Aula Prática 3/ Practical Class 3

Python Exercises

1A. Numerical Differentiation

Unless stated otherwise the following exercises are meant to be performed in jupyter notebook.
Type: conda activate PMN
Type: jupyter notebook
We can create a new Python notebook by selecting Python 3, usually this is called Python kernel.
Recall that in jupyter notebook to run a cell we issue: **Shift+Enter**

a) Consider the following values of the hydration free energy of ethane obtained from MD simulations (Table 1). Estimate the entropy of hydration at 298 K using the forward, backward, and central difference formulas.

Table 1 – Hydration free energy of ethane at three temperatures and 0.1 MPa.

T(K)	ΔG_{hyd} (kJ/mol)
278	7.88
298	9.68
318	11.36

Is ethane's poor solubility in water related to a high positive enthalpy or a low negative entropy?

b) Consider the general expression for the Taylor series of a function $f(x)$ around a,

$$f(x)=\sum_{n=0}\frac{f^{(n)}(a)}{0!}(x-a)^n$$

Derive the order of the central difference formula given by,

$$f'(x_j)=f^{(1)}(x_j)=\frac{f(x_{j+1})-f(x_{j-1})}{x_{j+1}-x_{j-1}}$$

c) Consider a reaction of decomposition of a chemical species A, into B and C, in aqueous solution,

$$a\mathrm{A}_{(\mathrm{aq})} \rightarrow b\mathrm{B}_{(\mathrm{aq})} + c\mathrm{C}_{(\mathrm{aq})}$$

with the stoichiometric coefficients, $a = b = c = 1$.

The concentration of A was measured at discrete time intervals - data displayed in **Table 1**.

Table 1 – Experimental concentration of species A along time.

time (s)	**[A] (mol/dm^3)**
0	0.1
10	0.085
20	0.072
30	0.061
40	0.052
50	0.044

Assuming a first order reaction:

(i) Estimate the instantaneous rate of decomposition of A at $t = 20$ s using the central difference formula to approximate the respective numerical derivative.

(ii) Assuming a first-order reaction, determine the rate constant k using the numerical derivative at $t = 20$ s.

Hint: The rate of a first order reaction can be written in the form:

$$\text{rate} = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]$$

Solution:

a) The entropy of solvation (hydration) can be obtained from,

$$\Delta S_{solv} = -\left(\frac{\partial \Delta G_{solv}}{\partial T}\right)$$

Using the backward, forward, and central difference formulas of numerical differentiation we get the following results:

Formula	ΔS_{hyd} (kJ mol^{-1} K^{-1})	$T\Delta S_{hyd}$ (kJ mol^{-1})	ΔH_{hyd} (kJ mol^{-1})
Backward	-0.090	-26.82	-17.14
Forward	-0.084	-25.03	-15.35
Central	-0.087	-25.93	-16.25

Ethane's poor solubility is due to a relatively large negative entropy, whereas enthalpy is small but negative – favoring solubility.

Solution:

b) Chek the book if you have doubts.

Solution:

c) The rate of reaction is given by (assuming a first order reaction),

$$\text{rate } = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{d[A]}{dt} = k[A]$$

(i) The rate of decomposition of A at $t = 20$ s can be estimated from,

$$\text{rate} = -\frac{d[A]}{dt} \approx -\frac{[A]_{30} - [A]_{10}}{30-10} = -\frac{0.061-0.085}{30-10} = 0.0012 \text{ Ms}^{-1}$$

(ii) The rate of reaction k is,

$$-\frac{d[A]}{dt} = k[A]$$

$$k = -\frac{d[A]}{dt}\frac{1}{[A]} = \frac{0.0012}{0.072} = 0.0167 \text{ s}^{-1}$$

Recall that,

$$
\begin{aligned}
&d[A] = -k[A]dt \\
&\int_{[A]_0}^{[A]} \frac{1}{[A]} d[A] = -k\int_{t_0}^{t} dt \\
&\ln[A] - \ln[A]_0 = -k(t - t_0) \\
&\ln[A] = \ln[A]_0 - kt
\end{aligned}
$$

and, therefore, the slope of ln[A] versus t is minus the rate of the reaction (-k). A value of k = 0.0164 s^{-1} is found from the slope, which is close to the value estimated above.