Chemistry BC3252y **Problem Set 1**

Mathematical and Numerical methods

Physical chemistry is replete with equations. In order to learn and appreciate the subject, it is absolutely necessary that you not get bogged down in the mathematics. This problem set is designed to review some math topics and perhaps introduce some others. A calculator is essential for problem solving. Be sure you have a calculator that includes logs and exponentials. Spend time becoming completely familiar with the use of your calculator. If your calculator is programmable, it is well worth your while to learn how to program it.

A. Review of Basic Operations

Logarithms and exponentials

Review the fundamental properties of logarithms illustrated in the equation below:

$$\log (ab/c)^n = n (\log a + \log b - \log c)$$

Most equations in physical chemistry that involve logs and exponentials are more easily expressed in base e. I will use the notation

ln x when I mean the base e (natural) log, and

log x when I mean the base 10 (common) log.

The inverse log function for base e is e^x, which may be written exp(x).

The relationship between the two can be derived as follows:

Suppose $y = \log x$. Then $x = 10^y$.

Take natural logs of both sides, $\ln x = \ln(10^y) = y (\ln 10) = (\ln 10)(\log x)$.

Thus <u>$\ln x = 2.303 \log x$</u> where $2.303 = \ln 10$.

Most calculations of logs and their inverse are automatic with modern calculators, but it is still important to understand how these work. One useful operation occurs when you have a negative quantity for a logarithm: you may write is as a positive decimal fraction minus the next lower integer. Thus

if $\log x = -9.432$ then $\log x = +0.568 - 10$

so $x = 10^{0.568} \times 10^{-10} = 3.698 \times 10^{-10}$

Your calculator does this automatically, but you should understand the operation nevertheless: sometimes numbers may exceed the exponent capacity of a calculator.

How do significant figures work in logarithms? An approximate rule for significant figures and logs: the digits to the right of the decimal in a logarithm (the mantissa) are significant. Thus if a number has two significant figures, its logarithm is written to the nearest hundredth (and vice versa). See the on-line sheet Significant Figures for two derivations of this result.

Example: if pH = 7.20, $[H^+]$ should be written 6.3×10^{-8} M.

Series

Review Taylor's theorem and the use of Taylor's and MacLauren's series.
To expand **f(x)** around the point **a**:

$$f(x) = f(a) + (x-a)\, f^{(1)}(a) + (x-a)^2 f^{(2)}(a)/2! + \ldots + (x-a)^n f^{(n)}(a)/n!$$

Where $f^{(n)}(a)$ is the nth derivative of the function f(x), evaluated at a.

Example: Show that $(1+x)^{-1} = 1 - x + x^2 - x^3 +$

$f(x) = 1/(1+x)^1$	$f(0) = +1$
$f'(x) = -1/(1+x)^2$	$f'(0) = -1$
$f''(x) = +2/(1+x)^3$	$f''(0) = +2$
$f^{(3)}(x) = -6/(1+x)^4$	$f^{(3)}(0) = -6$

thus $f(x) = 1 + (-1)x + (2)\, x^2/2 + (-6)x^3/6 = 1 - x + x^2 - x^3$

Differentiation

Review the rules for differentiation of simple algebraic and trigonometric functions. Be sure you know the criteria for the maxima and minima of a function.

Because thermodynamic functions often depend on several variables, thermodynamics makes extensive use of partial derivatives. Taking partial derivatives is quite straightforward: the derivative is taken with respect to one variable, while the others are held constant. The notation used is as follows: $(\partial f/\partial x)_y$ means take the derivative of the function f(x,y) with respect to x, holding y constant. Just as the regular derivative is the slope of the function f(x), so is the partial derivative a slope, bit in this instance the direction must be specified.

Example: if $f(x, y) = xy^2 - 3x^2$, $(\partial f/dx)_y = y^2 - 6x$, and $(\partial f/dy)_x = 2xy$.

We can take second partial derivatives, for example $(\partial^2 f/\partial y\partial x)$ means $\partial/\partial y[(\partial f/dx)_y]_x$. In other words, first take the partial derivative of the function with respect to x (holding y constant) and then take the partial derivative of the result with respect to y (holding x constant). Continuing with the above example, $(\partial^2 f/\partial y\partial x) = (\partial/\partial y)[y^2 - 6x] = 2y$, and $(\partial^2 f/\partial x\partial y) = (\partial/\partial x)[2xy] = 2y$.

