{\partial F}{\partial x} - k_b x^2 \frac{\partial F}{\partial x} + k_b N F x$$

$$\frac{\partial F}{\partial t} = k_b N (x-1) F + \left[-k_b x^2 - (k_f - k_b) x + k_f \right] \frac{\partial F}{\partial x}$$

Special Case:

$k_f = k_b = k$

$$\frac{1}{k}\frac{\partial F}{\partial t} = N(x-1)F + (1-x^2)\frac{\partial F}{\partial x}$$

$\tau = kt$

$d\tau = k\,dt$

$$\frac{\partial F}{\partial \tau} = N(x-1)F + (1-x^2)\frac{\partial F}{\partial x}$$

B.C.

$$F(x,t) = \sum P(n,t)\, x^n$$

I.C.

at $t=0$ $\quad P(n,t) = \delta_{n,0}$ $\quad [n_A = 0 \;\&\; n_B = N]$

$$F(x,0) = \sum \delta_{n,0}\, x^n = x^0 = 1$$

$$F(x=1) = \sum P_n = 1 \qquad F(1) = 1$$

consistent with IC

SS:

$$(1-x^2)\frac{\partial F}{\partial x} = N(1-x)F$$

$$\frac{1}{F}\frac{dF}{dx} = \frac{N}{1+x}$$

$$\ln F = N\int \frac{d(x+1)}{1+x} + C$$

$$\ln F = N\ln(1+x)\,C$$

$$F = C(1+x)^N$$

$$F(1) = 1 \qquad C\,2^N = 1 \Rightarrow C = 2^{-N}$$

$$F = 2^{-N}(1+x)^N$$

$$F = \sum P_n x^n$$

$$\left.\frac{\partial F}{\partial x}\right|_{x=1} = \sum n P_n x^{n-1} = \frac{1}{x}\sum n P_n x^n\Big|_{x=1} = \sum n P_n = \langle n\rangle$$

$$\left.\frac{\partial F}{\partial x}\right|_{x=1} = N\,2^{-N}(1+1)^{N-1} = N/2$$

$$\left.\frac{\partial^2 F}{\partial x^2}\right|_{x=1} = \sum n(n-1)P_n x^{n-2}\Big|_{x=1} = \frac{1}{x^2}\sum n(n-1)P(n)x^n = \langle n^2\rangle - \langle n\rangle$$

$$\left.\frac{\partial^2 F}{\partial x^2}\right|_{x=1} = N(N-1)2^{-N}(2)^{N-2} = \frac{N^2-N}{4}$$

$$\left.\frac{\partial F}{\partial x^2}\right|_{x=1} = \langle n^2\rangle - \langle n\rangle$$

$$\langle n^2\rangle = \frac{\partial^2 F}{\partial x^2} + \langle n\rangle = \frac{N^2-N}{4} + \frac{N}{2} = \frac{N^2}{4} + \frac{N}{4}$$

$$\sigma^2 = \langle n^2\rangle - \langle n\rangle^2 = \cancel{\frac{N^2}{4}} + \frac{N}{4} - \cancel{\frac{N^2}{4}} = \frac{N}{4}$$

$$\boxed{\sigma = \frac{\sqrt{N}}{2}}$$

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$$\frac{\partial F}{\partial \tau} = N(x-1)F + (1-x^2)\frac{\partial F}{\partial x}$$

$$F(x,\tau) = f(x)g(\tau)$$

$$f(x)\frac{\partial g}{\partial \tau} = g(\tau)(x-1)f(x) + g(\tau)(1-x^2)\frac{\partial f}{\partial x}$$

Divide by: $f \cdot g$:

$$\frac{1}{g}\frac{\partial g}{\partial \tau} = N(x-1) + (1-x^2)\frac{1}{f}\frac{\partial f}{\partial x} = \mu^2$$

$$\frac{\partial \ln g}{\partial \tau} = \mu^2$$

$$\ln g = \mu^2\tau + C'(x)$$

$$g = C(x)e^{\mu^2\tau}$$

$$\frac{d\ln f}{\partial x} = \frac{\mu^2 + (1-x)N}{(1-x^2)}$$

$$\ln f = \mu^2\int\frac{dx}{1-x^2} + \mu^2 N\int\frac{dx}{1+x} + Q(\tau)$$

$\mu^2 \ln(1+x)$

$$\int\frac{dx}{1-x^2} = \int\frac{\cos y\,dy}{\cos^2 y} = \int\frac{dy}{\cos y}$$

