A. a) $-\frac{d(I)}{dt} = k(I)(M)$, $-\frac{d(I)}{k(M)dt} = (I)$, $-\frac{d(I)}{d\nu} = (I)$ ← $k(M)dt = d\nu$

$\therefore (I) = (I)_0 e^{-\nu}$, for $t=0$, $\nu=0$

$\frac{d(A_2)}{dt} = k(I)(M) - k(A_2)(M)$, $\frac{d(A_2)}{d\nu} = (I) - (A_2) = (I)_0 e^{-\nu} - (A_2)$

$$e^{\nu}\frac{d(A_2)}{d\nu} + e^{\nu}(A_2) = (I)_0 e^{-\nu}\cdot e^{\nu}$$

$\frac{d}{d\nu}[e^{\nu}(A_2)] = (I)_0$, $(A_2) = \nu e^{-\nu}\cdot(I)_0$, $t=0, \nu=0, (A_2)=0$

$\therefore (A_2) = (I)_0 \nu e^{-\nu}$

$\frac{d(A_3)}{dt} = k(M)(A_2) - k(M)(A_3)$, $\frac{d(A_3)}{d\nu} = (I)_0 \nu e^{-\nu} - (A_3)$

$\frac{d}{d\nu}[e^{\nu}(A_3)] = (I)_0 \nu$, $(A_3) = (I)_0 \frac{\nu^2}{2} e^{-\nu}$

$\vdots$

$(A_4) = (I)_0 \frac{\nu^3}{2\cdot 3} e^{-\nu}$

$\vdots$

$(A_x) = (I)_0 \frac{\nu^{x-1}}{(x-1)!} e^{-\nu}$

$$\therefore X_x = \frac{(A_x)}{\sum_{x=1}^{\infty}(A_x)} = \frac{\cancel{(I)_0} \frac{\nu^{x-1}\cancel{e^{-\nu}}}{(x-1)!}}{\cancel{(I)_0 e^{-\nu}} \sum_{x=1}^{\infty}\frac{\nu^{x-1}}{(x-1)!}} = \frac{\nu^{x-1}}{(x-1)!\,e^{\nu}}$$

$\sum_{x=1}^{\infty}\frac{\nu^{x-1}}{(x-1)!} = e^{\nu}$

$$= \frac{e^{-\nu}\nu^{x-1}}{(x-1)!} \quad (1 \le x \le \infty)$$

which is highly peaked at $x = \nu$

b) $x! \approx \sqrt{2\pi}\, x^{x+\frac{1}{2}} e^{-x}$ Stirling's approximation

$$X_x = \frac{e^{-\nu}\nu^{x-1}}{(x-1)!} = \frac{x}{\nu}\frac{e^{-\nu}\nu^{x}}{x!} \approx \frac{e^{-\nu}\nu^{x}}{x!} \approx \frac{e^{-\nu}\,\nu^{x}}{\sqrt{2\pi}\,x^{x+\frac{1}{2}}e^{-x}}$$

$$= \frac{e^{-\nu}}{\sqrt{2\pi}}\cdot\frac{1}{\nu^{1/2}}\cdot\frac{\nu^{x+1/2}}{x^{x+1/2}}\cdot e^{x} = \frac{e^{-\nu}e^{x}}{\sqrt{2\pi\nu}}\cdot\left(\frac{\nu}{x}\right)^{x+\frac{1}{2}}$$

