CHEM1047 – Week 5 Lecture 2 – Differentials

☐ *Chapter 5 of Cockett and Doggett, "Maths for Chemists", Vol 1.*

☐ *Sections 4.12 and 9.5 of Steiner, "The Chemistry Maths Book", 2nd edition.*

The *differential* is a generalisation of the notion of small increment. In the discussion so far, we were working with finite increments (*e.g.* Δf and Δx) or with limit expressions in which those increments vanished after the limit was taken. Differential expressions combine those methods: dx stands for an increment of x that is infinitesimally small.

1. Formal definition of the differential

In mathematics, the differential is formally defined as the limit of a small increment:

$$\begin{gathered} f(x+\Delta x)=f(x)+f'(x)\Delta x-\varphi(x,\Delta x)\Delta x \\ \Downarrow \\ f(x+\Delta x)-f(x)=f'(x)\Delta x-\varphi(x,\Delta x)\Delta x \\ \Downarrow \\ \Delta f=f'(x)\Delta x-\varphi(x,\Delta x)\Delta x \\ \Downarrow \\ df=f'(x)dx \end{gathered} \tag{1}$$

Differential expressions are more compact and convenient than the expressions involving limits of finite increments. Equation (1) also clarifies the origin of *Leibniz's notation* for the derivative:

$$df=f'(x)dx \quad \Rightarrow \quad \frac{df}{dx}=f'(x) \tag{2}$$

Differentials will appear naturally in the construction of the definite integral where they correspond to infinitesimally small area or volume elements that the integral is adding up. The differential of a function may also be viewed as its local linear approximation.

2. Properties of differentials

The properties follow from the corresponding derivative properties. For sums and multiples:

$$d[f+g]=df+dg, \qquad d[\alpha f]=\alpha df \tag{3}$$

where α is a constant. For products and fractions:

$$d[fg]=fdg+gdf, \qquad d\left[\frac{f}{g}\right]=\frac{fdg-gdf}{g^2} \tag{4}$$

Here, d is not a variable or a function, but a *differential operator* – an instruction to compute the differential of whatever appears in front.

Differential notation is powerful – the chain rule that has taken a page of limit expressions a few lectures ago can now be derived in one line:

$$df=f'(g)dg, \quad dg=g'(x)dx \quad \Rightarrow \quad d\left[f(g(x))\right]=f'(g(x))g'(x)dx \tag{5}$$

Deriving the rule for differentiating inverse functions is also now straightforward:

$$\begin{aligned} y = f(x) \quad &\Rightarrow \quad \frac{dy}{dx} = f'(x) \\ x = f^{-1}(y) \quad &\Rightarrow \quad \frac{dx}{dy} = \left(\frac{dy}{dx}\right)^{-1} = \frac{1}{f'(x)} = \frac{1}{f'\left(f^{-1}(y)\right)} \end{aligned} \tag{6}$$

Example 1: calculate the differential of $\exp\left(-x^2/2\right)$.

Solution: from the definition in Equation (2)

$$d\left[\exp\left(-x^2/2\right)\right] = \exp\left(-x^2/2\right) d\left(-x^2/2\right) = -x\exp\left(-x^2/2\right) dx$$

Example 2: if $df/dx = \cos x$ and $x = t^3$, derive the expression for df/dt.

Solution: we can calculate dx and replace it

$$dx = 3t^2 dt \quad \Rightarrow \quad \frac{df}{dx} = \frac{df}{3t^2 dt} = \cos\left(t^3\right) \quad \Rightarrow \quad \frac{df}{dt} = 3t^2\cos\left(t^3\right)$$

Example 3: given that $y = a\sin(x)$, calculate dx/dy.

Solution: we can use the fact that dx/dy can be interpreted as a ratio of the two differentials

$$y = a\sin(x) \quad \Rightarrow \quad \frac{dy}{dx} = a\cos(x) \quad \Rightarrow \quad \frac{dx}{dy} = \frac{1}{a\cos(x)}$$

$$\frac{dx}{dy} = \frac{1}{a\sqrt{1-\sin^2(x)}} = \frac{1}{a\sqrt{1-y^2/a^2}} = \frac{1}{\sqrt{a^2-y^2}}$$

3. Differentials of multivariate functions

Multivariate functions change value if any of their arguments changes. The expression for the differential of a multivariate function therefore is:

$$df(x,y,z,...) = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz + ... \tag{7}$$

A subtle point here is that not every expression of the form

$$[...]dx + [...]dy + [...]dz + ... \tag{8}$$

is a differential of a well-behaved function because mixed second derivatives must be equal, *e.g.*:

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \tag{9}$$

A differential that satisfies this property is called an *exact differential*. Such differentials are important in thermodynamics because their integrals are path-independent. To find out if a particular expression is an exact differential, one must compare mixed second derivatives, for example:

$$g(x,y)\,dx + h(x,y)\,dy \qquad \begin{array}{ll} \dfrac{\partial g}{\partial y} = \dfrac{\partial h}{\partial x} & \text{exact differential} \\ \dfrac{\partial g}{\partial y} \neq \dfrac{\partial h}{\partial x} & \text{not an exact differential} \end{array} \tag{10}$$

Here, $g(x,y)$ and $h(x,y)$ are already first partial derivatives of something – see Equation (7) – and therefore only one further derivative, with respect to the other variable, needs to be calculated.

Mixed derivative relations are useful in thermodynamics. Consider the full differential of enthalpy:

$$H = U + PV \qquad dH = dU + PdV + VdP \tag{11}$$

From the second law of thermodynamics $dU = TdS - PdV$, and therefore

$$dH = TdS + VdP \tag{12}$$

For this to be an exact differential, we must have:

$$\frac{\partial T(P,S)}{\partial P} = \frac{\partial V(P,S)}{\partial S} \tag{13}$$

Such relations are called *Maxwell's relations*.

Example 4: calculate the differential of $f(x,y) = x\sin y$.

Solution: from the definition

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy = \frac{\partial}{\partial x}(x\sin y)\,dx + \frac{\partial}{\partial y}(x\sin y)\,dy =$$
$$= \sin(y)\,dx + x\cos(y)\,dy$$

Example 5: find out if $(x^2 - y^2)dx + 2xydy$ is an exact differential.

Solution: calculating mixed derivatives yields

$$\frac{\partial}{\partial y}(x^2 - y^2) = -2y \qquad \frac{\partial}{\partial x}(2xy) = 2y$$

The derivatives are not equal, and therefore the differential is not exact.