Lecture 1: Mathematical Background

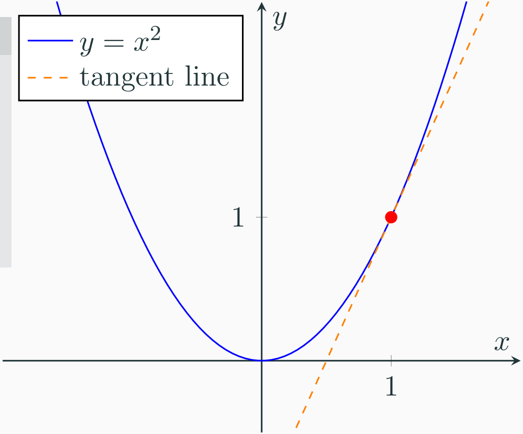
Calculus Review, Partial Derivatives

Derivatives

Derivative

Instantaneous rate of change of a function, represented by tangent line

$$\frac{df}{dx} = \lim_{\Delta x \to 0} \frac{f(x+\Delta x) - f(x)}{\Delta x}$$



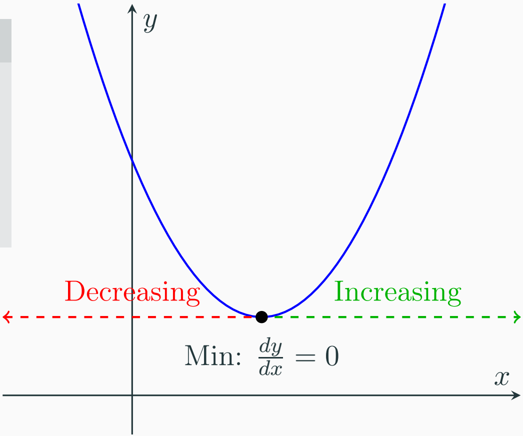
Common Derivative Rules

Chain Rule	$\frac{d}{dx}[f(g(x))] = f'(g(x))\, g'(x)$
Power Rule	$\frac{d}{dx}[x^n] = nx^{n-1}$
Product Rule	$\frac{d}{dx}[f(x)g(x)] = f'(x)g(x) + f(x)g'(x)$
Quotient Rule	$\frac{d}{dx}\left[\frac{f(x)}{g(x)}\right] = \frac{f'(x)g(x) - f(x)g'(x)}{g(x)^2}$
Exp/Log Rule	$\frac{d}{dx}[e^x] = e^x, \quad \frac{d}{dx}[\ln x] = \frac{1}{x}$

Meaning of First Derivative

Sign of First Derivative

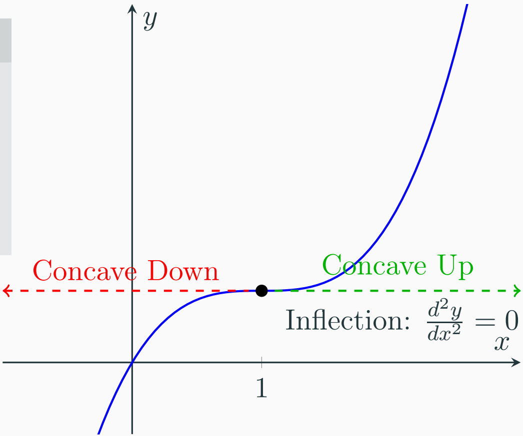
- $\frac{dy}{dx} = 0$, local min or max
- $\frac{dy}{dx} > 0$, function is increasing
- $\frac{dy}{dx} < 0$, function is decreasing



Meaning of Second Derivative

Sign of Second Derivative

- $\frac{d^2y}{dx^2} = 0$, inflection point
- $\frac{d^2y}{dx^2} > 0$, concave up
- $\frac{d^2y}{dx^2} < 0$, concave down



Integrals

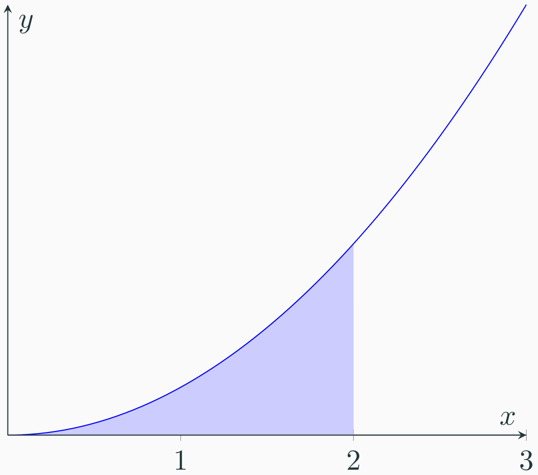
Integral

Antiderivative of a function

$$\int f(x)\,dx = F(x)+C, \quad F'(x) = f(x)$$

Also represents the area under a curve

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



Common Integral Rules

U Substitution	$\int f(g(x))g'(x)\,dx = \int f(u)\,du,\ u = g(x)$
Power Rule	$\int x^n\,dx = \frac{x^{n+1}}{n+1} + C$
Reciprocal Rule	$\int \frac{1}{x}\,dx = \ln\|x\| + C$
Exponential Rule	$\int e^x\,dx = e^x + C$

