Mathematical Review for Physical Chemistry

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   (a) Important derivatives
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1 Integration:

1.1 Integrals you should know:

1.1.1 Integrals involving x^n

$$\int ax^n\, dx = \frac{a}{n+1}x^{n+1} \tag{1}$$

$$\int \frac{a}{x}\, dx = a\ln x \tag{2}$$

$$\int \frac{a}{x^n}\, dx = -\frac{a}{(n-1)x^{n-1}} \tag{3}$$

1.1.2 Integrals involving sin,cos and e^x

$$\int \sin(ax)\, dx = -\frac{1}{a}\cos(ax) \tag{4}$$

$$\int \cos(ax)\, dx = \frac{1}{a}\sin(ax) \tag{5}$$

$$\int e^{ax}\, dx = \frac{1}{a}e^{ax} \tag{6}$$

1.2 Tricks for evaluating integrals:

When an integral is more complicated than the ones shown above, integral tables are often helpful. However, often the integral you are trying to solve and the ones in the tables do not look the same and you may need to apply some manipulations to get them into the "standard" form. Tricks that you may find helpful are described below:

1.2.1 Break the integral into steps

$$\int_{-\infty}^{\infty} F(x)\ dx = \int_{-\infty}^{0} F(x)\ dx + \int_{0}^{\infty} F(x)\ dx \tag{7}$$

$$= \int_{-\infty}^{a} F(x)\ dx + \int_{a}^{b} F(x)\ dx + \int_{b}^{\infty} F(x)\ dx \tag{8}$$

1.2.2 Change the dummy variable

Since the result of an integration is independent of the variable over which the integration is carried out, it can be treated as a dummy variable, e.g. the result does not depend on what label it is given. It can be called x, u or $Harry$ and the result will not change. Mathematically:

$$\int_{x=a}^{b} F(x)\ dx = \int_{u=a}^{b} F(u)\ du \tag{9}$$

1.2.3 Change of variables

If $u = kx$, then $x = u/k$,

$$dx = \frac{dx}{du}du = \frac{1}{k}du \tag{10}$$

$$\int_{x=a}^{b} F(x)\ dx = \frac{1}{k}\int_{u=ka}^{kb} F\left(\frac{u}{k}\right)\ du \tag{11}$$

1.2.4 Switching the limits of integration

Switching the limits of integration changes the sign of the integral:

$$\int_{x=a}^{b} F(x)\ dx = -\int_{x=b}^{a} F(x)\ dx \tag{12}$$

1.2.5 Integration by parts

$$\int_{x=a}^{b} u(x)\frac{dv(x)}{dx}\ dx = u(x)v(x)|_{x=a}^{b} - \int_{x=a}^{b} v(x)\frac{du(x)}{dx}\ dx \tag{13}$$

1.2.6 Other tricks

If the integrand contains sin's or cos's, you may find it necessary to utilize one or more of the trig identities reviewed below. If the integrand is even $[F(x) = F(-x)]$ then

$$\int_{-a}^{a} F(x)\ dx = 2\int_{0}^{a} F(x)\ dx \tag{14}$$

If the integrand is odd $[F(x) = -F(-x)]$

$$\int_{-a}^{a} F(x)\ dx = 0 \tag{15}$$

2 Derivatives

2.1 Ones you should know:

$$\frac{du^n}{dx} = nu^{n-1}\frac{du}{dx} \tag{16}$$

$$\frac{de^u}{dx} = e^u\frac{du}{dx} \tag{17}$$

$$\frac{d\ln x}{dx} = \frac{1}{x} \tag{18}$$

$$\frac{d\sin x}{dx} = \cos x \tag{19}$$

$$\frac{d\cos x}{dx} = -\sin x \tag{20}$$

2.2 Special relationships:

Chain rule:

$$\frac{d[F(u(x))]}{dx} = \frac{dF}{du}\frac{du}{dx} \tag{21}$$

Derivative of a product:

$$\frac{d(uv)}{dx} = \frac{du}{dx}v + u\frac{dv}{dx} \tag{22}$$

Derivative of a ratio:

$$\frac{d(u/v)}{dx} = \frac{v\left(\frac{du}{dx}\right) - u\left(\frac{dv}{dx}\right)}{v^2} \tag{23}$$

