

Chem 664

Solution to
Problem Set #2

A. (1) Given that $g(N, s) = \sum_N s^N F_N$

$$s \frac{d}{ds} g(N, s) = \sum_N s N s^{N-1} F_N = \sum_N N s^N F_N$$

$$s \frac{d^{(2)}}{ds^2} g(N, s) = \sum_N s N \cdot N s^{N-1} F_N = \sum_N N^2 s^N F_N$$

$$\vdots$$

$$s \frac{d^{(k)}}{ds^k} g(N, s) = \sum_N N^k s^N F_N, \quad \left[s \frac{d^{(k)}}{ds^k} g(N, s) \right]_{s=1} = \sum_N N^k F_N \equiv m_k$$

(2) If $F_N = (1-p)p^{N-1}$, $g(N, s) = (1-p)s \sum_{N=1}^{\infty} s^{N-1} p^{N-1} = \frac{(1-p)s}{(1-sp)}$

$$s \frac{d}{ds} g(N, s) = s \left[\frac{(1-p)}{(1-sp)} + \frac{(1-p)s(-p)(-1)}{(1-sp)^2} \right] = s \frac{1-p}{(1-sp)^2}$$

$$m_1 = 1 \frac{(1-p)}{(1-p)^2} = \frac{1}{1-p}$$

$$s \frac{d^{(2)}}{ds^2} g(N, s) = s \left[\frac{(1-p)}{(1-sp)^2} + \frac{5(1-p)(-p)(-2)}{(1-sp)^3} \right] = \frac{s(1-p)(1+sp)}{(1-sp)^3}$$

$$m_2 = \frac{1+p}{(1-p)^2}$$

$$s \frac{d^{(3)}}{ds^3} g(N, s) = s \frac{d}{ds} \left[\frac{(1-p)(1+sp)}{(1-sp)^3} \right] = s(1-p) \left[\frac{(1+2sp)(1-sp) + s(1+sp)(-3p)}{(1-sp)^4} \right]$$

$$= s(1-p) \left[\frac{1 + p - 2s^2p^2 + 3sp + 3s^2p^2}{(1-sp)^4} \right] = s(1-p) \left[\frac{1+4sp+p^2}{(1-sp)^4} \right]$$

$$m_3 = \frac{(1-p)(1+4p+p^2)}{(1-p)^4} = \frac{1+4p+p^2}{(1-p)^3}$$

$$s \frac{d^{(4)}}{ds^4} g(N, s) = (1-p)s \frac{d}{ds} \left[\frac{1+4sp+p^2}{(1-sp)^4} \right] = s(1-p) \left[\frac{1+8sp+3s^2p^2}{(1-sp)^4} \right]$$

$$+ \frac{(5+4s^2p+s^3p^2)4p}{(1-sp)^5} \Bigg]$$

$$= s(1-p) \left[\frac{1+11sp+11s^2p^2+s^3p^3}{(1-sp)^5} \right]$$

$$m_4 = \frac{1+11p+11p^2+p^3}{(1-p)^4}$$

Note here that $\sum$ of coefficients of the numerator for k th moment is $k!$ which is consistent with $k!/q^k$ in the cont. limit

$$A. (3) \quad G(N, s) = \int_0^{\infty} e^{-sN} F(N) dN$$

SPS2/2

$$\frac{d}{ds} G(N, s) = \int_0^{\infty} (-N) e^{-sN} F(N) dN = (-1) \int_0^{\infty} N e^{-sN} F(N) dN$$

$$\frac{d^2}{ds^2} G(N, s) = \int_0^{\infty} (-N)(-N) e^{-sN} F(N) dN = \int_0^{\infty} N^2 e^{-sN} F(N) dN$$

$$\vdots$$

$$\frac{d^k}{ds^k} G(N, s) = \frac{d^{(k)}}{ds^{(k)}} G(N, s) = (-1)^k \int_0^{\infty} N^k e^{-sN} F(N) dN$$