$x = \sin y$

$dx = \cos y\,dy$

$1-x^2 = \cos^2 y$

$x = \tan y = \frac{\sin y}{\cos y}$

$dx = \frac{\cos^2 y + \sin^2 y}{\cos^2 y} = \frac{1}{\cos^2 y}dy$

$1 - \tan^2 y = 1 - \frac{\sin^2 y}{\cos^2 y} = \frac{\cos^2 y - \sin^2 y}{\cos^2 y}$

$$\frac{1}{1-x^2} = \frac{1}{(1-x)(1+x)} = \frac{1}{2(1-x)} + \frac{1}{2(1+x)}$$

$$\frac{1}{2}\int_1 \frac{dx}{1-x} = -\int\frac{dx}{x-1} = -\int\frac{d(x-1)}{x-1} = -\ln(x-1)$$

$$\frac{d\ln f}{dx} = \frac{\mu^2 + N(1-x)}{1-x^2} = \frac{\mu^2}{2(1-x)} + \underbrace{\frac{\mu^2}{2(1+x)} + \frac{N}{1+x}}_{\frac{1}{1+x}\left(N+\frac{\mu^2}{2}\right)}$$

$$\ln f = -\frac{\mu^2}{2}\ln(1-x) + \left(N+\frac{\mu^2}{2}\right)\ln(1+x) + Q(\tau)$$

$$\begin{cases} f = (1-x)^{-\mu^2/2}(1+x)^{N+\frac{\mu^2}{2}}\cancel{Q(\tau)} \\ g = e^{\mu^2\tau}\cancel{C(x)} \end{cases}$$

$$(1-x)^{-\mu^2/2}(1+x)^{+\mu^2/2}$$

$$\Rightarrow \left(\frac{1+x}{1-x}\right)^{\mu^2/2}(1+x)^N e^{\mu^2\tau}$$

$$F = f\cdot g = C\,(1-x)^{-\mu^2/2}(1+x)^{N+\mu^2/2}e^{\mu^2\tau}$$

~~$F(x=1) =$~~

$$\frac{\partial F}{\partial\tau} = \mu^2 C(1-x)^{-\mu^2/2}(1+x)^{N+\mu^2/2}e^{\mu^2\tau}$$

$$N(x-1)F = -N\mu^2 C(1-x)^{-\mu^2/2+1}(1+x)^{N+\mu^2/2}e^{\mu^2\tau}$$

$$(1-x^2)\frac{\partial F}{\partial x} = (1-x)(1+x)\frac{\partial F}{\partial x} = (1-x)(1+x)\Big[\mu^2 C\left(-\frac{\mu^2}{2}\right)(1-x)^{-\mu^2/2-1}(1+x)^{N+\mu^2/2}e^{\mu^2\tau}$$

$$+\mu^2 C(1-x)^{-\mu^2/2}\left(N+\mu^2/2\right)(1+x)^{N+\mu^2/2-1}\Big]$$

$$= -\frac{\mu^4}{2}C(1-x^2)^{-\mu^2/2}(1+x)^{N+\mu^2/2+1} + \mu^2 C(1-x)^{-\mu^2/2+1}\left(N+\mu^2/2\right)(1+x)^{N+\mu^2/2}$$

$$\frac{\partial F}{\partial \tau} - (1-x^2)\frac{\partial F}{\partial x} - N(x-1)F = 0$$

$$\begin{cases} \dfrac{d\tau}{ds} = 1 \\ \dfrac{dx}{ds} = x^2 - 1 \\ \dfrac{dz}{ds} = N(x-1) \end{cases}$$

$$IC: \quad \tau(r,0) = 0, \quad x(r,0) = r, \quad z(r,0) = 1$$

$$\tau = s + c_1(r) \Rightarrow \tau = s$$

$$x = -\tanh(\tau - \operatorname{arctanh} r)$$

$$\frac{1}{x^2-1}dx = ds \Rightarrow -\operatorname{arc\,tanh} x = s + c_2(r) \Rightarrow \cancel{x = -\tanh(s + c_2(r))}$$

