Simpson's 1/3 Rule

Simpson's 1/3 Rule is a **numerical integration method** often used in **chemistry and chemical engineering** to approximate the **area under a curve** when the exact integral is difficult or impossible to calculate analytically. It's especially useful in experimental data analysis.

What is Simpson's 1/3 Rule?

Simpson's 1/3 Rule estimates the definite integral of a function by dividing the interval into an **even number of segments** and approximating each pair of sub intervals using a **parabola (second-degree polynomial)**.

Formula:

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Formula:

$$\int_a^b f(x)\,dx \approx \frac{h}{3}\left[f(x_0) + 4f(x_1) + 2f(x_2) + 4f(x_3) + \cdots + f(x_n)\right]$$

Where:

- $h = \frac{b-a}{n}$ (step size)
- n = even number of intervals
- $x_0, x_1, \ldots, x_n$ are the values of x over the interval

Application in Chemistry:

1. Titration Curve Analysis:

When you have experimental **pH vs volume** data, and you want to calculate the **total acid or base added**.

2. Calculating Enthalpy (ΔH):

For temperature vs heat added data, Simpson's rule helps approximate the **area under a heat curve**, giving the total energy change.

3. Absorbance vs Concentration (Beer-Lambert Law curves):

To find total absorbance over a range of wavelengths in **spectrophotometry**.

4. Rate of Reaction:

If you have discrete data for concentration over time, it helps to compute **total change** or **area under rate curves**.

Advantages:

More accurate than trapezoidal rule when the curve is not linear.

Ideal when the function is smooth and you have an even number of data points.

Important Condition:

The number of sub-intervals **must be even** (i.e., data must be in odd number of points: x_0 to x_n, with n even).

Example in Chemistry

Let's say you have 5 values of absorbance data across wavelengths:

wavelengths	absorbance
400	0.10
420	0.20
440	0.25
460	0.22
480	0.18

Use **Simpson's 1/3 Rule** to estimate the **area under the absorbance curve** from 400 nm to 480 nm.

Solution:

We are given:

a=400, b=480

Intervals: 400, 420, 440, 460, 480 → Total of 5 data points ⇒ 4 intervals → **Even number (n = 4)**

Step size:

Now apply the Simpson's 1/3 Rule:

$$\int_{400}^{480} A(\lambda)\, d\lambda \approx \frac{h}{3}[f(x_0) + 4f(x_1) + 2f(x_2) + 4f(x_3) + f(x_4)]$$

Substitute values:

$$= \frac{20}{3}[0.12 + 4(0.18) + 2(0.20) + 4(0.22) + 0.19]$$

$$= \frac{20}{3}(2.31) \approx 6.67 \text{ X } 2.31 \approx 15.41$$

The estimated **area under the absorbance curve** is approximately **15.41 absorbance·nm**.

A titration-based example using Simpson's 1/3 Rule in chemistry

Problem: During an acid-base titration, the **pH of a solution** was measured at various volumes of base added:

Volume of NaOH added (mL)	pH
0	2.0
5	3.1
10	4.8
15	7.0
20	9.2

Estimate the **area under the pH vs volume curve** from 0 mL to 20 mL using **Simpson's 1/3 Rule**.

Given: a= 0 , b=20

Number of interval =20 (even)

- $h = \frac{20-0}{4} = 5\,\text{mL}$

Let's assign:

- $f(x_0) = pH(0) = 2.0$
- $f(x_1) = pH(5) = 3.1$
- $f(x_2) = pH(10) = 4.8$
- $f(x_3) = pH(15) = 7.0$
- $f(x_4) = pH(20) = 9.2$

Now apply **Simpson's 1/3 Rule**:

$$\int_0^{20} \text{pH}\, dV \approx \frac{h}{3}\left[f(x_0) + 4f(x_1) + 2f(x_2) + 4f(x_3) + f(x_4)\right]$$

$=\frac{5}{3}[2.0+4(3.1)+2(4.8)4(7.0)9.2)]$

$=\frac{5}{3}$ X 61.2≈1.667 X 61.2≈102.0

The estimated **area under the pH-volume curve** is **approximately 102.0 pH·mL**.

This can represent the **total acidity or buffering capacity** depending on the context of the experiment.

A **thermochemistry example** using **Simpson's 1/3 Rule** to estimate the **enthalpy change (ΔH)** from experimental data.

Problem (Enthalpy-Temperature Example):

In a calorimetry experiment, heat was added to a substance, and the temperature was recorded at regular intervals. The data is as follows:

Time (min)	Temperature
0	25.0
0	28.5
4	32.1
6	35.6
8	39.0

Estimate the **total temperature rise (area under the T–time curve)** using **Simpson's 1/3 Rule**, which helps approximate the **total heat absorbed** if the heat flow is constant.

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a=0, b=8, n= 4 intervals (even)

Step size : h=$\frac{8-0}{4}$ = 2min

Let , T_0= 25.0, T_1= 28.5,T_2= 32.1,T_3= 35.6,T_4= 39.0

Apply **Simpson's 1/3 Rule:**

$$\int_0^8 T(t)\,dt \approx \frac{h}{3}\left[T_0 + 4T_1 + 2T_2 + 4T_3 + T_4\right]$$

Substitute the values:

$$= \frac{2}{3}\left[25.0 + 4(28.5) + 2(32.1) + 4(35.6) + 39.0\right]$$

$$=\frac{2}{3}(25.0+114.0+64.2+142.4+39.0)=\frac{2}{3} \times 384.6 \approx 256.4$$

The estimated **area under the temperature-time curve** is **approximately 256.4 °C·min**.

This is **proportional to the total heat absorbed** if the heat is applied uniformly (constant rate), and can be used to estimate **ΔH** when specific heat and mass are known:

ΔT = q=m.c.ΔT

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