Summary of Partial Differentiation

Let \( z = z(x,y) \) and \( a, c \) are constants

Examples

\( a) \quad z = x^2 + y^2 \) \hspace{1cm} \( d) \quad z = x^2 \)
\( b) \quad z = 3xy \) \hspace{1cm} \( e) \quad z = 3y \)
\( c) \quad z = ax^2 + y/c \) \hspace{1cm} \( f) \quad z = e^{-(x+y)} \)

1) \( \left( \frac{\partial z}{\partial x} \right)_y \) means consider everything but \( x \) constant (i.e. \( y \) is constant) and differentiate with respect to \( x \). The derivative is generally still a function of \( x \) and \( y \).

Examples:

\( a) \quad \left( \frac{\partial z}{\partial x} \right)_y = \left( \frac{\partial (x^2 + y^2)}{\partial x} \right)_y = \left( \frac{\partial x^2}{\partial x} \right)_y + \left( \frac{\partial y^2}{\partial x} \right)_y = 2x \)

\( b) \quad \left( \frac{\partial z}{\partial x} \right)_y = \left( \frac{\partial (3xy)}{\partial x} \right)_y = 3y \left( \frac{\partial x}{\partial x} \right)_y = 3y \)

\( f) \quad \left( \frac{\partial z}{\partial x} \right)_y = -e^{-(x+y)} \) \hspace{1cm} (Note this is still a function of \( x \) and \( y \).)

We can have \( \left( \frac{\partial z}{\partial y} \right)_x \) with analogous meaning:

\( c) \quad \left( \frac{\partial z}{\partial y} \right)_x = 1/c \) \hspace{1cm} \( d) \quad \left( \frac{\partial z}{\partial y} \right)_x = 0 \) \hspace{1cm} \( e) \quad \left( \frac{\partial z}{\partial y} \right)_x = 3 \)

2) The total differential equation of a function, \( z(x,y) \) is:

\[
dz = \left( \frac{\partial z}{\partial x} \right)_y \, dx + \left( \frac{\partial z}{\partial y} \right)_x \, dy
\]
an example from (a)

\[
dz = \left( \frac{\partial (x^2 + y^2)}{\partial x} \right)_y \, dx + \left( \frac{\partial (x^2 + y^2)}{\partial y} \right)_x \, dy
\]

\[= 2x \, dx + 2y \, dy\]

3) Mixed partial derivatives and second partial derivatives:

\[
\left( \frac{\partial^2 z}{\partial x^2} \right)_y = \left[ \frac{\partial}{\partial x} \left( \frac{\partial z}{\partial x} \right)_y \right]_y
\]

and the same can be said for \( \left( \frac{\partial^2 z}{\partial y^2} \right)_x \)

a) \( \left( \frac{\partial^2 z}{\partial x^2} \right)_y = 2 \)

b) \( \left( \frac{\partial^2 z}{\partial x^2} \right)_y = 0 \)

c) \( \left( \frac{\partial^2 z}{\partial y^2} \right)_x = 0 \)

f) \( \left( \frac{\partial^2 z}{\partial y^2} \right)_x = e^{(x+y)} \)

\[
\frac{\partial^2 z}{\partial x \partial y} = \left[ \frac{\partial}{\partial x} \left( \frac{\partial z}{\partial y} \right)_x \right]_y \quad \text{with a similar definition for} \quad \frac{\partial^2 z}{\partial y \partial x}
\]

a) \( \frac{\partial^2 z}{\partial x \partial y} = \left[ \frac{\partial}{\partial x} \left( \frac{\partial z}{\partial y} \right)_x \right]_y = \left[ \frac{\partial}{\partial x} (2y) \right]_y = 0 \)

b) \( \frac{\partial^2 z}{\partial x \partial y} = 3 \quad \frac{\partial^2 z}{\partial y \partial x} = 3 \)

Note: The fact that these mixed partial derivatives are equal is NOT a coincidence. It is generally true and a very important fact that,

if \( z = z(x,y) \Rightarrow \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x} \)

4) The differential form \( dz = M(x,y) \, dx + N(x,y) \, dy \) is derived from a function \( z = f(x,y) \), i.e.

\[
dz = \left( \frac{\partial z}{\partial x} \right)_y \, dx + \left( \frac{\partial z}{\partial y} \right)_x \, dy = M \, dx + N \, dy
\]

IF AND ONLY IF \( \left( \frac{\partial M}{\partial y} \right)_x = \left( \frac{\partial N}{\partial x} \right)_y \)
Examples: for \( dz = 2xy^2 \, dx + 2yx^2 \, dy \)

\[
M = 2xy^2 \quad \text{and} \quad N = 2yx^2
\]

\[
\left( \frac{\partial M}{\partial y} \right)_x = 4xy \quad \text{and} \quad \left( \frac{\partial N}{\partial x} \right)_y = 4xy
\]
The two partial derivatives are equal!!! Therefore a function, \( z = f(x,y) \) does exist. In fact, for this example, \( z = x^2y^2 \). In this case, the differential equation, \( dz \) is called an **exact differential**.

For \( dz = 2xy \, dx + 2yx^2 \, dy \) \quad M = 2xy \quad \text{and} \quad N = 2yx^2

\[
\left( \frac{\partial M}{\partial y} \right)_x = 2x \quad \text{and} \quad \left( \frac{\partial N}{\partial x} \right)_y = 4xy \quad \text{and} \quad \left( \frac{\partial M}{\partial y} \right)_x \neq \left( \frac{\partial N}{\partial x} \right)_y
\]

Therefore no function, \( z(x,y) \) exists that corresponds with this differential equation. A differential of this type is called an **inexact differential**.

