2.3: Exact and Inexact Partials and Euler's Test

Before we leave the subject of work, there is a property of path-dependent differentials like ∂w and ∂q that needs to be examined using multivariable calculus. Normally the change in a function $f(x)$ is $\frac{\partial f}{\partial x}$; however, when the function has two or more variables, i.e. $f(x,y)$, we must analyze the change in the function with respect to both x and y as: $\partial f(x,y) \approx \frac{\partial f}{\partial x} + \frac{\partial f}{\partial y}$. Now being good chemists, we know that if we are measuring the change in an observation (∂f) due to a change in an experimental condition (∂x), we then need to hold all other variables (here, y) constant and vice versa. To represent this, we change the notation as: $\partial f(x,y) \approx \left(\dfrac{\partial f}{\partial x}\right)_y + \left(\dfrac{\partial f}{\partial y}\right)_x$. However, this expression can't be fully correct as ∂f has the same units as the function f while $\left(\dfrac{\partial f}{\partial x}\right)_y$ has units of $\frac{f}{x}$. Another clue that something isn't quite right is that fact that ∂f is infinitesimally small, yet $\frac{\partial f}{\partial x}$ is finite.

"The solution is that the real partial is:

$$\partial f(x,y) = \left(\dfrac{\partial f}{\partial x}\right)_y \partial x + \left(\dfrac{\partial f}{\partial y}\right)_x \partial y \tag{2.3.1}$$

which is tantamount to calculating a change in the function (∂f) by following $f(x,y)$ in small steps (∂x) along the x-direction in an amount weighted by the slope $\frac{\partial f}{\partial x}$, and then doing the same in the y-direction as shown in Figure 2.6. To apply the lesson above, the partial of the function $f(x,y) = x \cdot y$ is:

$$\partial f(x,y) = \left(\dfrac{\partial x \cdot y}{\partial x}\right)_y \partial x + \left(\dfrac{\partial x \cdot y}{\partial y}\right)_x \partial y = y \cdot \partial x + x \cdot \partial y \tag{2.3.2}$$

This is an example of an exact differential, which means that there is a function $f(x,y)$ associated with $\partial f(x,y)$. Such a differential is said to be exact, and it is ***not path dependent***.

Thermodynamic variables that are exact include energy and entropy, but not work or heat as we have already shown that they depend on whether a process is reversible or irreversible. Since energy and entropy are not path dependent, we call them state variables, which means that their values are not derived from how the state came to exist. For example, the potential energy of a cat on a bookshelf is due to gravity and is a function of the height of the shelf. It doesn't matter how the cat got there, only that it is there! Hence, state function.

Inexact differentials are the opposite of the exact. An example is: $\partial f(x,y) = x \cdot \partial y$. This is ∼1/2 the exact differential in Equation 2.8, and as a result you could never write a function $f(x,y)$ that could be differentiated into $\partial f = x \cdot \partial y$. Work: $\partial w(P_{ext}, V) = -P_{ext} \cdot \partial V$ is clearly inexact because it is identical to: $\partial f(x,y) = x \cdot \partial y$, the letters are just different! This is why you haven't seen us write w =…, because work is only defined as a differential ∂w. As a result, work is path dependent and is ***not a state variable***.

Euler (pronounced Oiler!) introduced a test to examine whether a differential $\partial f(x,y)$ is exact or not:

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\left( \dfrac{\partial }{\partial y}{\frac{\partial f}{\partial x} \right)_y)}_x=\left( \dfrac{\partial }{\partial x}{\frac{\partial f}{\partial y} \right)_x)}_y        \label{2.9}
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This says when taking the derivative of an exact differential with respect to the variables, it doesn't matter what order you do the operations. Later we will prove that ∂w and ∂q are inexact differentials, but first we need to introduce energy.