Chemical Physics Cumulative Examination
September 16, 2009

The examination will focus on the application of mathematical series in the physical description of chemical systems and chemical processes. You should support your answers with brief justifications. Explain any assumptions you make when proposing solutions to the problems below. An equation sheet with constants, conversions, and integrals is provided.

Q1 (30 points): Consider the geometric series

$$s = \sum_{n=0}^{\infty} \frac{1}{2^n} \quad (1)$$

a) determine whether the series converges
b) determine which partial sum approximates the series to 1%
c) the series in Eq. 1 can be written in a more general form

$$s = \sum_{n=0}^{\infty} ar^n \quad (2)$$

determine the value for the series in equation 2
d) show that the partial sum for equation 2 is

$$S_n = a\left(\frac{1-r^n}{1-r}\right) \quad (3)$$

e) the molecular partition function is defined in the statistical mechanics of non-interacting molecules as the sum over all the states of one molecule

$$z = \sum_{i=0}^{\infty} \exp\left(\frac{-E_i}{k_B T}\right) \quad (4)$$

where i is an index specifying the state, E_i is the energy of state i, k_B is the Boltzmann constant, and T is absolute temperature. If we consider only the vibration of a diatomic molecule, to a good approximation the energy E_i can be expressed as

$$E_i = E_v = h\nu\left(v + \frac{1}{2}\right) \quad v = 0,1,2,\ldots \quad (5)$$

where ν is the vibrational frequency, v is the vibrational quantum number, and h is Planck's constant. Use your answer in Q1(c) to find the value of the partition function for vibration.

Q2 (20 points): A power series has the form

$$s(x) = a_0 + a_1(x-h) + a_2(x-h)^2 + a_3(x-h)^3 \ldots \quad (6)$$

and when h=0 it is called a Maclaurin series.

a) show that the formula in Eq. 7 below is correct for the coefficients in the vicinity of x=0 for an arbitrary function f(x) that can be represented by a Maclaurin series

$$a_n = \frac{1}{n!}\left(\frac{d^n f}{dx^n}\right)_0 \quad n = 1,2,3,\ldots \quad (7)$$

b) show that the Maclaurin series for e^x is

$$e^x = 1 + \frac{1}{1!}x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \frac{1}{4!}x^4 + \dots \quad (8)$$

c) the virial series is a power series used to represent the behavior of a non-ideal gas

$$\frac{P\overline{V}}{RT} = 1 + \frac{B_2}{\overline{V}} + \frac{B_3}{\overline{V}^2} + \frac{B_4}{\overline{V}^3} + \dots \quad (9)$$

the pressure virial equation of state, which is a Maclaurin series in P, also is a commonly used series equation of state.

$$P\overline{V} = RT + A_2 P + A_3 P^2 + A_4 P^3 + \dots \quad (10)$$

show that A_2 in Eq. 9 is equal to B_2 in Eq. 10

d) If two power series in the same independent variable are equal to each other, what can be said regarding the values of the corresponding coefficients in the series?

Q3 (15 points): A Taylor series expansion has the same functional form as Eq. 6 except that h is not equal to zero. The boiling temperature T of a solution can be determined from the mole fraction of pure solute X_1 using the relation

$$-\ln X_1 = \frac{\Delta H_v}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \quad (11)$$

where ΔH_v is the molar heat of vaporization, T_0 is the normal boiling point, and R is the gas constant.

a) find the Taylor series for ln(x) about x=1

b) the mole fraction of the solute X_2, assuming only one component in the solution other than the solvent, is $X_2 = 1 - X_1$. Use this relation, and your answer in Q3(a) to show that

$$X_2 + \frac{1}{2}X_2^2 + \frac{1}{3}X_2^3 + \dots = \frac{\Delta H_v}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \quad (12)$$

c) determine how large X_2 can be to truncate Eq. 12 to the form

$$X_2 \approx \frac{\Delta H_v}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \quad (13)$$

where the inaccuracy increases above 1%.