This result is general for continuous well-behaved functions, including all the important thermodynamic functions: $\boldsymbol{(\partial^2 f/\partial y\partial x) = (\partial^2 f/\partial x\partial y)}$. This fact is sometimes called an **Euler Reciprocity Relation** or **Clairault's Theorem**.

Integration between definite limits

Review the following and other simple integrals:

$$\int_{T_1}^{T_2} T^n dT = ? \qquad \int_{y_1}^{y_2} \frac{dy}{y} = ? \qquad \int_{Z_1}^{Z_2} \frac{dZ}{Z^n} = ?$$

Differential equations and finding the definite integral

Suppose you know that $f(T) = dV/dT$. If you know V_1 at T_1, how can you calculate V_2 at T_2?

Multiply $f(T) = dV/dT$ by dT to obtain a differential equation: $dV = f(T)\, dT$

Differential equations express how infinitesimal changes in one variable relate to those in others. Such equations must have a differential variable (like dx) in *each* term.

To integrate this equation, first <u>separate variables</u>: all terms that depend on V must be on the left hand side, with dV, and all terms involving T must be on the right, with dT. Constants can go anywhere. In this case, since f is a function of T only, we can integrate directly:

$$\int_{V_1}^{V_2} dV = V_2 - V_1 = \int_{T_1}^{T_2} f(T)dT$$

Exercises

A1) log x= –121.323. What is x?

A2) Show that $\int_{V_1}^{V_2} \frac{dV}{V} = \ln \frac{V_2}{V_1}$

A3) Use a Taylor's series expansion about the point x = 0 (a MacLauren series) to show that

$$\ln(1+x) = x - x^2/2 + x^3/3 - x^4/4 + \ldots$$

A4) $Y = (22.414 - 0.221\ p + 5.60 \times 10^{-3}\ p^2)$. Find p and Y at the minimum of Y(p).

A5) $\int_{298}^{1500} (9.8 \times 10^{-3}) T dT = ?$

A6) If dp/dT= 0.025 p and p = 1.24 when T = 25, find p when T = 125.

A7) $f(x, y) = 5x^2y + 3x/y - 14 \ln x$. Find $(\partial f/\partial x)_y$ and $(\partial f/\partial y)_x$. Show that $\partial^2 f/\partial x \partial y = \partial^2 f/\partial y \partial x$.

<u>B. Exact and Inexact Differentials</u>

A key point in the First Law of thermodynamics is that, whereas dq and dw are *inexact* differentials, dU, which is equal to the sum of dq and dw, is an *exact* differential. What does this mean mathematically? For a differential df involving variables x and y to be exact, there is a function f(x,y) such that

$$df = (\partial f/\partial x)_y\, dx + (df/\partial y)_x\, dy.$$

So for a differential equation with arbitrary coefficients a and b

$$df(x, y) = a(x, y)\, dx + b(x, y)\, dy$$

df is **exact** if $a(x, y) = (\partial f/\partial x)_y$ and $b(x, y) = (df/\partial y)_x$. [Observe that the (x, y) in the above equation indicates that f, a, and x are all functions of the variables x and y.] How can we know when this is true? Euler provided the answer for all well-behaved functions (and the functions on thermodynamics are all well-behaved).

The differential df is exact if and only if $(\partial^2 f/\partial x \partial y) = (\partial^2 f/\partial y \partial x)$.

Therefore $df = a(x, y)\, dx + b(x, y)\, dy$ is an exact differential if $(\partial a/\partial y)_x = (\partial b/\partial x)_y$.

Exercise B: Specify whether each of the following is an exact or inexact differential:

1) $du = (4xy^3)\, dx + (6x^2y^2)\, dy$

2) $dv = (2x^2y^3)\, dx + (3x^3y^2)\, dy$

3) $dw(p, V) = -p\, dV$

4) $dx(p,V) = -p\, dV - V\, dp$

C. Graphical methods

Frequently you will encounter a situation where you have data but no equation. A few years ago, students in thermodynamics and kinetics courses had to make lots of careful graphs by hand. Today, spreadsheet packages like Excel automate much of this, and often make the analysis of the graph much easier. You should develop the habit of using Excel routinely. Note that you almost always what an "XY (Scatter)" plot, not a "Line" plot (the latter places points at equal intervals along the abscissa).

