Univariate Calculus, Integration and Series: Introduction to Thermodynamics

1 Introduction to Integrals

Why do we care about integrals?

Integrals in natural science are widely used as they help understanding some phenomena. Some of the most common case uses of integrals are:

- Quantum chemistry. The expectation value of position is

$$\langle x \rangle = \int_{-\infty}^{\infty} x \, |\psi_0(x)|^2 \, dx,$$

  where

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{\alpha x^2}{2}}.$$

- Spectroscopy. The intensity of absorption or emission is related to the *transition dipole moment*, which is expressed as an integral:

$$\mu_{if} = \int \psi_f^*(\mathbf{r}) \, \hat{\mu} \, \psi_i(\mathbf{r}) \, d\mathbf{r},$$

  where ψ_i and ψ_f are the initial and final electronic states, and $\hat{\mu} = -e\mathbf{r}$ is the dipole operator. The value of this integral determines whether a transition is allowed and how intense the absorption or emission line will be. This gives rise to the *spectroscopic selection rule* for vibrational transitions and explain why spectra have the peaks and intensities observed in experiments.

- Thermodynamics. Integrals are used to calculate the work done on or by a system and the heat exchanged in processes such as expansion or compression. For example, the work associated with a pressure–volume change is given by

$$W = \int_{V_i}^{V_f} P(V) \, dV,$$

  where $P(V)$ is the pressure as a function of volume. In the special case of an ideal gas undergoing isothermal expansion, $P(V) = \frac{nRT}{V}$, so the work integral becomes

$$W = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln\left(\frac{V_f}{V_i}\right).$$

2 Deffinition

Integrals are sums.

Integrals were developed to compute the area under the curve (function). One of the most used numerical integration methods is the sum of "bins". Geometrically this sum represents the represents the sum of the areas of each rectangle, Fig. 3.1. This approach is know as *Riemann sum*. As we can observe, there is a limitation, depending on the topology of the function we may require more or less "rectangles" to correctly compute the area under the curve for a given function. In the infinite limit of number of "bins", $(x_i - x_j) \approx 0$, we can defined this sum as a limiting process,

$$\lim_{h\to 0}\sum_{i}^{N} f(\varepsilon_i)h = \int_a^b f(x)\,dx. \tag{1}$$

Eq. 1 is also known as *Riemann integral*. $f(x)$ is known as the **integrand**.

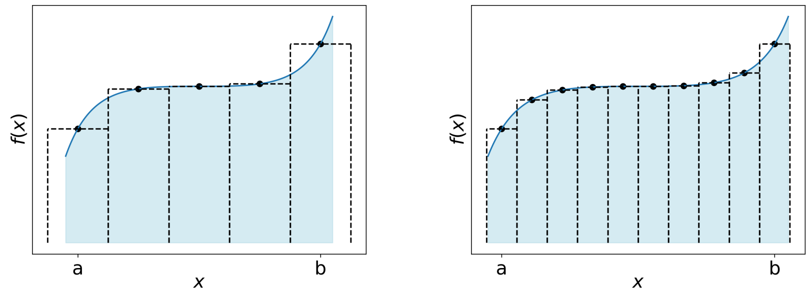


Figure 1: An illustration of integrals.

There are two different types of integrals commonly encountered in chemistry:

1. **Definite integrals**, which evaluate the area under a curve between two limits:

$$\int_a^b f(x)\,dx. \tag{2}$$

2. **Indefinite integrals**, which represent the family of antiderivatives of a function:

$$\int f(x)\,dx = \int_{-\infty}^{\infty} f(x)\,dx = F(x) + C, \tag{3}$$

where $F(x)$ is the antiderivative of $f(x)$, i.e. $\frac{d}{dx}F(x) = f(x)$, and C is an integration constant.

In summary, definite integrals are used to compute quantities between specific limits, while indefinite integrals provide the general antiderivative that can later be applied to many different problems.

3 Properties of integrals

Similar to derivatives, integrals have some nice properties that we can use to our advantage.

1. Integrals are linear operations

$$\int_a^b (f(x) + g(x))\,dx = \int_a^b f(x)\,dx + \int_a^b g(x)\,dx = F(a) - F(b) + G(a) - G(b) \tag{4}$$

or

$$\begin{aligned}\int_{-\infty}^{\infty} (f(x) + g(x))\,dx &= \int_{-\infty}^{\infty} f(x)\,dx + \int_{-\infty}^{\infty} g(x)\,dx && (5)\\ &= F(x) + C_f + G(x) + C_g && (6)\\ &= F(x) + G(x) + C && (7)\end{aligned}$$