$$(-1)^k \left[\frac{d^{(k)}}{ds^{(k)}} G(N, s) \right]_{s=0} = (-1)^k \int_0^{\infty} N^k e^{-0} F(N) dN$$

$$= \int_0^{\infty} N^k F(N) dN = \mu_k, \text{ Q.E.D.}$$

$$B. 1) \quad \alpha \leq 1, \quad (1-\alpha) \equiv \zeta, \quad w_N = \frac{N(N-1)}{2} \alpha^{N-2} (1-\alpha)^3$$

$$= \frac{N(N-1)}{2} \frac{\alpha^N}{\alpha^2} (1-\alpha)^3$$

$$w(N, \zeta) \approx \frac{N^2}{2} e^{-\zeta N} \zeta^3 \quad \text{where} \quad \frac{\alpha^N}{\alpha^2} \approx \alpha^N = (1-\zeta)^N$$

$$\approx e^{-\zeta N}$$

$$\& N-1 \approx N, \quad 0 \leq N \leq \infty$$

Normalization of $w(N, \zeta)$

$$\int_0^{\infty} \frac{N^2}{2} e^{-\zeta N} \zeta^3 dN = \frac{\zeta^3}{2} \frac{2!}{\zeta^3} = 1$$

$$\uparrow \int_0^{\infty} x^2 e^{-ax^2} dx = \frac{2!}{a^3}$$

$$\text{Hence } \mu(N, \zeta) = A \frac{N}{2} e^{-\zeta N} \zeta^3 \quad \text{since } \mu(N, \zeta) \propto \frac{w(N, \zeta)}{N}$$

$$1 = \frac{A}{2} \zeta^3 \int_0^{\infty} N e^{-\zeta N} dN = \frac{A}{2} \zeta^3 \frac{1!}{\zeta^2} = \frac{A\zeta}{2}, \quad \therefore A = \frac{2}{\zeta}$$

$$\mu(N, \zeta) = N e^{-\zeta N} \zeta^2$$

$$m_2 = \int_0^\infty N^2 n(N, \xi) = \xi^2 \int_0^\infty N^2 N e^{-\xi N} dN$$

$$= \xi^2 \frac{3!}{\xi^4} = \frac{3!}{\xi^2}$$

SPS2/3

$$m_3 = \xi^2 \int_0^\infty N^3 N e^{-\xi N} dN = \xi^2 \frac{4!}{\xi^5} = \frac{4!}{\xi^3}$$

$$N_3 = m_3/m_2 = 4/\xi = 4/(1-\alpha)$$

$$m_k = \frac{(k+1)!}{\xi^k}$$

$$N_w = m_2/m_1 = 3/\xi = 3/(1-\alpha)$$

B.2) Poisson distribution, $n_N = \frac{e^{-\nu} \nu^N}{(N-1)!}$ which is highly peaked at $N \approx \nu \gg 1$

$$\frac{\nu^{N-1}}{(N-1)!} = \frac{N \nu^{N-1}}{N!} = \left(\frac{N}{\nu}\right) \frac{\nu^N}{N!} \approx \frac{\nu^N}{N!} \text{ since } \left(\frac{N}{\nu}\right) \approx 1 \text{ when } n_N \text{ is finite}$$

$$n_N = \frac{e^{-\nu} \nu^N}{N!} \approx \frac{e^{-\nu} e^N}{(2\pi\nu)^{1/2}} \left(\frac{\nu}{N}\right)^{N+1/2}, \quad N! \approx (2\pi\nu)^{1/2} N^{N+1/2} e^{-N} \text{ (Stirling's approx)}$$

$$\left(\frac{\nu}{N}\right)^{N+1/2} = \left(1 - \frac{N-\nu}{N}\right)^{N+1/2} \approx \left(1 - \frac{N-\nu}{N}\right)^N = \left[\left(1 - \frac{N-\nu}{N}\right)^{N/\nu}\right]^\nu$$