3 Series Expansions of Functions

The first derivative of a function provides its slope, the second its curvature. This means that if we are interested in the behavior of a function near a specific point then a good approximation is obtained by using a second order polynomial:

$$F(x) \approx A(x-a)^2 + B(x-a) + C \tag{24}$$

Where $A = F''(a)/2$, $B = F'(a)$ and $C = F(a)$. At $x = a$ the relationship is exact, while at points near a the relationship provides a reasonable approximation to $F(x)$, the size of the error will depend on the size of the deviation of the function from being strictly quadratic [the importance of higher order terms in the expansion]. This idea becomes important in physical chemistry when one wants to study deviations from ideal behavior, for example, the behavior of gases near zero pressure (the ideal gas limit).
In general, the series expansion of a function can be written as:

$$F(x) = \sum_j \frac{F^{(j)}(a)}{j!}(x-a)^j \tag{25}$$

where $F^{(j)}(a)$ represents the jth derivative of $F(x)$ evaluated at $x = a$. Some particularly useful expansions (all about $x = 0$) and the values of x for which they converge are given below:

$$\begin{aligned}
e^x &= 1 + x + \frac{x^2}{2!} + \ldots + \frac{x^n}{n!} + \ldots; \quad [\text{all x}] && (26)\\
\ln(1+x) &= x - \frac{x^2}{2} + \frac{x^3}{3} - \ldots - (-1)^n\frac{x^n}{n} - \ldots; \quad [x^2 < 1] && (27)\\
\frac{1}{1+x} &= 1 - x + x^2 + \ldots + (-1)^n x^n + \ldots; \quad [x^2 < 1] && (28)\\
\frac{1}{1-x} &= 1 + x + x^2 + \ldots + x^n + \ldots; \quad [x^2 < 1] && (29)\\
\frac{1}{(1-x)^2} &= 1 + 2x + 3x^3 + \ldots + (n+1)x^n + \ldots; \quad [x^2 < 1] && (30)\\
\sqrt{1+x} &= 1 + \frac{x}{2} - \frac{x^2}{8} + \frac{x^3}{16} + \ldots; \quad [x^2 < 1] && (31)\\
\sin x &= x - \frac{x^3}{6} + \frac{x^5}{120} - \ldots; \quad [\text{all x}] && (32)\\
\cos x &= 1 - \frac{x^2}{2} + \frac{x^4}{24} - \ldots; \quad [\text{all x}] && (33)
\end{aligned}$$

4 Partial Derivatives

4.1 Definitions:

If a function depends on two or more variables, $f(x, y)$, then the *partial derivative* expresses the dependence of f on one of the variables when **all** other variables are held constant. Mathematically the partial derivative of f with respect to x at constant y is represented by:

$$\left(\frac{\partial f}{\partial x}\right)_y \tag{34}$$

By analogy to the one-dimensional definition of the differential of $z(x)$:

$$dz = \frac{dz}{dx}dx \tag{35}$$

The differential of $z(x, y)$ is given by:

$$dz(x, y) = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{36}$$

or more generally,

$$dz(x_1, x_2, \ldots, x_n) = \left(\frac{\partial z}{\partial x_1}\right)_{x_2,\ldots,x_n} dx_1 + \ldots + \left(\frac{\partial z}{\partial x_n}\right)_{x_1,x_2,\ldots,x_{n-1}} dx_n \tag{37}$$

Physically, the relationship of Eq. (36) says that if x is changed by a infinitesimal amount dx, the corresponding value of dz is $\left(\frac{\partial z}{\partial x}\right)_y dx$ and if y is changed by an infinitesimal amount dy, the corresponding change in z is given by $\left(\frac{\partial z}{\partial y}\right)_x$dy. If both x and y are changed by differential amounts then the change in z will be given by the sum of the individual changes, assuming dz is an exact differential (see the following section). For an exact differential, the order of differentiation does not matter:

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y = \left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x \tag{38}$$

which means the second derivative of $z(x, y)$ can be expressed unambiguously by

$$\frac{\partial^2 z}{\partial x \partial y} \equiv \frac{\partial^2 z}{\partial y \partial x} \tag{39}$$