On the other hand, as given by Hint, $\left(\frac{\nu}{x}\right)^{x+\frac{1}{2}} \approx \left(1-\frac{x-\nu}{x}\right)^{x} = e^{\ln\left(1-\frac{x-\nu}{x}\right)^{x}}$

$$= e^{\nu \ln\left(1-\frac{x-\nu}{x}\right)\frac{x}{\nu}}$$

$$\approx \exp\left\{\nu\left[-\frac{x-\nu}{\nu}-\frac{1}{2}\left(\frac{x-\nu}{\nu}\right)^2\right]\right\}$$

$$= e^{-x}\cdot e^{\nu}\cdot e^{-(x-\nu)^2/2\nu}$$

$$\therefore X(x) \approx \frac{e^{-\nu}e^{x}}{\sqrt{2\pi\nu}}\cdot e^{-x}\cdot e^{\nu}\cdot e^{-(x-\nu)^2/2\nu}$$

$$= \frac{1}{\sqrt{2\pi\nu}}\cdot e^{-(x-\nu)^2/2\nu} \qquad \text{Q.E.D.}$$

c) $$W(x) = \frac{x X(x)}{\int_0^\infty x X(x)\,dx}, \qquad \int_0^\infty x X(x)\,dx = \frac{1}{\sqrt{2\pi\nu}}\int_0^\infty x e^{-(x-\nu)^2/2\nu}\,dx$$

$$\begin{pmatrix} x-\nu \equiv u, & x=0,\ u=-\nu\to-\infty \\ & dx = du \\ & x = u+\nu \end{pmatrix}$$

$$\int_0^\infty x e^{-(x-\nu)^2/2\nu}\,dx = \int_{-\infty}^{\infty}(u+\nu)e^{-u^2/2\nu}\,du$$

$$= \underbrace{\int_{-\infty}^{\infty} u e^{-u^2/2\nu}\,du}_{=0} + \int_{-\infty}^{\infty}\nu e^{-u^2/2\nu}\,d\nu$$

u = odd func.

$e^{-u^2/2\nu}$ = even func.

$$= 2\nu\int_0^\infty e^{-u^2/2\nu}\,d\nu = 2\nu\,\frac{1}{2}\sqrt{\frac{\pi}{1/2\nu}} = \boxed{\nu\sqrt{2\pi\nu}}$$

$$\therefore W(x) = \frac{\frac{1}{\sqrt{2\pi\nu}}\,x e^{-(x-\nu)^2/2\nu}}{\nu} = \frac{1}{\sqrt{2\pi\nu^3}}\,x e^{-(x-\nu)^2/2\nu}$$

Q.E.D.

$$x_n = Q_1/Q_0, \quad x_w = Q_2/Q_1, \quad x_z = Q_3/Q_2$$

$$Q_1 = \nu, \quad Q_0 = 1, \quad x_n = \nu$$

$$Q_2 = \frac{1}{\sqrt{2\pi\nu}} \int_0^\infty x^2 e^{-(x-\nu)^2/2\nu} dx = \frac{1}{\sqrt{2\pi\nu}} \cdot \int_{-\infty}^{\infty} (u+\nu)^2 e^{-u^2/2\nu} du$$

$$= \frac{1}{\sqrt{2\pi\nu}} \left\{ \int_{-\infty}^{\infty} u^2 e^{-u^2/2\nu} du + 2\nu \int_{-\infty}^{\infty} u e^{-u^2/2\nu} du + \nu^2 \int_{-\infty}^{\infty} e^{-u^2/2\nu} du \right\}$$

$$= \frac{1}{\sqrt{2\pi\nu}} \cdot \left\{ 2 \cdot \frac{1}{2^2(\frac{1}{2\nu})} \sqrt{\frac{\pi}{1/2\nu}} + 0 + 2\nu^2 \frac{1}{2}\sqrt{\frac{\pi}{1/2\nu}} \right\} = \underline{\underline{\nu + \nu^2}}$$

$$Q_3 = \frac{1}{\sqrt{2\pi\nu}} \int_0^\infty x^3 e^{-(x-\nu)^2/2\nu} dx = \frac{1}{\sqrt{2\pi\nu}} \int_{-\infty}^{\infty} (u+\nu)^3 e^{-u^2/2\nu} du$$