$$\left(\frac{\nu}{N}\right)^N = \exp\left[\ln\left(\frac{\nu}{N}\right)^N\right] = \exp\left[\nu \ln\left(1 - \frac{N-\nu}{N}\right)^{N/\nu}\right]$$

whereas

$$\left(1 - \frac{N-\nu}{N}\right)^{N/\nu} = 1 - \left(\frac{N-\nu}{N}\right) + \dots$$

thus,

$$\ln\left(1 - \frac{N-\nu}{N}\right)^{N/\nu} \approx \ln\left[1 - \left(\frac{N-\nu}{N}\right) + \dots\right] \approx \ln\left[1 - \left(\frac{N-\nu}{\nu}\right)\right] = -\frac{N-\nu}{\nu} - \frac{(N-\nu)^2}{2! \nu^2} - \dots$$

$$\therefore \nu \ln\left(1 - \frac{N-\nu}{N}\right)^{N/\nu} \approx \nu \left[-\frac{N-\nu}{\nu} - \frac{(N-\nu)^2}{2! \nu^2} - \dots\right]$$

$$\approx -(N-\nu) - \frac{(N-\nu)^2}{2\nu} - \dots$$

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

$$n_N \approx \frac{e^{-\nu} \cdot e^N}{(2\pi\nu)^{1/2}} \cdot e^{-N} \cdot e^{+\nu} \cdot e^{-(N-\nu)^2/2\nu} = \frac{1}{(2\pi\nu)^{1/2}} e^{-(N-\nu)^2/2\nu}$$

SPS2/5

$$\left[\frac{d}{ds} G(N, s) \right]_{s=0} = \left(\frac{\lambda s}{2} - 1 \right) \nu G(N, s) \Big|_{s=0} = -\nu$$

$$m_1 = +\nu$$

$$\begin{aligned} \frac{d^2}{ds^2} G(N, s) &= \nu G(N, s) + \nu(s-1)\nu(s-1)G(N, s) \\ &= [\nu + \nu^2(s-1)^2] G(N, s) \text{ where } G(N, s) \Big|_{s=0} = 1 \\ m_2 &= \nu + \nu^2 \end{aligned}$$

$$\begin{aligned} \frac{d^3}{ds^3} G(N, s) &= \frac{d}{ds} \{ [\nu + \nu^2(s-1)^2] G(N, s) \} \\ &= 2\nu^2(s-1)G(N, s) + [\nu + \nu^2(s-1)^2]\nu(s-1)G(N, s) \\ &= [3\nu^2(s-1) + \nu^3(s-1)^3] G(N, s) \\ m_3 &= 3\nu^2 + \nu^3 \end{aligned}$$

$$N_3 = m_3/m_2 = \frac{3\nu^2 + \nu^3}{\nu + \nu^2} \approx \nu$$

$$N_w = m_2/m_1 = \frac{\nu + \nu^2}{\nu} = 1 + \nu \approx \nu$$

C. (1.35) $W_N = p^{N-1} N (1-p)^2$, $\ln W_N = (N-1)\ln p + \ln N + 2\ln(1-p)$

Since at $N_{\max}$, $W_{N_{\max}} > 0$, $\frac{dW_N}{dN} = \frac{d \ln W_N}{dN}$

$$\left. \frac{d \ln W_N}{dN} \right|_{N_{\max}} = \ln p + \frac{1}{N_{\max}} = 0, \quad N_{\max} = \frac{1}{\ln(\frac{1}{p})}$$

$$\begin{aligned} \text{If } p \lesssim 1, \quad \ln\left(\frac{1}{p}\right) &= \ln\left[\frac{1}{1-1+p}\right] = \ln\left[\frac{1}{1-(1-p)}\right] \\ &= \ln[1 + (1-p) + (1-p)^2 + \dots] \approx \ln[1 + (1-p)] \\ &\approx (1-p) + \frac{(1-p)^2}{2!} + \dots \approx (1-p) \end{aligned}$$