Whether prepared by hand or by computer, all graphs should have a title (which should not repeat what is on the axes) as well as labels on both axes, including units where appropriate. The automatic scales on the axes are often fine, but sometimes it may be important to override them. Please *always* get rid of the gray background on Excel graphs. Include a legend only when more than one set of data appears on a graph. The legend distinguishes the curves by using different symbols. If your columns (or rows) of data include labels in the first row (or column), and if you included this row when you set up the graph, the legend will have informative labels.

When plotting data by hand, one often draws the best straight line by eye, making a careful effort to have the line pass as close to the data as possible, with some points above and others below. A less subjective way is to use the method if least squares. The relevant equations are given in the on-line document :The Method of Least Squares". Excel has several built-in ways to do a least squares fit. The easiest is to use the *trendline* function on the graph. Be sure to check the option "display equation on chart" before pressing "OK". If the equation displays insufficient digits, highlight the equation and press the "increase decimal" button on the tool bar. (When you need uncertainties on slope and intercept, the Excel *Linest* function is recommended. See course web site for instructions for *Linest*.)

Exercise C

The volume of 1.0000 g of SO_2 gas at 273.15 K is measured as a function of pressure with the following results.

p (atm)	0.25000	0.50000	0.70000	1.00000
V (L/g)	1.39124	0.69150	0.49164	0.34170

Draw a graph of pV vs. p for this data. Find the intercept (the limit of pV at zero pressure) and the slope (which is the second virial coefficient for this gas). Report each with the correct units.

D. Numerical methods of approximation

You will encounter situations where you have an equation that cannot be solved directly (analytically). The solution nevertheless exists, and can be obtained by numerical methods. A properly converged approximate method is no less correct that an analytical solution. The best method often depends on the particular equation. Three methods will be described here.

Educated guesswork

Suppose we wished to find a positive root to the cubic equation

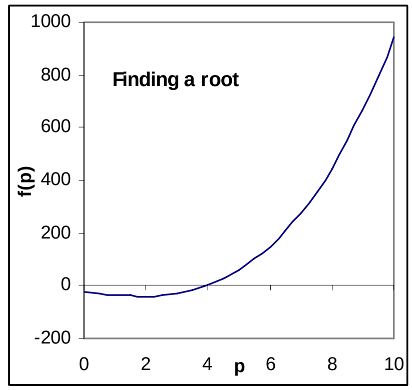
$$f(p) = p^3 + p^2 - 13p - 25 = 0$$

It is easy to see that a real positive root exists. For very large p, the cubic term dominates, so the polynomial is positive. When p is zero, f(p) is –25. Somewhere between the function must pass through zero; it may do so either one or three times.

Make a guess, say p= 5. Evaluate f(p): 625 +25 –75 –25 = 550. Since this is positive, a root is between 0 and 5. Therefore, try a smaller value, say 2: f(2): 8 +4 –26 –25 = –39. So a root is between 2 and 5. Continue closing in on the answer until the desired accuracy is obtained. If you have a programmable calculator, program the polynomial and this goes very quickly. Suppose we desired 3 significant figure accuracy:

Guess	1	2	3	4	5	6	7	8
p	5	2	3	4	3.9	3.95	3.93	3.92
f(p)	550	–39	–28	3	–1.17	0.88	0.05	–0.36

To the nearest hundredth, the root is 3.93.



Guesswork using Excel

Using Excel, one can plot the function for a grid of p values, and look at its behavior. The result is shown on the right, with an initial interval of [0, 10]. The single root is clearly close to 4. If the spreadsheet is set up so the initial value and increment are easily changed, it is quite easy to locate the root to any desired precision.

Successive approximation

A rapidly convergent scheme can be devised when the equation can be recast so that the unknown enters into the expression as a small correction. The Van der Waals' equation of state provides an example $(\mathbf{p} + \mathbf{n}^2 a/\mathbf{V}^2)(\mathbf{V} - \mathbf{n}b) = \mathbf{nRT}$.