Q4: (35 points) Fourier series are sine and cosine functions which can be applied to problems with periodic solutions to reach series convergence rapidly. For example, a Fourier series that represents a periodic function of period 2L is

$$f(x) = a_0 + \sum_{n=1}^{\infty} a_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{\infty} b_n \sin\left(\frac{n\pi x}{L}\right) \quad (14)$$

a) show that the basis functions in the series in Eq. 14 are periodic with period 2L

b) the property of orthogonality is typically used to find the coefficients of a Fourier series. Define the three equations for orthogonality for Eq. 14.

c) find the expressions for a_0 and a_n.

d) find the Fourier series to represent the function f(x) = x for the interval $-L < x < L$

e) plot the resulting series in Q4(d) in the range $-3L < x < 3L$

$k = 1.3805 \times 10^{-16}$ erg K^{-1} = 1.3805×10^{-23} J K^{-1}
$h = 6.6256 \times 10^{-27}$ erg s = 6.6256×10^{-34} J s
1 J = 1.439×10^{20} kcal mol^{-1} = 1×10^{7} erg = 6.242×10^{18} eV = 5.034×10^{22} cm^{-1} = 0.2390 cal
1 atm = 760 torr = 1.01325 bar = 1.01325×10^{5} Pa

Integrals

$$\int \sin ax\, dx = -\frac{1}{a}\cos ax$$

$$\int \sin^2 ax\, dx = \frac{x}{2} \quad \frac{\sin 2ax}{4a}$$

$$\int \sin^3 ax\, dx = -\frac{1}{3a}\cos ax\left[\sin^2 ax + 2\right]$$

$$\int \sin ax \cos ax\, dx = \frac{1}{2a}\sin^2 ax$$

$$\int x\sin^2 ax\, dx = \frac{x^2}{4} - \frac{x\sin 2ax}{4a} - \frac{\cos 2ax}{8a^2}$$

$$\int x^2\sin^2 ax\, dx = \frac{x^3}{6} - \left(\frac{x^2}{4a} - \frac{1}{8a^3}\right)\sin 2ax - \frac{x\cos 2ax}{4a^2}$$

$$\int \cos ax\, dx = \frac{1}{a}\sin ax\, dx$$

$$\int \cos^2 ax\, dx = \frac{x}{2} + \frac{\sin 2ax}{4a}$$

$$\int \cos^3 ax\, dx = \frac{1}{a}\sin ax - \frac{1}{3a}\sin^3 ax$$

$$\int x\cos^2 ax\, dx = \frac{x^2}{4} + \frac{x\sin 2ax}{4a} + \frac{\cos 2ax}{8a^2}$$

$$\int x^2\cos^2 ax\, dx = \frac{x^3}{6} + \left(\frac{x^2}{4a} - \frac{1}{8a^3}\right)\sin 2ax + \frac{x\cos 2ax}{4a^2}$$

$$\int_0^\infty x^{2n}e^{-ax^2}\, dx = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}a^n}\left(\frac{\pi}{a}\right)^{1/2} \quad (n \text{ positive integer})$$

$$\int_0^\infty x^{2n+1}e^{-ax^2}\, dx = \frac{n!}{2a^{n+1}} \quad (n \text{ positive integer})$$

$$\int_0^\infty x^n e^{-ax}\, dx = \frac{n!}{a^{n+1}} \quad (n \text{ positive integer})$$

$$\int_0^\infty e^{-ax^2}\, dx = \left(\frac{\pi}{4a}\right)^{1/2}$$

$$\int_0^\infty xe^{-ax^2}\, dx = \frac{1}{2a}$$

$$\int \sin(a+bx)dx = -\frac{1}{b}\cos(a+bx)$$

$$\int \cos(a+bx)dx = \frac{1}{b}\sin(a+bx)$$

$$\int x\sin(x)dx = \sin(x) - x\cos(x)$$

$$\int x\cos(x)dx = \cos(x) + x\sin(x)$$

$$\int x^2\sin(x)dx = 2x\sin(x) - (x^2-2)\cos(x)$$

$$\int x^2\cos(x)dx = 2x\cos(x) + (x^2-2)\sin(x)$$

$$\int \sin(x)\cos(x)dx = \frac{\sin^2(x)}{2}$$

$$\int \sin^2(x)\cos^2(x)dx = \frac{1}{8}\left[x - \frac{\sin(4x)}{4}\right]$$

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Q1 a) Convergence of $S = \sum_{n=0}^{\infty} \frac{1}{2^n}$

Ratio test

$$r = \lim_{n\to\infty} \frac{\frac{1}{2^{n+1}}}{\frac{1}{2^n}} = \lim_{n\to\infty} \frac{2^n}{2^{n+1}} = \lim_{n\to\infty} \frac{\cancel{2^n}}{\cancel{2^n}\cdot 2} = \frac{1}{2}$$

since $r<1$, series converges

Q1 b) partial sum approximates the series to 1% for $s = \sum_{n=0}^{\infty} \frac{1}{2^n}$

$$\text{Total sum} = 1 + \frac{1}{2} + \frac{1}{4} + \frac{1}{8} + \cdots$$

$$= 1 + \frac{1}{2}\left(1 + \frac{1}{2} + \frac{1}{4} + \frac{1}{8} \cdots\right)$$

$$S = 1 + \frac{1}{2} S \qquad \text{here } \underline{\underline{S=2}}$$

for partial sum 1%, remaining partial sum = 0.02
what is first term that contributes at this level?