5) An important derivative relationship is the chain rule:

\[
\left( \frac{\partial z}{\partial x} \right) = \left( \frac{\partial z}{\partial u} \right) \left( \frac{\partial u}{\partial x} \right), \text{ Where } u \text{ is a function of } x.
\]

6) In thermodynamics, kinetics and quantum mechanics we rarely use \( x, y, z \) as variables. We use measurable quantities such as enthalpy (H), entropy (S), and concentrations ([A]) and determine how these quantities might vary with other measurable quantities such as: temperature or pressure or time. Therefore you must get used to seeing derivatives, partial derivatives and mixed derivatives in terms of chemical properties.

Examples: a. \( \left( \frac{\partial H}{\partial T} \right)_p \) is defined as how the enthalpy changes with temperature holding pressure constant.

b. \( \left( \frac{\partial G}{\partial P} \right)_{T,n} \) how does the Gibbs energy change with respect to pressure holding temperature and the number of moles constant.
c. \( \frac{\partial^2 A}{\partial V \partial T} = \left[ \frac{\partial}{\partial V} \left( \frac{\partial A}{\partial T} \right)_V \right] \) means to take the derivative of \( A \) with respect to \( T \) holding volume constant. Then take that answer, and differentiate with respect to \( V \) holding \( T \) constant.

d. If we have the solution to a partial derivative we can easily express this as a differential equation. For example:

\( \left( \frac{\partial U}{\partial T} \right)_V = C_V \) Where \( U \) is the internal energy of a system and \( C_V \) is the heat capacity at constant volume. Therefore the differential equation may be written as:

\[ dU = C_V \, dT \]

7) Below is a list of common derivatives and integrals that we will use throughout this course.

\[ \frac{d}{dx}[c]=0 \quad \frac{d}{dx}[x^n]=n \, x^{n-1} \quad \frac{d}{dx}[c \, f(x)]=c \, \frac{d}{dx}[f(x)] \]

\[ \frac{d}{dx}[g(x) + f(x)]=\frac{d}{dx}[g(x)] + \frac{d}{dx}[f(x)] \text{, subtraction is done in a similar way.} \]

\[ \frac{d}{dx}[e^x]=e^x \quad \frac{d}{dx}[\ln x]=\frac{1}{x} \quad \frac{d}{dx}[g(x) \cdot f(x)]=g(x) \frac{d}{dx}[f(x)] + f(x) \frac{d}{dx}[g(x)] \]

\[ \frac{d}{dx}[\sin x]=\cos x \quad \frac{d}{dx}[\cos x]= -\sin x \quad \frac{d}{dx}\left[\frac{f(x)}{g(x)}\right]=\frac{g(x) \frac{d}{dx}[f(x)] - f(x) \frac{d}{dx}[g(x)]}{(g(x))^2} \]
5) You should be familiar with integration by u-substitution.

Example:

Evaluate: \[ \int 3x^2 \sqrt{x^3 - 1} \, dx \]

-If we let \( u = x^3 - 1 \), then \( du/dx = 3x^2 \)
Therefore \( du = 3x^2 \, dx \), then

\[ \int 3x^2 \sqrt{x^3 - 1} \, dx = \int u^{1/2} \, du = \frac{u^{3/2}}{3/2} + C = \frac{2}{3} (x^3 + 1)^{3/2} + C \]
Problems- Partial differentiation

\[ z = z(x,y) \text{ and } a, b \text{ are constants.} \]

1. Compute \( \left( \frac{\partial z}{\partial x} \right)_y, \left( \frac{\partial z}{\partial y} \right)_x, \frac{\partial^2 z}{\partial x \partial y}, \frac{\partial^2 z}{\partial y \partial x} \)

   a) \( z = x^2y + 3y \)
   b) \( z = y\ln x + x\ln x \)
   c) \( z = 6x^3 \)
   d) \( z = 5e^x + y \)
   e) \( z = \sqrt{xy} \)

2. a) For \( PV = nRT \), determine \( \left( \frac{\partial V}{\partial T} \right)_p \) directly

   b) \( P = \frac{RT}{V-b} \), solve for \( \left( \frac{\partial P}{\partial V} \right)_T \) and \( \left( \frac{\partial P}{\partial T} \right)_V \), \( R \) and \( b \) are constants

3. Obtain differential equations, \( dz \) of the following:

   a) \( z = 3xy + x^2 \)
   b) \( z = ae^{-x} + ye^x \)
   c) \( z = x^4y^2 + 3x^2y^3 + \cos(ax) \)

4. For each of the differential equations in problem 3, verify that \( \left( \frac{\partial M}{\partial y} \right)_x = \left( \frac{\partial N}{\partial x} \right)_y \) where \( dz = Mdx + Ndy \).

5. Determine which of the following are inexact differentials. Show your work.

   a) \( (3x^2)dx + (3y^2x)dy \)
   b) \( (2xy)dx + (x^2 + 3)dy \)
   c) \( 2xdx + 2ydy \)
   d) \( ye^{-x}dx + xe^{-y}dy \)

6. Using the chain rule, determine the derivative of each of the following functions.

   a) \( z = 4 \cos(x^3) \)

   b) \( z = \sin(x^2 + 9) \)
   c) \( z = e^{x^3} \)
Evaluate the following integrals:

a. \( \int (x^2 + x) \, dx \)

b. \( \int 4 \cos x \, dx \)

c. \( \int -\frac{nRT}{V} \, dV \)

(n,R,T are constant)

d. \( \int_{3}^{10} \left(2x^{3/4}\right) \, dx \)

e. \( \int_{V_1}^{V_2} P \, dV \) (P is constant)

f. \( \int_{V_1}^{V_2} \frac{RT}{V - b} - \frac{a}{V^2} \, dV \)

(a, R,T are constants)

g. \( \int_{0}^{\infty} v^2 e^{-mv^2} \, dv \), m is a constant