Hence $N_{\max} = \frac{1}{1-p} = N_n$

p	0.99	0.995	0.998
N_n	100	200	500
$N_{\max}$	99.5	199.5	499.5

$$(i) \quad n_N(p) = \frac{(N+f-2)!}{(f-1)!(N-1)!} p^{N-1} (1-p)^f \text{ for } N\text{-mer with } f\text{-branch}$$

$p^{N-1} (1-p)^f$ is analog of MPD with termination probability for each f branch

$(N-1 + f-1) = \#$ of objects whose permutation is $(N+f-2)!$

$$\text{Distinct combinations} = \frac{(N+f-2)!}{(f-1)!(N-1)!}$$

$$\text{Thus, } n_N(p) = \frac{(N+f-2)!}{(f-1)!(N-1)!} p^{N-1} (1-p)^f, \quad f=1, \quad n_N(p) = \frac{(N-1)!}{0!(N-1)!} p^{N-1}$$

Normalization:

$$\sum_{N=1}^{\infty} n_N(p) = (1-p)^f \sum_{N=1}^{\infty} \frac{(N+f-2)!}{(f-1)!(N-1)!} p^{N-1} \quad \left[\begin{array}{l} = p^{N-1} (1-p) \\ \text{MPD} \end{array} \right]$$

$$= (1-p)^f \left\{ \frac{(f-1)!}{(f-1)!0!} p^0 + \frac{f!}{(f-1)!1!} p + \frac{(f+1)!}{(f-1)!2!} p^2 + \dots \right\}$$

$$= (1-p)^f \left\{ 1 + fp + \frac{(f+1)f}{2!} p^2 + \frac{(f+2)(f+1)f}{3!} p^3 + \dots \right\}$$

$$= (1-p)^f \cdot \frac{1}{(1-p)^f} = 1, \text{ normalized}$$

$$(ii) \quad N_n \stackrel{?}{=} \frac{(f-1)p+1}{1-p}$$

$$g(N, s) = \sum s^N n_N(p) = (1-p)^f \left\{ s \frac{(f-1)!}{(f-1)!} p^0 + s^2 \frac{f!}{(f-1)!} p + s^3 \frac{f(f+1)}{2!} p^2 + \dots \right\}$$

$$m_1(N) = \left[s \frac{d}{ds} g(N, s) \right]_{s=1} \quad \left[\begin{array}{l} = (1-p)^f \frac{s}{(1-sp)^f} \end{array} \right]$$

$$= \left[s (1-p)^f \left\{ \frac{1}{(1-sp)^f} + \frac{fs p}{(1-sp)^{f+1}} \right\} \right]_{s=1}$$

$$= \left[(1-p)^f \cdot \frac{s(1-sp) + fs^2 p}{(1-sp)^{f+1}} \right]_{s=1} = \left[(1-p)^f \frac{(f-1)s^2 p + s}{(1-sp)^{f+1}} \right]_{s=1}$$

$$= \frac{(f-1)p+1}{(1-p)}, \quad \text{Q.E.D.} \quad \text{If } f=1, \quad m_1 = \frac{1}{1-p}, \text{ MPD mult}$$

(iii) To prove that $\frac{N_w}{N_n} \approx 1 + \frac{1}{f}$

$$\begin{aligned}
 m_2(N) &= \left\{ s \frac{d}{ds} \left[(1-p)^f \frac{(f-1)s^2 p + s}{(1-sp)^{f+1}} \right] \right\}_{s=1} \\
 &= \left\{ s(1-p)^f \left[\frac{(f-1)2sp+1}{(1-sp)^{f+1}} + \frac{[(f-1)s^2 p + s](f+1)p}{(1-sp)^{f+2}} \right] \right\}_{s=1} \\
 &= (1-p)^f \left\{ \frac{(f-1)2p+1}{(1-p)^{f+1}} + \frac{[(f-1)p+1](f+1)p}{(1-p)^{f+2}} \right\} \\
 &= \frac{(1-p)[(f-1)p+1 + (f-1)p] + [(f-1)p+1](f+1)p}{(1-p)^2} \\
 &= \frac{[(f-1)p+1](1+pf) + (1-p)(f-1)p}{(1-p)^2}
 \end{aligned}$$

