Theoretical Methods in Chemistry

Problem Class 1 : Autumn 2004

Tutors Sheet

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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 nth 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 nth 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 $\frac{n}{2}[2a + (n-1)d]$
- 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. $1-\frac{1}{3}+\frac{1}{9}-\frac{1}{27}+\frac{1}{81}-\dots$

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

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

Tutor Note:

a. A GP with a=1 and r = -1/3 as |r| < 1 it converges to $a\left(\frac{1}{1-r}\right)=1.\left(\frac{1}{1+\frac{1}{3}}\right)=\frac{3}{4}$

b. A GP with a=250 and r=3/5 converging to $250\left(\frac{1}{1-\frac{3}{5}}\right)=625$

c. A GP with a=1, r=-1/2 converging to 2/3.

For those students who struggle with these ideas it is a good idea to sketch the sequence of partial sums, S_n, and "see" the convergence of the series.

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.

Tutor Note:

For this to be a geometric sequence we must have a consistent common ratio,

$r=\frac{x+1}{x-1}=\frac{3(x-2)}{(x+1)}$; or

$3(x-2)(x-1)=(x+1)^2$

$2x^2-11x+5=(2x-1)(x-5)=0,\ \textit{two solutions},$

$x=\frac{1}{2}\ \textit{or}\ x=5$

So there are two possible geometric sequences a=-1/2, r=-3 and a=4, r=5/3 so the two possible 6^{th} terms – ar^5 are $\frac{3^5}{2}$ and $4\left(\frac{5}{3}\right)^5$

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

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

Tutor Note:

a. $a_n = \frac{n^2}{n^2+1}$ so $\lim_{n\to\infty} a_n = \frac{n^2}{n^2} = 1$
the series diverges by the n[th] term test (note: failing the n[th] term test means that it really does diverge)

b. $a_n = \frac{n+3}{n^2+10n}$ so $\lim_{n\to\infty} a_n = \lim_{n\to\infty}\frac{n}{n^2} = \lim_{n\to\infty}\frac{1}{n} = 0$
the series does not diverge by the n[th] term test (note: which does not mean that it will converge – further tests are required).

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.

Tutor Note:

This was covered in Lecture 1: rewrite the series as;

$$S = 1+\frac{1}{2}+\frac{1}{3}+\frac{1}{4}+\frac{1}{5}+\frac{1}{6}+\frac{1}{7}+\ldots = 1+\frac{1}{2}+\left(\frac{1}{3}+\frac{1}{4}\right)+\left(\frac{1}{5}+\frac{1}{6}+\frac{1}{7}+\frac{1}{8}\right)+\ldots$$

written this way is easy to see that each bracket must be bigger than ½ --- (2 terms in the first bracket, smallest term ¼ => its value is bigger that 2x ¼ = ½ ; fours terms in the next bracket, smallest term 1/8 etc etc.

So;

$$S > 1 + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \ldots$$

Which diverges slowly but surely.

As a prelude to the next question point out that the technique here was to compare the test series to the comparison series given by;

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

noting that this series must be smaller than S and yet this series diverges….

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

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

Tutor Note:

Similar to the previous question but now compare to a series based on the *largest* term in each bracket; - the test series, S, must be less than the comparison series, ie:

$$S < 1 + \left(\frac{1}{2^2} + \frac{1}{2^2}\right) + \left(\frac{1}{4^2} + \frac{1}{4^2} + \frac{1}{4^2} + \frac{1}{4^2}\right) + \ldots$$
$$= 1 + \frac{2}{2^2} + \frac{4}{4^2} + \frac{8}{8^2} + \ldots$$
$$= 1 + \frac{1}{2} + \frac{1}{4} + \frac{1}{8} + \ldots$$

But, this is a Geometric Progression with a=1, r = ½ and so it converges to $a\left(\frac{1}{1-r}\right)$ or 2.

As the comparison series is always greater than the test series … the test series must also converge.

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

Tutor Note:

$$S=\sum_{n=1}^{\infty}\frac{1}{n^3}=1+\left(\frac{1}{2^3}+\frac{1}{3^3}\right)+\left(\frac{1}{4^3}+\frac{1}{5^3}+\frac{1}{6^3}+\frac{1}{7^3}\right)+\ldots$$

$$S<1+\frac{2}{2^3}+\frac{4}{4^3}+\frac{8}{8^3}+\ldots$$

$$=1+\frac{1}{2^2}+\frac{1}{4^2}+\frac{1}{8^2}+\frac{1}{16^2}+\ldots$$

$$S<\sum_{n=1}^{\infty}\frac{1}{n^2}$$

Where the last step follows because S < a series which contains only some of the positive definite terms in the $1/n^2$ series so it must be a smaller sum.

And in question 3 we proved that $1/n^2$ converges, so the comparison series converges so our test series converges. Similar arguments lead to the conclusion that $1/n^4$, $1/n^5$ etc all converge.

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. $\sum_{n=1}^{\infty}\frac{n^2}{n^3-\frac{1}{2}}$

Tutor Note:

a. Easy, compare with the series $\sum_{n=1}^{\infty}\frac{n}{n^3}=\sum_{n=1}^{\infty}\frac{1}{n^2}$ and we proved the convergence of this in question 3. The logic is….