$$= \frac{1}{\sqrt{2\pi\nu}} \left\{ \int_{-\infty}^{\infty} u^3 e^{-u^2/2\nu} du + \int_{-\infty}^{\infty} 3u^2\nu e^{-u^2/2\nu} du + \int_{-\infty}^{\infty} 3u\nu^2 e^{-u^2/2\nu} du + \int_{-\infty}^{\infty} \nu^3 e^{-u^2/2\nu} du \right\}$$

$$= \frac{1}{\sqrt{2\pi\nu}} \left\{ 0 + 3\nu \cdot \frac{2}{2^2(\frac{1}{2\nu})} \sqrt{2\pi\nu} + 0 + 2\nu^3 \frac{1}{2} \sqrt{2\pi\nu} \right\}$$

$$= \underline{\underline{3\nu^2 + \nu^3}}$$

$$x_w = \frac{\nu + \nu^2}{\nu} = \nu + 1 \approx \nu$$

$$x_z = \frac{3\nu^2 + \nu^3}{\nu + \nu^2} = \frac{\nu(\nu^2+\nu) + 2\nu}{\nu + \nu^2} = \nu + \frac{2\nu}{\nu+\nu^2} = \nu + \frac{2}{1+\nu} \approx \nu$$

B. $$F_1 = \frac{-d(M_1)/dt}{-d(M_1+M_2)/dt} = \frac{k_{11}(M_1\cdot)(M_1) + k_{21}(M_2\cdot)(M_1)}{(k_{11}\text{ step}) + (k_{21}\text{ step}) + (k_{12}\text{ step}) + (k_{22}\text{ step})}$$

$$= \frac{[k_{11}(M_1\cdot)(M_1)/k_{21}(M_2\cdot)(M_2)] + [\cancel{k_{21}(M_2\cdot)}(M_1)/\cancel{k_{21}(M_2\cdot)}(M_2)]}{\frac{k_{11}(M_1\cdot)(M_1)}{k_{21}(M_2\cdot)(M_2)} + \frac{\cancel{k_{21}(M_2\cdot)}(M_1)}{\cancel{k_{21}(M_2\cdot)}(M_2)} + \frac{k_{12}(M_1\cdot)\cancel{(M_2)}}{k_{21}(M_2\cdot)\cancel{(M_2)}} + \frac{k_{22}\cancel{(M_2\cdot)(M_2)}}{k_{21}\cancel{(M_2\cdot)(M_2)}}}$$

From $k_{21}(M_2\cdot)(M_1) = k_{12}(M_1\cdot)(M_2)$

$$(M_1\cdot)/(M_2\cdot) = \frac{k_{21}(M_1)}{k_{12}(M_2)}$$

SPS#3/A

$$F_1 = \frac{\frac{k_{11}(M_1)}{\cancel{k_{21}}(M_2)}\cdot\frac{\cancel{k_{21}}(M_1)}{k_{12}(M_2)} + \frac{(M_1)}{(M_2)}}{\frac{k_{11}}{k_{12}}\left[\frac{(M_1)}{(M_2)}\right]^2 + \frac{(M_1)}{(M_2)} + \frac{\cancel{k_{12}}}{\cancel{k_{21}}}\cdot\frac{\cancel{k_{21}}(M_1)}{\cancel{k_{12}}(M_2)} + \frac{k_{22}}{k_{21}}}$$

$$= \frac{r_1\left[\frac{(M_1)}{(M_2)}\right]^2 + \frac{(M_1)}{(M_2)}}{r_1[\quad]^2 + 2\frac{(M_1)}{(M_2)} + r_2} = \frac{r_1(f_1^2/f_2^2) + (f_1/f_2)}{r_1(f_1^2/f_2^2) + 2(f_1/f_2) + r_2}$$

$$f_1 = \frac{(M_1)}{(M_1)+(M_2)}, \quad f_2 = \frac{(M_2)}{(M_1)+(M_2)}; \quad r_1 \equiv k_{11}/k_{12}, \quad r_2 \equiv k_{22}/k_{21}$$

$$= \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}, \quad Q.E.D.$$

b), d) See next page

c) To prove $\frac{f(1-F)}{F} = r_2 - r_1(f^2/F)$, which is used to extract r_1, r_2 from the exptl f_1 & F_1

where $f \equiv f_1/f_2$ & $F \equiv F_1/F_2$

Proof: start with $F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$, $F_2 = \frac{r_2 f_2^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$