$$N_w = m_2(N)/m_1(N) = \frac{1+pf}{(1-p)} + \frac{p(f-1)}{(f-1)p+1}$$

If $f=1$, $N_w = \frac{1+p}{1-p}$ which is of MPD

$$N_w/N_n = \frac{\frac{1+pf}{(1-p)} + \frac{p(f-1)}{(f-1)p+1}}{\frac{(f-1)p+1}{(1-p)}} = \frac{1+pf}{(f-1)p+1} + \frac{p(1-p)(f-1)}{[(f-1)p+1]^2}$$

$$\begin{aligned}
 &\approx \underbrace{\frac{1+f}{f}}_{\substack{\uparrow \\ p \rightarrow 1}} + \underbrace{\frac{(1-p)(f-1)}{f^2}}_{\substack{\uparrow \\ f \rightarrow 0}} \approx 1 + \frac{1}{f}
 \end{aligned}$$

$$\begin{aligned}
 N_w/N_n &\approx 2 \quad (\text{MPD result}) \\
 &\quad \uparrow \\
 &\quad f=1
 \end{aligned}$$

E. (1.37)

We use the notations given in Handout #5-1

$$(i) n_N = \frac{(N_n - 1)^{N-1}}{(N-1)!} e^{(1-N_n)} = \frac{\nu^{N-1} e^{-\nu}}{(N-1)!}, \quad \nu \equiv N_n - 1$$

$$(ii) w_N = \frac{N n_N}{\sum N n_N}, \quad \sum_{N=1}^{\infty} N n_N = e^{-\nu} \sum \frac{N \nu^{N-1}}{(N-1)!}$$

$$= e^{-\nu} (1 \cdot \frac{\nu^0}{0!} + 2 \cdot \frac{\nu^1}{1!} + 3 \cdot \frac{\nu^2}{2!} + 4 \cdot \frac{\nu^3}{3!} + \dots)$$

$$= (1+\nu) e^{-\nu} \cdot e^{\nu} = 1+\nu = N_n$$

$$\therefore w_N = \frac{N \nu^{N-1} e^{-\nu}}{(1+\nu)(N-1)!}$$

$$(iii) N_w = \sum N w_N$$

$$= \sum \frac{N^2 \nu^{N-1} e^{-\nu}}{(1+\nu)(N-1)!}$$

$$= \frac{e^{-\nu}}{(1+\nu)} (1^2 \frac{\nu^0}{0!} + 2^2 \frac{\nu^1}{1!}$$

$$+ 3^2 \frac{\nu^2}{2!} + 4^2 \frac{\nu^3}{3!} + \dots)$$

$$= \frac{e^{-\nu}}{(1+\nu)} (1 + 4\nu + \frac{9}{2!} \nu^2 + \frac{16}{3!} \nu^3 + \dots) = \frac{e^{-\nu}}{(1+\nu)} \cdot e^{\nu} (1 + 3\nu + \nu^2)$$

$$e^{\nu} (1 + 3\nu + \nu^2) = 1 + \nu + \frac{\nu^2}{2!} + \frac{\nu^3}{3!} + \frac{\nu^4}{4!} + \dots$$

$$+ 3\nu + 3\nu^2 + 3 \frac{\nu^3}{2!} + 3 \frac{\nu^4}{3!} + \dots$$

$$+ \nu^2 + \nu^3 + \frac{\nu^4}{2!}$$

$$= 1 + 4\nu + \frac{8+1}{2!} \nu^2 + \frac{1+9+6}{3!} \nu^3 + \frac{1+12+12}{4!} \nu^4 + \dots$$

