Course on Numerical Integration for Chemistry
Midpoint Rule: Theory, Errors, and Applications

Numerical Methods Applied to Chemistry

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1 Introduction: Why Does Chemistry Need Numerical Integration?

In theoretical and experimental chemistry, integration is omnipresent:

- **Thermodynamics:** Computing the compression/expansion work of a gas, $W = -\int_{V_1}^{V_2} P(V)\,dV$.
- **Chemical Kinetics:** Determining cumulative concentrations or calculating reaction time.
- **Analytical Chemistry:** Measuring the area under the curve of a peak in chromatography (HPLC, GC) or spectroscopy (UV-Vis, NMR) to quantify a chemical species.

In laboratory practice, analytical functions $f(x)$ are rarely known in a simple closed form. Most often, we work with discrete experimental data: a table of measurements (e.g., pressure measured at various volumes, or absorbance measured at different wavelengths). Numerical integration allows us to calculate the area under these experimental data points without knowing the exact equation of the curve.

2 Physical Meaning: Integral vs. Discrete Formulation

It is essential to thoroughly understand the correspondence between the continuous world (theoretical mathematics) and the discrete world (experimental measurement).

2.1 Continuous formulation: $\int_a^b f(x)\,dx$

In the mathematical expression:

$$I = \int_a^b f(x)\,dx$$

- The symbol $\int$ represents the continuous sum (an elongated S standing for *summa*).
- $f(x)$ represents the measured physical quantity (e.g., Pressure P, Absorbance A, Chromatographic signal S).
- **The role of dx:** dx is an infinitesimal increment of the variable x (an infinitely small, ideal, and theoretical variation). It confers the physical dimension to the integral (e.g., if $f(x)$ is in Pascals and x in m^3, $f(x)dx$ is in Joules).

2.2 Discrete formulation: $\sum_{i=1}^{n} f(x_i)\,\Delta x$

In experimental reality or on a computer, one cannot sum an infinite number of points. We partition the interval $[a, b]$ into n subintervals of finite width:

$$\Delta x = h = \frac{b-a}{n}$$

The integral is then approximated by a finite sum:

$$I \approx \sum_{i=1}^{n} f(x_i)\,\Delta x$$

- The symbol $\sum$ represents the discrete sum of n terms.
- **The role of Δx:** Δx is the measurement step size or grid spacing. It is a finite and measurable quantity (e.g., recording a spectrum every $\Delta\lambda = 1$ nm, or taking a kinetic data point every $\Delta t = 5$ s).
- **The limit process:** As the number of points approaches infinity ($n \to \infty$), the step size approaches zero ($\Delta x \to 0$). The discrete sum then converges to the continuous integral:

$$\lim_{\Delta x \to 0} \sum_{i=1}^{n} f(x_i)\,\Delta x = \int_a^b f(x)\,dx$$

3 Midpoint Rule

3.1 Geometric principle

On each subinterval $[x_{i-1}, x_i]$, instead of evaluating the function at the left or right endpoint, it is evaluated at the midpoint of the segment:

$$m_i = \frac{x_{i-1} + x_i}{2}$$

We approximate the area under the curve over this subinterval using a rectangle of width Δx and height $f(m_i)$.

3.2 Composite formula

For n subintervals of equal width $\Delta x = \frac{b-a}{n}$:

$$I_{\text{midpoint}} = \Delta x\,[f(m_1) + f(m_2) + \cdots + f(m_n)] = \Delta x \sum_{i=1}^{n} f\left(x_{i-1} + \frac{\Delta x}{2}\right)$$

3.3 Integration error

The overall truncation error $E_{\text{midpoint}} = I_{\text{exact}} - I_{\text{midpoint}}$ is theoretically expressed as:

$$E_{\text{midpoint}} = \frac{(b-a)^3}{24n^2}\,f''(\xi) = \frac{(b-a)\,(\Delta x)^2}{24}\,f''(\xi)$$

where ξ is an unknown point located within the interval $[a, b]$, and f'' denotes the second derivative of f.

In practice (Absolute error bound):

$$|E_{\text{midpoint}}| \leq \frac{(b-a)\,(\Delta x)^2}{24} M_2 = \frac{(b-a)^3}{24n^2} M_2$$

with $M_2 = \max_{x \in [a,b]} |f''(x)|$.

3.4 Application Example: How to Use the Error Bound Formula?

In practice, a chemist does not only seek to calculate a value, but also wants to guarantee that the numerical error does not exceed a specified threshold ϵ (for example, $\epsilon = 0.1$ J).

Problem Statement: We wish to calculate the expansion work of one mole of an ideal gas from $V_1 = 1.0$ L to $V_2 = 2.0$ L at $T = 300$ K. The function to integrate is the pressure $P(V) = \frac{nRT}{V} = \frac{2494.2}{V}$ (expressed in Joules per liter, with $nRT \approx 2494.2$ J).

Question: What is the minimum number of subintervals n required to guarantee a maximum absolute error of $|E_{\text{midpoint}}| \leq 0.1$ J?

Step-by-Step Solution:

1. **Computation of the second derivative $f''(V)$:**

$$f(V) = \frac{2494.2}{V} \implies f'(V) = -\frac{2494.2}{V^2} \implies f''(V) = \frac{4988.4}{V^3}$$

2. **Determination of $M_2 = \max_{V \in [1,2]} |f''(V)|$:** The function $|f''(V)| = \frac{4988.4}{V^3}$ is strictly decreasing over the interval [1.0, 2.0]. Its maximum is therefore reached at the lower bound $V = 1.0$ L:

$$M_2 = |f''(1.0)| = \frac{4988.4}{1.0^3} = 4988.4 \text{ J} \cdot \text{L}^{-2}$$

3. **Setting up the accuracy inequality:** We apply the formula with $(b - a) = 2.0 - 1.0 = 1.0$ L:

$$|E_{\text{midpoint}}| \leq \frac{(b-a)^3}{24n^2} M_2 = \frac{(1.0)^3 \times 4988.4}{24n^2} = \frac{207.85}{n^2}$$

4. **Solving for the number of subdivisions n:** We require this upper bound to be less than or equal to the maximum allowable error $\epsilon = 0.1$ J:

$$\frac{207.85}{n^2} \leq 0.1 \implies n^2 \geq \frac{207.85}{0.1} = 2078.5 \implies n \geq \sqrt{2078.5} \approx 45.59$$

5. **Conclusion:** Since n must be an integer, we must choose at least $n = 46$ **subdivisions** (which corresponds to a volume step size of $\Delta V = \frac{1.0}{46} \approx 0.0217$ L) to guarantee that the numerical error in the work calculation will not exceed 0.1 J.