$F_2 = 1 - F_1$

Hence, $F = \frac{r_1 f_1^2 + f_1 f_2}{r_2 f_2^2 + f_1 f_2} = \frac{r_1 f^2 f_2^2 + f f_2^2}{r_2 f_2^2 + f f_2^2} = \frac{r_1 f^2 + f}{r_2 + f}$

$f_1 = f f_2$

$$1 - F = \frac{r_2 + f - r_1 f^2 - f}{r_2 + f} = \frac{r_2 - r_1 f^2}{r_2 + f}$$

$$f\frac{(1-F)}{F} = f\cdot\frac{r_2 - r_1 f^2}{r_1 f^2 + f} = \frac{r_2 - r_1 f^2}{r_1 f + 1} = \frac{r_2 + r_2 r_1 f - r_2 r_1 f - r_1 f^2}{1 + r_1 f}$$

$$= \frac{r_2(1 + r_1 f) - r_1(r_2 f + f^2)}{1 + r_1 f} = r_2 - r_1 f^2 \cdot \frac{(r_2 + f)}{f + r_1 f^2}$$

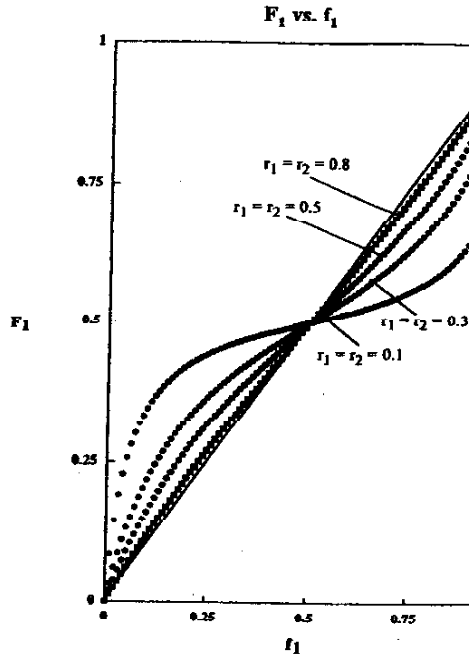
$$= r_2 - r_1\left(\frac{f^2}{F}\right), \quad Q.E.D.$$

e) Styrene $Q_1 = 1.0$, $e_1 = -0.8$; Vinyl acetate $Q_2 = 0.026$, $e_2 = -0.25$ (Table 5.2)

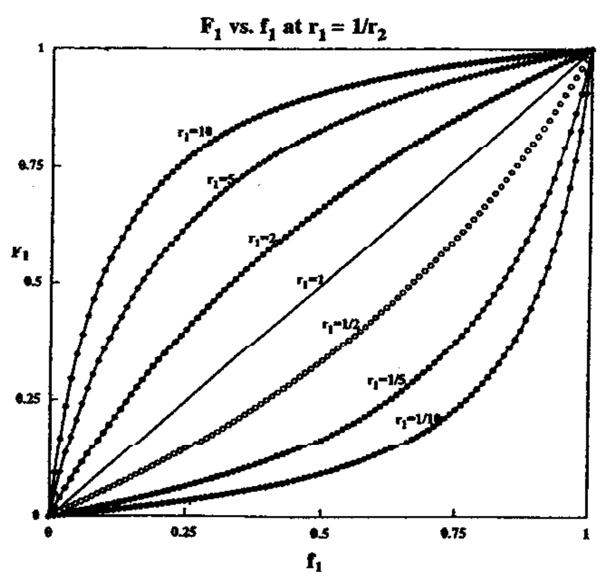
$r_1 = (Q_1/Q_2)\exp[-e_1(e_1 - e_2)] = (1.0/0.026)\cdot\exp[0.8(-0.8+0.25)] \simeq 25$ (55) found