$\overset{n=1}{\frac{1}{2} = 0.5}$ $\overset{n=2}{\frac{1}{4} = 0.25}$ $\overset{n=3}{\frac{1}{8} = 0.125}$ $\overset{n=4}{\frac{1}{16} = 0.0625}$ $\overset{n=5}{\frac{1}{32} = 0.0317}$

$\overset{n=6}{\boxed{\frac{1}{64} = 0.0156}}$

need first seven terms.

$$S = 1 + \frac{1}{2} + \frac{1}{4} + \frac{1}{8} + \frac{1}{16} + \frac{1}{32} + \frac{1}{64} = \boxed{1.9844}$$

Q1 c) $S = \sum_{n=0}^{\infty} ar^n$, what is value of s?

$$S = a + ar + ar^2 + ar^3 + \cdots)$$

$$= a + r(a + ar + ar^2 + \cdots) = a + rs$$

$$\boxed{S = \frac{a}{1-r}}$$

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Q1 d)

$$S_n = a + ar + ar^2 + .. + ar^{n-1}$$

$$= a(1 + r + r^2 + r^{n-1}) \cdot \frac{(1-r)}{(1-r)}$$

$$\boxed{= a\frac{(1-r^2)}{(1-r)}}$$

Q1 e)

$$Z = \sum_{i=0}^{\infty} e^{-E_i/k_bT} \qquad E_i = E_v = h\nu(v+\tfrac{1}{2})$$

$$Z_{vib} = \sum_{v=0}^{\infty} e^{-h\nu(v+\frac{1}{2})/k_bT}$$

$$= \sum_{v=0}^{\infty} e^{-h\nu v/k_bT} e^{-h\nu/2k_bT}$$

$$= e^{-h\nu/2k_bT} \sum_{v=0}^{\infty} e^{-h\nu v/k_bT} \qquad \text{set } x = h\nu/k_BT$$

$$e^{-x/2} \sum_{v=0}^{\infty} e^{-xv}$$

geometric series of form

$$S = \sum ar^n$$

where $a = 1$

$r = e^{-x}$

$n = v$

$$S = \frac{a}{1-r} = \frac{1}{1-e^{-x}}$$

$$\boxed{Z_{vib} = e^{-x/2}/(1-e^{-x})\ ;\ x = h\nu/k_BT}$$

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Q2 a) Maclaurin series $h = 0$

$$S(x) = f(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \dots$$

about $x = 0$

$$a_0 = 0$$

$$a_1 = \frac{d\, f(x)}{1\, dx} \qquad a_n = \frac{d^n f(x)}{n!\, dx^n} \text{ about } x = 0$$

$$a_2 = \frac{d^2 f(x)}{2\, dx^2} \qquad \boxed{a_n = \frac{1}{n!}\left(\frac{d^n f}{dx^n}\right)_0}$$

$$a_3 = \frac{d^3 f(x)}{2 \cdot 3\, dx^3}$$

$$\vdots$$

Q2 b) Maclaurin series $e^x = 1 + \frac{1}{1!}x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 \dots$

$$S(x) = e^x = a_0 + a_1 x + a_2 x^2 + \dots$$

$$a_n = \frac{1}{n!}\left(\frac{d^n f}{dx^n}\right)_0 = \frac{1}{n!}\left(\frac{d^n e^x}{dx^n}\right)_0$$

$$a_0 = 1$$

$$a_1 = \frac{1}{1!}\left(\frac{d e^x}{dx}\right)_0 = \frac{e^x}{1!} = \frac{1}{1!}$$

$$a_2 = \frac{1}{2!}\left(\frac{d^2 e^x}{dx^2}\right)_0 = \frac{e^x}{2!} = \frac{1}{2!}$$

$$a_3 = \frac{1}{3!}\left(\frac{d^3 e^x}{dx^3}\right)_0 = \frac{e^x}{3!} = \frac{1}{3!}$$

$$\boxed{e^x = 1 + \frac{1x}{1!} + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \dots}$$

