Theoretical Methods in Chemistry

Problem Class 1 : Autumn 2004

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Notes on Sequences and Series

- The limit of a sequence $\{a_n\}$ is written $L = \lim_{n\to\infty}(a_n)$ and exists if an n exists such that $|L - a_n| < \varepsilon$ for any $\varepsilon > 0$
  A sequence may be *convergent*, *divergent* or *conditionally convergent*
- The infinite series $\sum_{n=1}^{\infty} a_n$ is convergent if $L = \lim_{n\to\infty} S_n = \lim_{n\to\infty}\left(\sum_{i=1}^{n} a_i\right)$ exists, ie: the sequence of its partial sums converges.
- The n^{th} term test states that a series diverges if $\lim_{n\to\infty} a_n \neq 0$ - that is, if its terms to not decay to 0 the series diverges. Note: passing the n^{th} term test is not a guarantee of convergence.
- The sum of an arithmetic series, $a + (a+d) + (a+2d) + \ldots + (a+(n-1)d)$, is $\frac{n}{2}\left[2a + (n-1)d\right]$
- The sum of a geometric series, $a + ar + ar^2 \ldots + ar^{(n-1)}$ is $a\frac{(1-r^n)}{(1-r)}$
- An infinite geometric series converges, if $|r| < 1$, to $a\left(\frac{1}{1-r}\right)$
- The harmonic series is $\sum_{n=1}^{\infty}\frac{1}{n}$, and is divergent, while the alternating harmonic series is $\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}$ which is conditionally convergent.

Some exercises with geometric sequences and series.

1. Find the sums of the following series;

   a. $1 - \frac{1}{3} + \frac{1}{9} - \frac{1}{27} + \frac{1}{81} - \ldots$

b. $250 + 150 + 90 + 54 + \dots$

c. $1 - \frac{1}{2} + \frac{1}{4} - \frac{1}{8} + \frac{1}{16} - \frac{1}{32} + \dots$

2. The first three terms of a geometric sequence are $x-1$, $x+1$ and $3(x-2)$ find the two possible values for the sixth term.

Convergence of infinite series

The geometric series considered above can be analysed and manipulated easily because they are amenable to analytic summation. Unfortunately not all series are geometric series. In the general case there is no single test for convergence and a little more thought and inspiration is required;

1. For each of the following series state the n^{th} term and use the n^{th} term test to determine if the series is divergent.

a. $\frac{1}{2} + \frac{4}{5} + \frac{9}{10} + \frac{16}{17} + \frac{25}{26} + \dots$

b. $\sum_{n=1}^{\infty} \frac{n+3}{n^2 + 10n}$

As discussed in Lecture 1 the convergence of a series can often be analysed by bracketing terms – essentially by creating a *comparison* series;

2. Prove that the harmonic series $\sum_{n=1}^{\infty} \frac{1}{n}$ is divergent.

3. Prove that $\sum_{n=1}^{\infty} \frac{1}{n^2}$ is convergent.

   Hint: try grouping the terms as $1 + \left(\frac{1}{2^2} + \frac{1}{3^2} \right) + \left(\frac{1}{4^2} + \frac{1}{5^2} + \frac{1}{6^2} + \frac{1}{7^2} \right) + \dots$

4. What does question 3. tell us about the series $\sum_{n=1}^{\infty} \frac{1}{n^3}$? Or, in fact the set of

   series $\sum_{n=1}^{\infty} \frac{1}{n^p} \, for \;\; p > 1$?

5. Demonstrate the convergence or divergence of the following series by forming suitable comparison series..
    a. $\sum_{n=1}^{\infty} \frac{n}{n^3+1}$
    b. $\sum_{n=1}^{\infty} \frac{5^n}{7^n+1}$
    c. $\sum_{n=1}^{\infty} \frac{n^2}{n^3-\frac{1}{2}}$

These ideas can now be applied to some problems in Chemistry.

Sequences and Series in Chemistry

Notes on Thermodynamics

Firstly we need to recall some thermodynamics;

For a system characterised by a set of energy levels ε_j the *partition function*, Z, can be computed using the following series;

$$Z(T,N,V...) = \sum_{j=1}^{allstates} e^{-\varepsilon_j / k_B T}$$

From the partition functional all macroscopic properties of the system can be computed – energy, pressure, entropy, magnetisation etc etc.

For example – the total energy is an ensemble average over all of the microstates of the system;

$$\langle E \rangle = \sum_i \varepsilon_i p_i = \frac{\sum_i \varepsilon_i e^{-\varepsilon_i / k_B T}}{\sum_i e^{-\varepsilon_i / k_B T}} = \frac{\sum_i \varepsilon_i e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}$$

Where p_i is the probability of a microstate which is given by the exponential (remember the Boltzman distribution), and β is simply a shorthand for $1/k_B T$.

From this it should be clear that;

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}_{N,V} = -\frac{\partial \ln(Z)}{\partial \beta}_{N,V}$$

As you study *statistical mechanics* and *thermodynamics* you will find that any macroscopic variable can be computed once Z is known.

The complexity of the series which must be summed to find Z depends, of course, on the system under study – based on what we have learned about series thus far a surprising number of systems can be studied analytically – others require more fancy maths or, more usually, numerical methods.

The Vibrational Energy of a Diatomic Molecule

To a good approximation a diatomic molecule is a *simple harmonic oscillator* for which the energy levels are;

$$\varepsilon_n = (n + \frac{1}{2})\hbar\omega \qquad n = 0, 1, 2, 3\ldots$$

Where ω is the fundamental frequency of the harmonic potential (see Lecture 3 for more about this).

6. Compute the vibrational partition function for a gas of diatomic molecules at temperature T and use it to obtain an expression for the average vibrational energy of the gas.
   Find the low and high temperature limits for the average vibrational energy – do they make sense ?

   Hint: we will see in Lecture 3 that for small x, $e^x \approx 1 + x$

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