Partial Derivatives: Key Idea

Simple Derivative

$$\frac{d}{dx}(x) = 1$$

Derivative with Constant

$$\frac{d}{dx}(3x) = 3\frac{d}{dx}(x) = 3 \cdot 1 = 3$$

Partial Derivative

$$\frac{\partial}{\partial x}(yx) = y\frac{d}{dx}(x) = y \cdot 1 = y$$

Key Idea: Differentiate with respect to the variable, treat other variables as constant

Partial Derivatives

Partial Derivative

Measures rate of change with respect to a single variable, while keeping all other variables constant.
Notation: $\frac{d}{dx}$ = derivative $\frac{\partial}{\partial x}$ = partial

Example:

$$f(x, y) = x^2 y + 3y$$

$$\frac{\partial f}{\partial x}$$

$$f(x, y) = y \cdot x^2 + 3y$$
$$\frac{\partial f}{\partial x} = y \cdot 2x = 2xy$$

$$\frac{\partial f}{\partial y}$$

$$f(x, y) = x^2 \cdot y + 3y$$
$$\frac{\partial f}{\partial y} = x^2 + 3$$

Total Differential

Total Differential

For a function $f(x, y)$, the total differential is:

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

For a function $f(x, y, z)$:

$$df = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz$$

Subscripts indicate which variables are held constant

Gas Laws and Partial Derivatives

Recall from General Chemistry:

- Boyle's Law: At constant T, $PV = \text{constant}$
- Charles' Law: At constant P, $\frac{V}{T} = \text{constant}$
- Avogadro's Law: At constant T, P, $V \propto n$
- Ideal Gas Law: $PV = nRT$

Boyle's Law Partials:

$$V = \frac{c_1}{P}$$

Take the partial derivative wrt P:

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(\frac{c_1}{P}\right) = -\frac{c_1}{P^2}$$

Charles' Law Partials:

$$V = c_2 T$$

Take the partial derivative wrt T:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial}{\partial T}(c_2 T) = c_2$$

Ideal Gas Law, Formal Derivation

Experimentally, it is observed that for a fixed n, V only depends on T and P:

$$V = f(T, P)$$

Take the total differential:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

Using Charles' law and Boyle's law:

$$\left(\frac{\partial V}{\partial T}\right)_P = c_2 \quad \text{(Charles' Law)}$$
$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{c_1}{P^2} \quad \text{(Boyle's Law)}$$

Ideal Gas Law, Formal Derivation

Substitute partial derivatives into total differential:

$$dV = c_2\, dT - \frac{c_1}{P^2}\, dP$$

Use Charles' law and Boyle's law to rewrite in terms of V:

$$V = c_2 T \implies c_2 = \frac{V}{T} \quad \text{and} \quad V = \frac{c_1}{P} \implies c_1 = PV$$

$$dV = \frac{V}{T}\, dT - \frac{V}{P}\, dP$$

Rearrange:

$$\frac{dV}{V} = \frac{dT}{T} - \frac{dP}{P}$$

Ideal Gas Law, Formal Derivation

Integrate both sides:

$$\int \frac{dV}{V} = \int \frac{dT}{T} - \int \frac{dP}{P} \implies \ln V = \ln T - \ln P + C$$

Simplifying:

$$\ln V = \ln \frac{T}{P} + C$$

Exponentiate both sides:

$$V = e^{\ln \frac{T}{P} + C} = \frac{T}{P} e^{C} = \frac{T}{P} \cdot C'$$

Ideal Gas Law, Formal Derivation

The n dependence is in C':

$$V = \frac{T}{P} \cdot C'(n)$$

From Avogadro's law, at fixed T and P, $V \propto n$:

$$V = k(T, P) \cdot n$$

Therefore:

$$C'(n) \propto n \implies C'(n) = n \cdot R$$

Substituting back:

$$V = \frac{T}{P} \cdot (nR) = \frac{nRT}{P} \implies \boxed{PV = nRT}$$