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Q2(c) Eq. 9 can be written as

$$P = \frac{RT}{\bar{V}} + \frac{RTB_2}{\bar{V}^2} + \frac{RTB_3}{\bar{V}^3} + \cdots$$

this must be equal to the expression in Eq 10

$$P = \frac{RT}{\bar{V}} + \frac{A_2 P}{\bar{V}} + \frac{A_3 P^2}{\bar{V}} + \cdots$$

convert to series in $\frac{1}{\bar{V}}$ by substituting 1st equation wherever P appears in 2nd equation

$$P = \frac{RT}{\bar{V}} + \frac{A_2}{\bar{V}}\left(\frac{RT}{\bar{V}} + \frac{RTB_2}{\bar{V}^2} + \frac{RTB_3}{\bar{V}^3} + \cdots\right) + \frac{A_3}{\bar{V}}\left(\frac{RT}{\bar{V}} + \frac{RTB_2}{\bar{V}^2} + \frac{RTB_3}{\bar{V}^3}\right)^2 + \cdots$$

since we are only interested in $1/\bar{V}^2$ term:

$$P = \frac{RT}{\bar{V}} + \frac{A_2 RT}{\bar{V}^2} + \cancel{\frac{A_3 RT}{\bar{V}^2}} \cdots + O\left(\frac{1}{\bar{V}}\right)^3$$

where O designates all terms with $\frac{1}{\bar{V}^3}$ and higher

comparison of this relation with Eq. 9 modified shows that

$$\frac{A_2 RT}{\bar{V}^2} = \frac{B_2 RT}{\bar{V}^2} \qquad \boxed{A_2 = B_2}$$

Q2 d) if $s(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \cdots = f(x) = b_0 + b_1 x + \cdots$

$a_0 = b_0$

$a_1 = b_1$

$a_2 = b_2$

$\vdots$

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Q3 a) $\frac{d\ ln(x)}{dx} = \frac{1}{x}$, and at $x=1$ $\frac{1}{x} = 1$

$\frac{\partial^2 ln(x)}{dx} = -\frac{1}{x^2}$, and at $x=1$ $-\frac{1}{x^2} = -1$

regular pattern follows such that

$$ln(x) = (x-1) - \frac{1}{2}(x-1)^2 + \frac{1}{3}(x-1)^3 + \frac{1}{4}(x-1)^4$$

since $\left(\frac{d^n f}{dx^n}\right)_1 = (-1)^{n-1}(n-1)!$

Q3 b) for $X_2 = 1 - x_1$ $x_1 = 1 - x_2$, substitute into Q3(a)

$$ln(1-x_2) = -x_2 - \frac{1}{2}x_2^2 - \frac{1}{3}x_2^3 + \dots$$

$$\boxed{-ln\ x_2 = x_2 + \frac{1}{2}x_2^2 + \frac{1}{3}x_2^3 + \dots \cong \frac{\Delta H_v}{R}\left(\frac{1}{T_0} - \frac{1}{T_1}\right)}$$

Q3 c) want to find where $S_3 \geq 0.01 \cdot S$ for the series

$$S_3 = \frac{\frac{1}{3}x_2^3}{\cancel{x_2}} \geq 0.01\ x_2$$

$$\frac{1}{3}x_2^2 - 0.01\ \cancel{x_2} = 0$$

$$\sqrt{x_2^2} = \sqrt{0.03}$$

$$\boxed{x_2 > 0.173}$$

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6

Q4 a) Basis functions for Fourier Series Periodic

$\sin\left(\frac{n\pi x}{L}\right)$ periodic by 2L

$$\sin\left(\frac{n\pi\{x+2L\}}{L}\right) = \sin\left(\frac{n\pi x}{L} + 2n\pi\right)$$

$$= \sin\left(\frac{n\pi x}{L}\right)\underbrace{\cancel{\cos(2n\pi)}}_{+1} + \cos\left(\frac{n\pi x}{L}\right)\underbrace{\cancel{\sin(2n\pi)}}_{0}$$

for integer n

$$= \sin\left(\frac{n\pi x}{L}\right) ✓$$

$\cos\left(\frac{n\pi x}{L}\right)$ periodic by 2L

$$\cos\left(\frac{n\pi(x+2L)}{L}\right) = \cos\left(\frac{n\pi x}{L} + 2n\pi\right)$$

$$= \cos\left(\frac{n\pi x}{L}\right)\overbrace{\cancel{\cos(2n\pi)}}^{1} + \sin\left(\frac{n\pi x}{L}\right)\overbrace{\cancel{\sin(2n\pi)}}^{0}$$

for integer n

$$= \cos\left(\frac{n\pi x}{L}\right) ✓$$

Q4 b) orthoganality

$$\int_{-L}^{L} \cos\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)dx = L\,\delta_{mn}$$

$$\int_{-L}^{L} \cos\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx = 0$$

$$\int_{-L}^{L} \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx = L\,\delta_{mn}$$