2. Constants do not affect integrals

$$\int af(x)\,dx = a\int f(x)\,dx \tag{8}$$

3. Constants

$$\int a\,dx = a\int \,dx = ax + C \tag{9}$$

4. Polynomials, $n \neq -1$

$$\int x^n\,dx = \frac{x^{n+1}}{n+1} + C \tag{10}$$

5. Polynomials, $n = -1$

$$\int \frac{1}{x}\,dx = lnx + C \tag{11}$$

6. Polynomials, $n = -1$

$$\int e^x\,dx = e^x + C \tag{12}$$

7. Trigonometric functions

$$\int \cos(x)\,dx = \sin(x) + C \tag{13}$$

$$\int \sin(x)\,dx = -\cos(x) + C \tag{14}$$

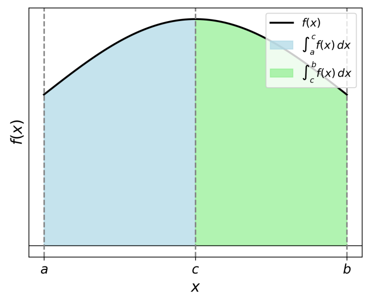
Exercise: Compute the integral of $f(x) = c$ within the interval a and b.

$$\int_a^b c\,dx = c\int_a^b \,dx = cx|_a^b = c(b-a) \tag{15}$$

3.1 Adding Integrals

We can also add two adjacent intervals together:

$$\int_a^b f(x)\,dx = \int_a^c f(x)\,dx + \int_c^b f(x)\,dx \tag{16}$$



3.2 Change of variable

Some times it is convenient to use a chain of variable to make the integral easier. This is similar to the chain rule in derivatives.

Exercise: Compute the integral of $f(x) = e^{ax}$. We can define $u = ax$, the total differential of u is

$$du = \left(\frac{\partial u}{\partial x}\right) dx = a\,dx, \qquad \text{meaning} \qquad dx = \frac{1}{a}\,du. \tag{17}$$

$$\int e^{ax}\,dx = \frac{1}{a}\int e^u\,du = \frac{1}{a}e^u + c = \frac{e^{ax}}{a} + c \tag{18}$$

4 Integration by parts

Integration by parts is one of the most used methods for computing the integral of complex functions. Integration by parts is defined as,

$$\int udv = uv - \int vdu, \tag{19}$$

where u and v are both functions of x; $u = u(x)$. In Spanish, there is a good mnemonic to memorize integration by parts.

un **d**ia **v**i **u**na **v**aca **v**estida **d**e **u**niforme. [1]

Exercise: Evaluate the following integral

$$\begin{aligned} \int f(x)dx &= \int 10 + \left(\frac{x}{10}\right)^3 e^{\left(\frac{x}{10}\right)^2}\,dx & (20)\\ &= 10\int dx + \int \left(\frac{x}{10}\right)^3 e^{\left(\frac{x}{10}\right)^2}\,dx & (21) \end{aligned}$$

Let's focus on the second integral and use a change of variable, $u = \left(\frac{x}{10}\right)^2$,

$$\begin{aligned} \int \left(\frac{x}{10}\right)^3 e^{\left(\frac{x}{10}\right)^2}\,dx &= \int \left(\frac{x}{10}\right)^3 \frac{50}{x} e^u\,du & (22)\\ &= \int \left(\frac{x}{10}\right)^3 \frac{50}{x} e^u\,du = 5\int \left(\frac{x}{10}\right)^2 e^u\,du & (23)\\ &= 5\int ue^u\,du & (24) \end{aligned}$$

[1] One day I saw a cow dressed in uniform

For this integral it is convenient to use the following definitions for u and v,

$$u = u \qquad \text{and} \qquad du = du \tag{25}$$
$$dv = e^u du \qquad \text{and} \qquad v = \int dv = \int e^u du = e^u \tag{26}$$

Plugging these equations into Eq. 4, we get,

$$\int ue^u du \quad = \quad ue^u - \int e^u du = ue^u - e^u = e^u\left(u-1\right). \tag{27}$$

Let's bring back the definitions based on x,

$$\int \left(\frac{x}{10}\right)^3 e^{\left(\frac{x}{10}\right)^2} dx \quad = \quad 5\int ue^u du = 5e^{\left(\frac{x}{10}\right)^2}\left(\left(\frac{x}{10}\right)^2 - 1\right) \tag{28}$$

The full integral of $f(x)$ is,

$$\int 10 + \left(\frac{x}{10}\right)^3 e^{\left(\frac{x}{10}\right)^2} dx \quad = \quad 10x + \frac{1}{20}e^{\left(\frac{x}{10}\right)^2}\left(x^2 - 100\right) + C \tag{29}$$

Exercise 1: Evaluate the following integral

$$\int f(x)dx \quad = \quad \int x\sin(x)\; dx. \tag{30}$$

$$u = x \qquad \text{and} \qquad du = dx \tag{31}$$
$$dv = \sin(x)\; dx \qquad \text{and} \qquad v = \int dv = \int \sin(x)\; dx = -\cos(x) \tag{32}$$

$$\int f(x)dx \quad = \quad \int x\sin(x)\; dx = x\;\cos(x) - \left(\int -\cos(x)\; dx\right) \tag{33}$$
$$= \quad x\;\cos(x) + \sin(x) + C. \tag{34}$$