$$\cancel{r = -\tanh(c_2(r))}$$

$$\frac{dz}{ds} = N(-\tanh(s + c_2(r)) - 1)z$$

$$d \ln z = \int N(-\tanh(s + c_2(r)) - 1)\,ds + c_3(r)$$

$$z(s) = -N\ln - \frac{-\cosh(s) + \sinh(s) r}{\sqrt{1-r^2}} + c_3(r)$$

$$z(0) = \frac{1}{2}\ln(1-r^2)N + c_3(r) = 1 \Rightarrow c_3(r) = 1 - \frac{1}{2}\ln(1-r^2)N$$

$$z(s) = -N\ln + \frac{\cosh(s) - \sinh(s) r}{\sqrt{1-r^2}} + 1 - \frac{1}{2}\ln(1-r^2)N$$

$$s = t, \quad r = \tanh(\tau + \operatorname{arctanh}(x))$$

$$\tau(s) = s$$

$$x(s) = -\tanh(s + c_2(r))$$

$$z(s) = c_3(r)\left[\tanh(s + c_2(r)) - 1\right]^{N/2}\left[\tanh(s + c_2(r) + 1\right]^{N/2} e^{-Ns}$$

$$z(s) = c_3(r)\,(-x(s) - 1)^{N/2}\,(-x(s) + 1)^{N/2}\, e^{-\cancel{Ns}}$$

$$\cancel{z(s) = c_3(r)\,(1 - x^2)^{N/2}\, e^{-Ns}\,(-1)^{N/2}}$$

$$\cancel{z(0) = 1 \qquad x(0) = r}$$

$$\cancel{c_3(r)\,(1 - r^2)^{N/2} = 1 \Rightarrow c_3(r) = \frac{1}{(1 - r^2)^{N/2}}}$$

$$z(s) = (-1)^{N/2} c_3(r)\,(1 + x)^{N/2}(1 - x)^{N/2} e^{-N\tau}$$

$$z(0) = \overset{\text{ignore}}{(\cancel{-1})^{N/2}}\, c_3(r)\,(1 + r)^{N/2}(1 - r)^{N/2} = 1$$

$$c_3(r) = (1 - r)^{-N/2}(1 + r)^{-N/2}$$

$$\left[\begin{array}{l} c_2(r) = \operatorname{arctan} r \\ r = \tanh(\tau + \operatorname{arctanh}(x)) \end{array}\right.$$

$$F(x, \tau) = \cancel{z(r)}\; \cancel{c_3(\tau)} = \frac{(1 + x)^{N/2}(1 - x)^{N/2} e^{-N\tau}}{\left(1 - \tanh^2(\tau + \operatorname{arctanh}(x))\right)^{N/2}}$$

$$\cancel{z(0) = (-1)^{N/2} c_3(r)}$$

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$$\frac{dx}{x^2-1} = \frac{1}{2}\ln\frac{x-1}{x+1} = \cancel{E}s + c$$

$$\cancel{\ln\frac{x-1}{x+1} = e'' \Rightarrow x-1 = e''(x+1)}$$

$$\cancel{x(e''-1) = 2}$$

$$\frac{1}{2}\ln\frac{x-1}{x+1} = s + c'$$

$$\ln\left(\frac{x-1}{x+1}\right)^{1/2} = s + c'$$

$$\cancel{\ln\frac{x-1}{x+1} = \sqrt{s+c'}}$$

$$\cancel{\frac{x-1}{x+1} = e^{(s+c')}}$$

$$\left(\frac{x-1}{x+1}\right)^{1/2} = e^{s}e^{c''}$$

$$\frac{x-1}{x+1} = e^{2s}e^{c''}$$

$$x-1 = e^{2s}e^{c'''}(x+1)$$

$$x(e^{2s}e^{c''}-1) = -e^{2s}e^{c''}-1$$

$$x = \frac{e^{2s}e^{c'''}+1}{1-e^{2s}e^{c'''}} = \frac{e^{+s}e^{c''}+e^{-s}}{e^{-s}-e^{+s}e^{c''}}$$

$$e'' = e^{c''}$$

$$x = \frac{e^{+s}e^{+c}+e^{-s-c}}{e^{-s-c}-e^{+s+c}}$$