where $\delta_{mn} = 1$ for $m=n$
$\delta_{mn} = 0$ for $m \neq n$

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Q4 c) use athogamity, multiply 14 by

$$\int_{-L}^{L} \cos\left(\frac{m\pi x}{L}\right) dx$$

$$\int_{-L}^{L} f(x) \cos\left(\frac{m\pi x}{L}\right) dx = \sum_{n=0}^{\infty} a_n \int_{-L}^{L} \cos\left(\frac{n\pi x}{L}\right) \cos\left(\frac{m\pi x}{L}\right) dx$$

$$+ \sum_{n=0}^{\infty} b_n \int_{-L}^{L} \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{m\pi x}{L}\right) dx$$

all terms on right vanish except for $n = m$ ~~n=m~~

$$\int_{-L}^{L} f(x) \cos\left(\frac{m\pi x}{L}\right) dx = a_m \int_{-L}^{L} \cos\left(\frac{m\pi x}{L}\right) \cos\left(\frac{m\pi x}{L}\right) = L a_m$$

$$= a_m L$$

$$\boxed{a_n = \frac{1}{L} \int_{-L}^{L} f(x) \cos\left(\frac{n\pi x}{L}\right) dx}$$

for a_0

$$\int_{-L}^{L} f(x) \cancel{\cos}(0) dx = a_0 \int_{-L}^{L} \cancel{\cos(0)} \cancel{\cos(0)} dx$$

$$\int_{-L}^{L} f(x) dx = a_0 2L$$

$$\boxed{a_0 = \frac{1}{2L} \int_{-L}^{L} f(x) dx}$$

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Q4 d) $f(x) = x$ for $-L < x < L$

$$x = a_0 + \sum_{n=1}^{\infty} a_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{\infty} b_n \sin\left(\frac{n\pi x}{L}\right)$$

$$a_0 = \frac{1}{2L}\int_{-L}^{L} x\,dx = \frac{1}{2L}\left|\frac{x^2}{2}\right|_{-L}^{L} = \frac{1}{2L}\left|\frac{L^2}{2} + \frac{L^2}{2}\right|$$

$$= \frac{1}{2L}(L^2) = \boxed{\frac{L}{2}}$$

$$a_n = \frac{1}{L}\int_{-L}^{L} x \cos\left(\frac{n\pi x}{L}\right) dx = \cancel{\frac{1}{L}\left[\cos(x) + x\sin(x)\right]_{-L}^{L}}$$

NEED THIS INTEGRAL

$$= \frac{1}{L}\left| \frac{L}{n\pi}\cos\left(\frac{n\pi x}{L}\right) + \frac{xL}{n\pi}\sin\left(\frac{n\pi x}{L}\right)\right|_{-L}^{L}$$

$$= \frac{\cancel{L}\,1}{\cancel{L}n\pi}\left|\cos\left(\frac{n\pi x}{L}\right) + x\sin\left(\frac{n\pi x}{L}\right)\right|_{-L}^{L}$$

$$= \frac{1}{n\pi}\left(\cos(n\pi) + L\sin(n\pi) - \underbrace{\cos(-n\pi)} + L\sin(-n\pi)\right)$$

$$-1 \quad + 0 \qquad +1 \qquad 0$$

$$= \cancel{\frac{1}{n\pi}}\,0$$

$$b_n = \frac{1}{L}\int_{-L}^{L} f(x)\sin\left(\frac{n\pi x}{L}\right)dx$$

$$= \frac{2}{L}\int_{0}^{L} x\sin\left(\frac{n\pi x}{L}\right)dx = \frac{2\cancel{L}}{\cancel{L}n\pi}\left|\frac{L}{n\pi}\sin\left(\frac{n\pi x}{L}\right) - x\cos\frac{n\pi x}{L}\right.\cancel{x\sin\left(\frac{n\pi x}{L}\right)}\Bigg|_{0}^{L}$$

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$$b_n = \frac{2}{n\pi} \left| \sin\left(\frac{n\pi x}{L}\right) - x\cos\left(\frac{n\pi x}{L}\right) \right|_0^L$$

$$= \frac{2}{n\pi} \left| \sin(n\pi) - L\cos(n\pi) - \cancel{\sin(0)}\ \cancel{0} \right|$$

$$= \frac{2}{n\pi} \left| 0 + L(-1)^{n-1} \right.$$

$$= \frac{2L}{n\pi}(-1)^{n-1}$$

$$\boxed{f(x) = \sum_{n-1}^{\infty} \frac{2L}{n\pi}(-1)^{n-1} \sin\frac{n\pi x}{L}}$$

Q4 e) plot the result. for $-3L \le x \le 3L$

should be repeating function of x