$r_2 = (Q_2/Q_1)\exp[-e_2(e_2 - e_1)] = (0.026/1.0)\cdot\exp[0.25(-0.25+0.8)] \simeq 0.03$ (0.01)

B. b)


F1 vs. f1
r1 = r2 = 0.8
r1 = r2 = 0.5
r1 = r2 = 0.3
r1 = r2 = 0.1
F1
f1
0
0.25
0.5
0.75
1

B. d)


F1 vs. f1 at r1 = 1/r2
r1=10
r1=5
r1=2
r1=1
r1=1/2
r1=1/5
r1=1/10
F1
f1
0
0.25
0.5
0.75
1

C. a) $\sum_{x=0}^{n} P(x,n) = \sum_{x=0}^{n} \frac{n!}{x!(n-x)!} p^x q^{n-x} = (p+q)^n = 1$

$p \equiv 1-q$

b)
$$P(4,4) = \frac{4!}{4!\,0!}\left(\frac{1}{2}\right)^4 = \frac{1}{16}$$
$$P(3,4) = \frac{4!}{3!\,1!}\left(\frac{1}{2}\right)^4 = \frac{4}{16} = \frac{1}{4}$$
$$P(2,4) = \frac{4!}{2!\,2!}\left(\frac{1}{2}\right)^4 = \frac{6}{16} = \frac{3}{8}$$
$$P(1,4) = \frac{4!}{1!\,3!}\left(\frac{1}{2}\right)^4 = \frac{4}{16} = \frac{1}{4}$$
$$P(0,4) = \frac{4!}{0!\,4!}\left(\frac{1}{2}\right)^4 = \frac{1}{16}$$

$$\sum = \frac{2}{16} + \frac{8}{16} + \frac{6}{16} = 1$$

c) See next page

d) See next page

e) $P(x,n) = \frac{n!}{x!(n-x)!} p^x q^{n-x} \xrightarrow[p=q=\frac{1}{2}]{n\to\infty} P(m,n) = \sqrt{\frac{2}{\pi n}}\, e^{-m^2/2n}$

$\downarrow p=q=\frac{1}{2},\ m \equiv n-2x$

$P(m,n) = \frac{n!}{\left(\frac{n+m}{2}\right)!\left(\frac{n-m}{2}\right)!}\left(\frac{1}{2}\right)^n \xrightarrow{n\to\infty}$

Stirling's approx

$x! \cong \sqrt{2\pi}\cdot x^{x+\frac{1}{2}}\cdot e^{-x}$

$-n \le m \le n$

$\begin{pmatrix} x=0,\ m=n \\ x=n,\ m=-n \end{pmatrix}$

The proof is given by Handout for limits

Addendum: $m = n-2x$,

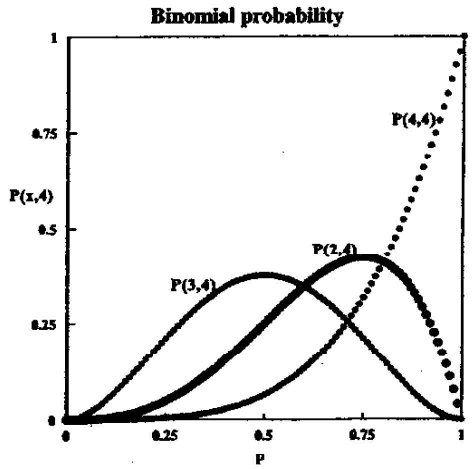
x	m
0	n
1	$n-2$
2	$n-4$
$\vdots$	
$\frac{n}{2}$	0
$\vdots$	
n	$-n$