$$= 1 + 4\nu + \frac{9}{2!} \nu^2 + \frac{16}{3!} \nu^3 + \frac{25}{4!} \nu^4 + \dots$$

$$\therefore N_w = \frac{\nu^2 + 3\nu + 1}{\nu + 1}$$

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

$$N_w / N_n = \frac{N_n^2 + N_n - 1}{N_n^2} = 1 + \frac{1}{N_n} - \frac{1}{N_n^2} \approx 1 + \frac{1}{N_n}$$

$$PDI = 1.01 \text{ if } N_n = 100$$

F. (1.40)

SPS 2/9

$$T/c = RT \left(\frac{1}{M_n} + A_2 c + \dots \right)$$

Units in cgs: pressure $\frac{\text{dyn}}{\text{cm}^2} = \frac{\text{erg}}{\text{cm}^3} = 10^{-1} \text{ Pa}$

$$\text{dyn} = g \cdot \frac{\text{cm}}{\text{s}^2} = 10^{-3} \text{ kg} \frac{10^{-2} \text{ m}}{\text{s}} = 10^{-5} \text{ N}$$

$$\frac{\text{dyn}}{\text{cm}^2} = \frac{10^{-5} \text{ N}}{10^{-4} \text{ m}^2} = 10^{-1} \text{ N/m}^2 = 10^{-1} \text{ Pa}$$

Thermal energy

$$RT = 8.314 \cdot 10^7 \frac{\text{erg}}{\text{mol} \cdot \text{K}} \cdot 296.15 \text{ K} = 2.46 \cdot 10^{10}$$

$$= 8.314 \cdot \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot 296.15 \text{ K} = 2.46 \cdot 10^3$$

$$T/c \Rightarrow \frac{\text{dyn/cm}^2}{\text{g/cm}^3} = \frac{g \cdot \frac{\text{cm}}{\text{s}^2} / \text{cm}^2}{\text{g/cm}^3} = \frac{1/\text{s}^2 \cdot \text{cm}}{1/\text{cm}^3} = \text{cm}^2/\text{s}^2$$

$$A_2 \Rightarrow \frac{\text{cm}^2/\text{s}^2}{\frac{\text{erg}}{\text{mol}} \cdot \frac{\text{g}}{\text{cm}^3}} = \frac{\frac{\text{cm}^2/\text{s}^2}{\text{mol} \cdot \text{s}^2} \cdot \frac{\text{g}}{\text{cm}^3}}{\frac{\text{g} \cdot \text{cm}^2}{\text{mol} \cdot \text{s}^2} \cdot \frac{\text{g}}{\text{cm}^3}} = \text{mol} \cdot \text{cm}^3/\text{g}^2$$

$$C (\text{g/cm}^3) \quad 2 \cdot 10^{-3} \quad 4 \cdot 10^{-3} \quad 6 \cdot 10^{-3} \quad 8 \cdot 10^{-3} \quad 10 \cdot 10^{-3}$$

$$T/c (\text{dyn/cm}^2) \quad 508 \quad 1040 \quad 1580 \quad 2150 \quad 2740$$

$$T/c (\text{cm}^2/\text{s}^2) \quad 2.54 \cdot 10^5 \quad 2.60 \cdot 10^5 \quad 2.63 \cdot 10^5 \quad 2.69 \cdot 10^5 \quad 2.74 \cdot 10^5$$

$$\text{Intercept: } 2.45 \cdot 10^5$$

$$\text{Slope: } 2.5 \cdot 10^6$$

$$M_n = \frac{8.314 \cdot 10^7 \cdot 2.9615 \cdot 10^2}{2.45 \cdot 10^5}$$

$$\approx 10^5 \text{ g/mol}$$

$$A_2 = \frac{2.5 \cdot 10^6}{8.314 \cdot 10^7 \cdot 2.9615 \cdot 10^2}$$

$$\approx 10^{-4} \text{ mol} \cdot \text{cm}^3/\text{g}^2$$