Exercise 2: Evaluate the following integral

$$\int f(x)dx \quad = \quad \int x^2\ln(x)\; dx. \tag{35}$$

$$u = \ln(x) \qquad \text{and} \qquad du = \frac{1}{x}\; dx \tag{36}$$
$$dv = x^2\; dx \qquad \text{and} \qquad v = \int dv = \int x^2\; dx = \frac{x^3}{3} \tag{37}$$

$$\int f(x)dx \quad = \quad \int x^2\ln(x)\; dx = \frac{x^3}{3}\ln(x) - \int\left(\frac{x^3}{3}\right)\left(\frac{1}{x}\right)\; dx \tag{38}$$
$$= \quad \frac{x^3}{3}\ln(x) - \frac{x^3}{9} + C. \tag{39}$$

Exercise 2.1: Evaluate the following integral

$$\int f(x)dx \quad = \quad \int x^2\ln(x)\; dx, \tag{40}$$

but now let's use the different possible choice of u and dv.

$$u = x^2 \quad \text{and} \quad du = 2x\,dx \tag{41}$$
$$dv = \ln(x)\,dx \quad \text{and} \quad v = \int dv = \int \ln(x)\,dx = x\ln(x) - x \tag{42}$$

$$\begin{aligned}
\int x^2 \ln(x)\,dx &= \int \ln(x)\,x^2\,dx = (x\ln(x) - x) - \int (x\ln(x) - x)\,(2x)\;dx \\
\int x^2 \ln(x)\,dx &= (x\ln(x) - x) - 2\int x^2\;\ln(x)\,dx + \int 2x^2\,dx, \qquad (43)
\end{aligned}$$

from these equations we can observe that the integral $\int x^2 \ln(x)\;dx$, appears on the left- and right-hand side. We can move $2\int x^2\;\ln(x)\;dx$ to the left-hand side and add it with the initial integral, giving us,

$$\begin{aligned}
\int x^2 \ln(x)\,dx + 2\int x^2\;\ln(x)\,dx &= 3\int x^2\;\ln(x)\,dx = \left(x^2\right)(x\ln(x) - x) + \int 2x^2\,dx, \qquad (44)\\
\int x^2\;\ln(x)\,dx &= \frac{1}{3}\left(\left(x^3\ln(x) - x^3\right) + \int 2x^2\,dx\right) = \frac{1}{3}\left(x^3\ln(x) - x^3\right) + \frac{2}{3}\int x^2\,dx
\end{aligned}$$

The last step is to solve $\int x^2\,dx$, which give us, $\int x^2\,dx = \frac{x^3}{3}$. Combining all these, we get,

$$\begin{aligned}
\int x^2\;\ln(x)\,dx &= \frac{1}{3}\left(x^3\ln(x) - x^3\right) + \left(\frac{2}{3}\right)\frac{x^3}{3} + C \qquad (45)\\
&= \frac{1}{3}x^3\ln(x) + x^3\left(-\frac{1}{3} + \frac{2}{9}\right) + C = \frac{1}{3}x^3\ln(x) - \frac{x^3}{9} + C \qquad (46)
\end{aligned}$$

We got exactly the same as in **Exercise 2**.

Exercise 3: Evaluate the following integral

$$\int f(x)dx = \int x^2 e^x\,dx. \tag{47}$$

$$u = x^2 \quad \text{and} \quad du = 2x\,dx \tag{48}$$
$$dv = e^x\,dx \quad \text{and} \quad v = \int dv = \int e^x\,dx = e^x \tag{49}$$

$$\int x^2 e^x\,dx = x^2\,e^x - \int e^x\,2x\;dx = x^2\,e^x - 2\int e^x\,x\;dx \tag{50}$$

The integral $\int e^x\,x\;dx$ can also be solved using integration by parts, using,

$$u_2 = x \quad \text{and} \quad du_2 = dx \tag{51}$$
$$dv_2 = e^x\,dx \quad \text{and} \quad v_2 = \int dv = \int e^x\,dx = e^x \tag{52}$$

$$\int e^x\,x\;dx = x\,e^x - \int e^x\,dx = x\,e^x - e^x + C. \tag{53}$$

Combining all these we get,

$$\begin{aligned}
\int x^2 e^x\,dx &= x^2\,e^x - 2\int e^x\,x\;dx = x^2\,e^x - 2\left(x\,e^x - e^x\right) + C \qquad (54)\\
&= e^x\left(x^2 - 2x + 2\right) + C. \qquad (55)
\end{aligned}$$