$P(x,n) = \frac{n!}{x!(n-x)!}\left(\frac{1}{2}\right)^n$ maximizes when $x = \frac{n}{2}$

$P(m,n) = \frac{n!}{\left(\frac{n+m}{2}\right)!\left(\frac{n-m}{2}\right)!}\left(\frac{1}{2}\right)^n$ maximizes when $m=0$

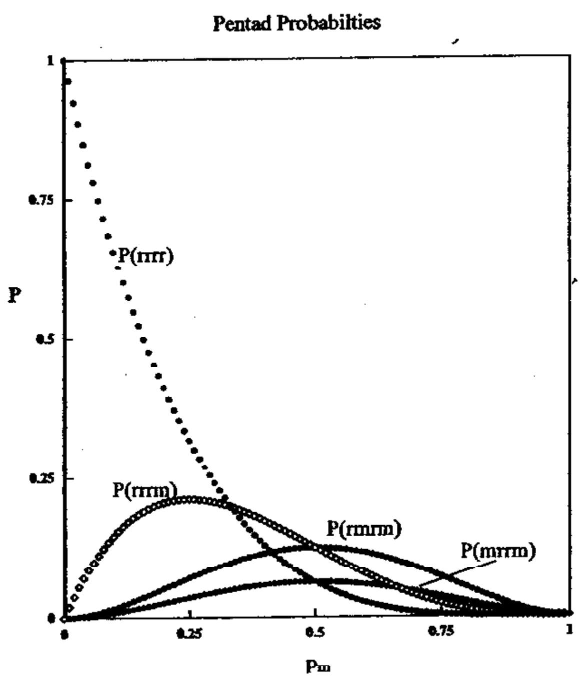
$\underbrace{P(m,n) = \sqrt{\frac{2}{\pi n}}\, e^{-m^2/2n}}_{\text{1D Gaussian}}$ maximizes when $m=0$

C. c)



$$\mathbb{P}(x,4) = \frac{4!}{x!(4-x)!} \cdot p^x (1-p)^{4-x}$$

d)



All sequences of pentad

mmmm

(rmmm, mmmr)

(mrmm, mmrm)

(rrmm, mmrr)

(rmrm, mrmr)

rmmr

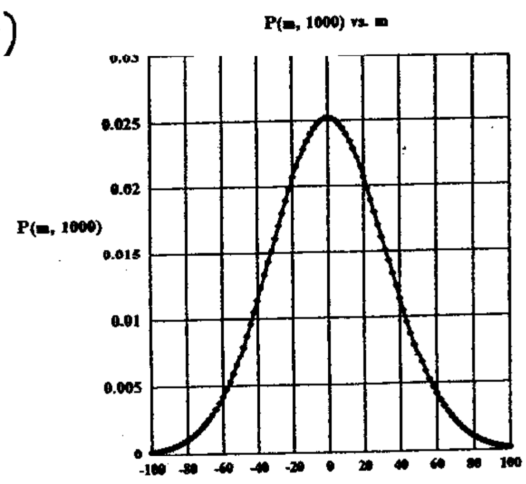
mrrm

(mrrr, rrrm)

(rmrr, rrmr)

rrrr

e)



$$\mathbb{P}(m,1000) = \left(\frac{2}{1000\pi}\right)^{1/2} e^{-m^2/2000}$$

$$\mathbb{P}(0,1000) = \left(\frac{2}{1000\pi}\right)^{1/2} = 0.0252$$

$$Q_1 = \int_{-\infty}^{\infty} m\,\mathbb{P}(m,1000)\,dm = \left(\frac{2}{1000\pi}\right)^{1/2} \int_{-\infty}^{\infty} \underbrace{m}_{\text{odd}}\ \underbrace{e^{-m^2/2000}}_{\text{even}}\,dm = 0$$