Calculus: Useful Formulas and Concepts for CHEM 2010

If you don't know them already, the following rules and formulas of calculus will be *very useful* to you in studying physical chemistry. I am giving them with no derivation or explanation: just look at them as a kind of "toolkit" of mathematical rules that you need to go on with your studies of chemistry (or physics). You would normally see the theory and applications of these rules in a second or third calculus course.

1. Derivative of functions of many variables

Suppose you have a function of two variables $f(x, y)$. When you take its derivative with respect to x, $\partial f/\partial x$, treat the other variable (y) as if it were a constant; when you take its derivative with respect to y, treat x as if it were a constant. Here are examples of this rule:

$$\begin{aligned}
f(x,y) &= x^2 y \ ; \ \frac{\partial f}{\partial x} = 2xy \ ; \ \frac{\partial f}{\partial y} = x^2 \ ; \ \frac{\partial f}{\partial z} = 0 \\
f(x,y) &= (x^2-1)\sin y \ ; \ \frac{\partial f}{\partial x} = 2x\sin y \ ; \ \frac{\partial f}{\partial y} = (x^2-1)\cos y \\
f(x,y) &= x^2 e^{xy} \ ; \ \frac{\partial f}{\partial x} = 2xe^{xy} + x^2 y e^{xy} \ ; \ \frac{\partial f}{\partial y} = x^3 e^{xy}
\end{aligned}$$

2. Mixed second derivatives.

A symbol like $\frac{\partial^2 f(x,y)}{\partial x \partial y}$ means "*take the derivative of $f(x, y)$ with respect to (wrt) y, then take the derivative of the resulting function wrt x*".

$$\frac{\partial^2 f(x,y)}{\partial x \partial y} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)$$

But *the order of differentiation does not affect the result*[a]. So

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)$$

3. Sums of Integrals.

$$\begin{aligned}
\int_0^{+\infty} f(x)\,dx &= \int_0^2 f(x)\,dx + \int_2^{+\infty} f(x)\,dx \\
\int_0^1 f(x)\,dx &= \int_0^{0.8} f(x)\,dx + \int_{0.8}^1 f(x)\,dx \\
\int_{-\infty}^{+\infty} f(x)\,dx &= \int_{-\infty}^0 f(x)\,dx + \int_0^{+\infty} f(x)\,dx
\end{aligned}$$

etc.

$$\int_a^b f(x)\,dx = \int_a^c f(x)\,dx + \int_c^b f(x)\,dx$$

where $a < c < b$. This formula becomes obvious if you sketch a function $f(x)$ and its integral (area under the curve) between the limits a to c, and c to b, with $a < c < b$.

4. Multiple Integrals.

In calculating multiple integrals of functions of many variables like

$$I = \int_{x_a}^{x_b}\int_{y_a}^{y_b} f(x,y)\,dxdy$$

rules analogous to 1. and 2. still apply, namely:
(i) when integrating $f(x,y)$ wrt x, treat y as if it were a constant (and vice-versa), and (ii) a double integral wrt x and y as written above means "*integrate*

[a]except for strange functions that almost never occur in physical chemistry.

wrt y between the limits y_a and y_b, and then integrate the resulting function wrt x between the limits x_a and x_b". However, the order in which you calculate the two integrals does not matter. Here is an example.

$$\begin{aligned}
\int_{x_a}^{x_b}\int_{y_a}^{y_b} x^2 y\, dx dy &= \int_{x_a}^{x_b} x^2\, dx \int_{y_a}^{y_b} y\, dy \\
&= \left[\frac{x^3}{3}\right|_{x_a}^{x_b} \times \left[\frac{y^2}{2}\right|_{y_a}^{y_b} \\
&= \frac{1}{6}\left(x_b^3 - x_a^3\right)\left(y_b^2 - y_a^2\right)
\end{aligned}$$

5. Taylor series — See Silbey page 885.

6. Total differential

The total differential df of a function of two variables $f(x, y)$ is, by definition

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy$$

This is readily generalized to functions of more than 2 variables, for example, for $f(x, y, z)$

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz$$

7. Implicit functions.

This comes up mostly in thermodynamics. Suppose we have a function of two variables $f(x, y)$ and y is itself a function of x, then we have

$$\frac{dy}{dx} = -\frac{\partial f/\partial x}{\partial f/\partial y}$$

Likewise, if we have a function of 3 variables $f(x, y, z)$ and each of the 3 variables is actually a function of the other two, $x \equiv x(y, z)$, $y \equiv y(x, z)$, and $z \equiv z(x, y)$, then

$$
\begin{aligned}
\frac{\partial y}{\partial x} &= -\frac{\partial f/\partial x}{\partial f/\partial y} \\
\frac{\partial z}{\partial y} &= -\frac{\partial f/\partial y}{\partial f/\partial z} \\
\frac{\partial x}{\partial z} &= -\frac{\partial f/\partial z}{\partial f/\partial x} \\
\frac{\partial z}{\partial x} &= -\frac{\partial f/\partial x}{\partial f/\partial z} = 1 \div \left(\frac{\partial x}{\partial z}\right) \\
&etc.
\end{aligned}
$$