Chemistry 553

Problem set 1

Due: 14 January 2011

1. Dill and Bromberg, 2nd ed, P(problem) 2.1
2. Sum the series:
$$S(m) = \sum_{i=0}^{\infty} k^m p^k \tag{1}$$
for $m = 2, m = 3$.
3. P4.5
4. P4.6
5. P4.13
6. Derive
$$\ln N! \simeq N \ln N - N + \ln(\sqrt{2\pi N}) \tag{2}$$
starting from the expression for the gamma function
$$\Gamma(N+1) = N! = \int_0^{\infty} dx e^{-x} x^N = \int_0^{\infty} dx e^{N g(x)} \qquad g(x) = \ln x - x/N \tag{3}$$
The integrand is sharply peaked about x^*. Derive x^*, and expand $g(x)$ about the maximum to quadratic order,
$$g(x) = g(x^*) - \frac{1}{2N^2}(x - x^*)^2 \tag{4}$$
Substitute $g(x)$ into the gamma-function integral and perform the integration. The approximation for $\ln N!$ should result.

Problem set 1

1. P2.1

$$W = N! / \{(N-M)!\, M!\}$$ where N = # of sites

and M = # of indistinguishable particles

$$W_a = \frac{20!}{(20-15)!\,15!} = \frac{20\cdot 19\cdot 18\cdot 17\cdot 16}{5\cdot 4\cdot 3\cdot 2\cdot 1} = \frac{19\cdot 18\cdot 17\cdot 16}{6}$$

$$= 15504$$

$$W_b = \frac{16!}{(16-15)!\,15!} = 16$$

$$W_c = 1$$

2.

$$S(M) = \sum_{k=0}^{\infty} k^M p^k = \left(p\frac{\partial}{\partial p}\right)^M \sum_{k=0}^{\infty} = \left(p\frac{\partial}{\partial p}\right) \frac{1}{1-p}$$

so that $$S(2) = \left(p\frac{\partial}{\partial p}\right)^2 \frac{1}{1-p} = \frac{p(1+p)}{(1-p)^3}$$

$$S(3) = \left(p\frac{\partial}{\partial p}\right)^3 \frac{1}{1-p} = \frac{p(1+4p+p^2)}{(1-p)^4}$$

3 P4.5a

$$f(x,y) = -(x-a)^2 - (y-b)^2$$

constraint $y - kx = 0$

$$df = -2(x-a)dx - 2(y-b)dy$$

constraint: $k\,dx - dy = 0$

so

$$df = [-2(x-a) + k\lambda]dx + [-2(y-b) - \lambda]dy = 0$$

or $k\lambda = 2(x-a)$, $y - b = -\lambda/2$

$x = \frac{1}{2}k\lambda + a$, $y = b - \lambda/2$

but $y = kx \Rightarrow b - \frac{\lambda}{2} = [\frac{1}{2}k\lambda + a]k$

$$\therefore \lambda = \frac{b-ak}{\frac{1}{2}k^2 + \frac{1}{2}} = \frac{2(b-ak)}{1+k^2}$$

so that

$$x = \frac{1}{2}\frac{k \cdot 2(b-ak)}{1+k^2} + a$$

$$x = \frac{k(b-ak)}{1+k^2} + a = \frac{a}{1+k^2} + \frac{bk}{1+k^2}$$

and

$$y = b - \frac{(b-ak)}{1+k^2} = \frac{b + (ak - b)}{1+k^2}$$

$$Y = \frac{bk^2}{1+k^2} + \frac{ak}{1+k^2}$$

3. P4.5 b

$$f(x,y) = (x-x_0)^2 + (y-y_0)^2 \quad \text{subject to} \quad y = 2x$$

$$df = 2(x-x_0)\,dx + 2(y-y_0)\,dy$$

constraint $\lambda[dy - 2dx]$

so that

$$df\Big|_{\text{constraint}} = \left[2(x-x_0) - 2\lambda\right]dx + \left[2(y-y_0) + \lambda\right]dy = 0$$