Suppose we wish to solve for V. The equation is cubic, so direct inversion is not practical. (There is a cubic formula, but it is very cumbersome.) We know that pV= nRT is good to within about 1% at pressures of one atmosphere or less, so the terms involving *a* and *b* are small. We thus rearrange the equation

$$V = nRT/[p + n^2a/V^2] + nb$$

We have not yet solved for V because it still appears on both sides of the equation. But on the right hand side the term which involves V is small. We solve this equation successively. Make a first guess, ignoring the small terms, the terms with a and b. (In this case, this reduces to the ideal gas result: V = nRT/p.) Substitute this V into the right-hand side, getting an improved value for V. Continue until the result has converged to the desired accuracy. Again, a programmable calculator speeds the job.

Example: Consider 1.0000 mole of O_2 gas at 300.00 K and 1.0000 atmosphere. What is V? (The Van der Waals' constants are $a = 1.36$ L^2-atm/mole^2 and $b = 0.0318$ L/mole.)

For the initial guess, V = nRT/p = 24.6162 L.

Guess number	1	2	3
V (L)	24.6162	24.5929	24.5928

As the data had five significant figures, the answer is converged in three iterations, V= 24.593 L.

Other methods: your calculator may have a **Solver** function. If you know how to use it, that is fine. If you use this to find an answer, please always say this clearly (e.g. "answer found with Solver function of TI-95 calculator"). It is a good idea to know how to use other methods too!

Exercises

D1) A virial equation for N_2 at 0°C is

$$Z = pV/nRT = 1 - 0.4690 \times 10^{-3}\, p + 3.849 \times 10^{-6}\, p^2 - 3.083 \times 10^{-9}\, p^3 + 0.760 \times 10^{-12}\, p^4$$

a. Calculate the volume occupied by one mole of N_2 gas at exactly 0°C and 50.000 atm pressure. What percent error would the ideal gas law make at this pressure?

b. Write the expression for the slope of Z vs. p. Calculate the slope at 0.10, 0.50, 1.0 and 10.0 atmospheres.

Is it valid to say that at pressures up to a few atmospheres the slope is essentially constant? Note that this is equivalent to saying that the terms of the virial equation above the second are negligible at low pressures.

D2) Atkins (7/e) give the following Van der Waals' constants for N_2 gas: $a = 1.408$ L^2-atm/mol and $b = 0.03913$ L/mol. Calculate to five significant figures the volume occupied by one mole of N_2 gas at exactly 0°C and 50 atm pressure. What is the percent deviation between this answer and that of the virial equation (1.a)?

E. Explicit and Implicit Differentiation

Suppose you have a function involving the variables (x, y, and z), along with various constants. The function implies that (x, y, and z) all depend on each other. How do you find the derivative $(\partial x/\partial y)_z$? The direct (explicit) way to proceed is to solve the original function for x, and then take the partial derivative, as indicated. But sometimes the first step is not straightforward: the function may be cubic in x, or involve x in some way that you cannot easily solve for x. You can still find the derivative, using a technique called **implicit differentiation**. This method is sometimes easier that direct differentiation even when the direct method is possible.

To differentiate implicitly, operate on the original function, term-by-term, with the operator $(\partial/\partial y)_z$. This produces a new equation which includes one or more terms linear in $(\partial x/\partial y)_z$. Rearrange this equation, solving for $(\partial x/\partial y)_z$.

Example: $xy = A + Bxz + Cx$, what is $(\partial x/\partial y)_z$?

This can be done directly. First solve for x: $x(y - Bz - C) = A \rightarrow x = A/(y - Bz - C)$

Now take the derivative: $(\partial x/\partial y)_z. = \{-A/(y - Bz - C)^2\}$

Find the same derivative implicitly. First operate on the original equation with $(\partial/\partial y)_z$:

$(\partial/\partial y)_z.\{xy = A + Bxz + Cx\} \rightarrow y\,(\partial x/\partial y)_z + x = Bz\,(\partial x/\partial y)_z + C\,(\partial x/\partial y)_z$

$(\partial x/\partial y)_z\,(y - Bz - C) = -x \rightarrow (\partial x/\partial y)_z = -x/\{(y - Bz - C)\}$. Is this result the same? Yes!

Substitute for x: $(\partial x/\partial y)_z = -[A/(y - Bz - C)]/\{(y - Bz - C)\} = \{-A/(y - Bz - C)^2\}$

Exercise E

$pV = RT + bp$. Find the derivative $(\partial p/\partial V)_T$ both explicity and implicitly, and verify that the answers are the same. b is a constant that depends only on T.