4.2 An Example:

$$\begin{aligned}
z(x, y) &= x^3 + 4x^2y + 12xy^2 + 7y^3 \\
\left(\frac{\partial z}{\partial x}\right)_y &= 3x^2 + 8xy + 12y^2 \\
\left(\frac{\partial z}{\partial y}\right)_x &= 4x^2 + 24xy + 21y^2 \\
\left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x &= 8x + 24y \\
\left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y &= 8x + 24y
\end{aligned}$$

4.3 Important relationships

If f can be written as a function of either $\{x, y\}$ where these variables are functions of $\{u, v\}$ so that:

$$\begin{aligned} x &= x(u,v) \\ y &= y(u,v) \end{aligned}$$

by the chain rule [Eq. (21)],

$$\left(\frac{\partial f}{\partial u}\right)_v = \left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial u}\right)_v + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial u}\right)_v \tag{40}$$

NOTE the variables appear in specific pairs - for example, derivatives with respect to x are taken at constant y and derivatives with respect to u are taken at constant v. This general relationship simplifies to some important relationships

4.3.1 $u = x$ and $v = z$

$$\begin{aligned} \left(\frac{\partial f}{\partial x}\right)_z &= \left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial x}\right)_z + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \\ &= \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \end{aligned} \tag{41}$$

since $\left(\frac{\partial x}{\partial x}\right)_z = 1$

4.3.2 $u = x$, $v = z$ and $f = z$

$$\begin{aligned} \left(\frac{\partial z}{\partial x}\right)_z &= \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \\ \left(\frac{\partial z}{\partial x}\right)_y &= -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \end{aligned} \tag{42}$$

since $\left(\frac{\partial z}{\partial x}\right)_z = 0$. Using the relationship:

$$\left(\frac{\partial z}{\partial x}\right)_y \frac{1}{\left(\frac{\partial x}{\partial z}\right)_y} \tag{43}$$

Eq. (42) can be rewritten as:

$$-1 = \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \tag{44}$$

5 Exact and Inexact Differentials

Functions, like U or H, have the property that their value depends only on the state of the system and not how it arrived at that state. These functions are called state functions and change in their values resulting from a change in the state of the system depends only on the starting and ending points, but not how they arrived there. The differentials of these functions are called *exact differentials*. Mathematically this means that the differential of a state function $f(x,y)$ is given by:

$$\begin{aligned} df &= \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy && (45) \\ &= M(x,y)dx + N(x,y)dy && (46) \end{aligned}$$

Eq. (38) says that:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{47}$$

which is often taken as the definition of exactness. Differentials for which this relationship does not hold, or where the changes depend on the path are called inexact differentials and are represented by df. Examples of inexact differentials in thermodynamics are dq and dw since the work done on a system or the heat absorbed by the system depend on the path the system takes to get from its initial to final state.

6 Properties of Logs:

$$\begin{aligned} \log(a) + \log(b) &= \log(ab) && (48) \\ \log(a) - \log(b) &= \log(a/b) && (49) \\ \log(a)^n &= n\log(a) && (50) \\ \ln(a) &= \ln(10)\log_{10}(a) = 2.303\log_{10}(a) && (51) \end{aligned}$$

7 Review of Trigonometry

$$\begin{aligned}
\sin(a+b) &= \sin(a)\cos(b)+\sin(b)\cos(a) && (52)\\
\sin(a-b) &= \sin(a)\cos(b)-\sin(b)\cos(a) && (53)\\
\cos(a+b) &= \cos(a)\cos(b)-\sin(a)\sin(b) && (54)\\
\cos(a-b) &= \cos(a)\cos(b)+\sin(a)\sin(b) && (55)\\
\cos(2a) &= \cos^2(a)-\sin^2(a)=2\cos^2(a)-1=1-2\sin^2(a) && (56)\\
\sin(2a) &= 2\sin(a)\cos(a) && (57)\\
\cos^2(a) &= \frac{1}{2}\left(\cos(2a)+1\right) && (58)\\
sin^2(a) &= \frac{1}{2}\left(1-\cos(2a)\right) && (59)
\end{aligned}$$