$$\Rightarrow \quad x - x_0 - \lambda = 0$$

$$x = x_0 + \lambda, \quad y - y_0 = -\lambda/2, \quad y = y_0 - \lambda/2$$

$$2x = y \Rightarrow \quad 2x_0 + 2\lambda = y_0 - \lambda/2$$

$$2x_0 - y_0 = -\frac{5}{2}\lambda$$

$$\therefore \quad \lambda = \frac{2}{5}(y_0 - 2x_0)$$

and $x = x_0 + \frac{2}{5}(y_0 - 2x_0) = \frac{1}{5}x_0 + \frac{2}{5}y_0$

$$y = y_0 - \frac{1}{5}(y_0 - 2x_0) = \frac{4}{5}y_0 + \frac{2x_0}{5}$$

which satisfies $2x = y$

4. P4.6

$$f = x^2 + 3y^2$$
$$y = 5u + 3$$

$$df = \left(\frac{df}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

change $dy \rightarrow \left(\frac{dy}{\partial u}\right)_x du$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial u}\right)_x du$$

$$= 2x\,dx + 6y \cdot 5\,du = 2x\,dx + 30y\,du$$

$$\therefore \left(\frac{\partial f}{\partial u}\right)_x = \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial u}\right)_x, \text{ and ; } \left(\frac{\partial f}{\partial u}\right)_x = 30y$$

$$\left(\frac{\partial f}{\partial u}\right)_x = 30(5u+3), \quad @\ u=1, \left(\frac{\partial f}{\partial u}\right)_x = 240$$

5. P4.13

a) $$\frac{2nRT}{(V-nb)^2}\,dV + \frac{R(V-nb)}{nb^2}\,dT$$

$\frac{\partial}{\partial T}$ $\qquad$ $\frac{\partial}{\partial V}$ $\qquad$ not exact

$$\frac{2nR}{(V-nb)^2} \overset{?}{=} \frac{R}{nb^2}$$

whereas

$$\frac{-nRT}{(V-nb)^2}\,dV + \frac{nR}{(V-nb)}\,dT$$

Take $\frac{\partial}{\partial T}$, take $\frac{\partial}{\partial V}$

$$\frac{\partial}{\partial T}\left(\frac{-nRT}{(V-nb)^2}\right) = \frac{-nR}{(V-nb)^2} = \frac{\partial}{\partial V}\left(\frac{nR}{V-nb}\right)$$

$\therefore$ an exact differential.

6.

$$N! = \int_0^\infty dx\, e^{-x} x^N = \int_0^\infty dx\, e^{-x}\, e^{\ln x^N}$$

so $$N! = \int_0^\infty dx\, \exp(-x + N\ln x) = \int_0^\infty dx\, \exp(Ng(x))$$

where $Ng(x) = -x + N\ln(x) = N\left\{\ln(x) - \frac{x}{N}\right\}$

$$g(x) = \ln(x) - \frac{x}{N} = \ln(x^*) - \frac{x^*}{N} + (x-x^*)\frac{\partial g(x)}{\partial x}$$
$$+ \frac{1}{2}(x-x^*)^2\frac{\partial^2 g}{\partial x^2} + \cdots$$

$$\frac{\partial}{\partial x}g(x) = \frac{1}{x} - \frac{1}{N} = 0 \Rightarrow x^* = N$$

$$\frac{\partial^2 g(x)}{\partial x^2} = -\frac{1}{x^2} = -\frac{1}{N^2}$$ so that

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

so now,

$$N! = \int_0^\infty dx \, \exp\left(N\left[g(N) - \frac{1}{2N^2}(x-N)^2\right]\right)$$

$$= \exp(Ng(N)) \underbrace{\int_0^\infty dx \, \exp\left(-\frac{1}{2N}(x-N)^2\right)}_{(2\pi N)^{1/2}}$$

so $\ln(N!) = Ng(N) + \ln(2\pi N)^{1/2}$

$$Ng(N) = N[\ln(N) - 1]$$

and $\ln(N!) = N\ln(N) - N + \frac{1}{2}\ln(2\pi N)$

as required.