

## 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.**

$T(K)$	$\Delta G_{\text{hyd}} \text{ (kJ/mol)}$
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?

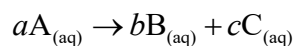
**b)** Consider the general expression for the Taylor series of a function  $f(x)$  around  $a$ ,

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

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,



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 <sup>3</sup> )
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:

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

**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	$\Delta S_{hyd}$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$T\Delta S_{hyd}$ (kJ mol <sup>-1</sup> )	$\Delta H_{hyd}$ (kJ mol <sup>-1</sup> )
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) Check 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,

$$d[A] = -k[A]dt$$

$$\int_{[A]_0}^{[A]} \frac{1}{[A]} d[A] = -k \int_{t_0}^t dt$$

$$\ln[A] - \ln[A]_0 = -k(t - t_0)$$

$$\ln[A] = \ln[A]_0 - kt$$

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