The comparison and test series only differ in that the denominator in every term of the comparison series is greater by 1 ie: each term is smaller that the corresponding term in the test series which converges; so the comparison series must also converge.

b. $\sum_{n=1}^{\infty} \frac{5^n}{7^n+1}$, again compare to $\sum_{n=1}^{\infty} \frac{5^n}{7^n} = \sum_{n=1}^{\infty}\left(\frac{5}{7}\right)^n$ which is a GP with a=5/7 and r=5/7 and therefore converges. So the test series, in which each term is smaller, must also converge.

c. Now we have *subtraction* in the denominator and so compare to the *smaller* series $\sum_{n=1}^{\infty} \frac{n^2}{n^3} = \sum_{n=1}^{\infty} \frac{1}{n}$ which is the harmonic series and as shown in question 2 this is divergent so our test series must also diverge.

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;

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

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, $e^x \approx 1 + x$

Tutor Note:

Firstly, this is a fairly extensive investigation and it would be remarkable if any of the students could complete it without assistance;

Given the energy levels the partition function is,

$$Z = \sum_{n=0}^{\infty} e^{-\beta\varepsilon_n} = e^{-\frac{1}{2}\beta\hbar\omega}\left(e^0 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + e^{-3\beta\hbar\omega} + \ldots\right)$$

The series in brackets is a geometric series with first term e^0=1 and common ratio $e^{-\beta\hbar\omega}$ which therefore sums to;

$$a\left(\frac{1}{1-r}\right) = \left(\frac{1}{1-e^{-\beta\hbar\omega}}\right)$$

and so,

$$Z(T) = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{e^{\frac{1}{2}\beta\hbar\omega} - e^{-\frac{1}{2}\beta\hbar\omega}}$$

or, if you prefer hyperbolic trig. functions;

$$Z(T) = \left(2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right)^{-1}$$

because the hyperbolic sin function is;

$$\sinh(\theta) = \frac{1}{2}\left(e^{\theta} - e^{-\theta}\right)$$

The average energy is given by;

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

So….

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial}{\partial\beta}\left(\frac{1}{e^{\frac{1}{2}\beta\hbar\omega} - e^{-\frac{1}{2}\beta\hbar\omega}}\right)$$

$$= -\frac{1}{Z}\left\{-\left(e^{\frac{1}{2}\beta\hbar\omega} - e^{-\frac{1}{2}\beta\hbar\omega}\right)^{-2}\left(\frac{1}{2}\hbar\omega e^{\frac{1}{2}\beta\hbar\omega} + \frac{1}{2}\beta\hbar\omega e^{-\frac{1}{2}\beta\hbar\omega}\right)\right\}$$

$$\langle E \rangle = \frac{1}{2}\hbar\omega\frac{\left(e^{\frac{1}{2}\beta\hbar\omega} + e^{-\frac{1}{2}\beta\hbar\omega}\right)}{\left(e^{\frac{1}{2}\beta\hbar\omega} - e^{-\frac{1}{2}\beta\hbar\omega}\right)}$$

which, if you prefer, can be rewritten as,

$$\langle E \rangle = \frac{1}{2}\hbar\omega\coth\left(\frac{1}{2}\beta\hbar\omega\right)$$

Low temperature limit:

$$\beta = {}^{1}\!/_{kT} \rightarrow \infty$$

$$e^{-\frac{1}{2}\beta\hbar\omega} \rightarrow 0$$

$$e^{+\frac{1}{2}\beta\hbar\omega} \rightarrow big$$

so,

$$\langle E\rangle \to \frac{1}{2}\hbar\omega\frac{\left(e^{\frac{1}{2}\beta\hbar\omega}\right)}{\left(e^{\frac{1}{2}\beta\hbar\omega}\right)}=\frac{1}{2}\hbar\omega$$

This is exactly what we would expect, each molecule is in its vibrational ground state.

High Temperature Limit:

$$\beta = {}^{1}\!/_{kT} \to 0$$

$$e^{-\frac{1}{2}\beta\hbar\omega} \to 1-\frac{1}{2}\beta\hbar\omega$$

$$e^{+\frac{1}{2}\beta\hbar\omega} \to 1+\frac{1}{2}\beta\hbar\omega$$

and so,

$$\langle E\rangle \to \frac{1}{2}\hbar\omega\left\{\frac{\left(1+\frac{1}{2}\beta\hbar\omega\right)+\left(1-\frac{1}{2}\beta\hbar\omega\right)}{\left(1+\frac{1}{2}\beta\hbar\omega\right)-\left(1-\frac{1}{2}\beta\hbar\omega\right)}\right\}$$

$$=\frac{1}{2}\hbar\omega\left(\frac{2}{\beta\hbar\omega}\right)=\frac{1}{\beta}$$

$$=k_B T$$

At high temperature many energy levels are populated and the average vibrational energy is k_BT which, we live in hope, is familiar ????

In this problem the *microscopic* energy levels of the vibrations of a molecule have been connected to the *macroscopic* average thermal energy of a gas and we find the phenomenological (thermodynamic) result of kT per degree of freedom (our molecules had one degree of freedom).

Boltzman must have been very excited when he figured out things like this for the first time. Up to that point temperature was ill defined – related somehow to the "motion of the molecules.. faster means hotter". Through the $e^{-\varepsilon/kT}$ of the Boltzman distribution he *redefined temperature* in a quantitative way – it is related to the probability of occupying particular energy levels.
Then, when you compute the average energy of a gas you get the right answer – hoorah!

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