9.1: Partial Differentiation

The development of thermodynamics would have been unthinkable without calculus in more than one dimension (multivariate calculus) and partial differentiation is essential to the theory.

'Active' Variables

When applying partial differentiation it is very important to keep in mind, which symbol is the variable and which ones are the constants. Mathematicians usually write the variable as x or y and the constants as a, b or c but in Physical Chemistry the symbols are different. It sometimes helps to replace the symbols in your mind.

For example the van der Waals equation can be written as:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \tag{9.1.1}$$

Suppose we must compute the partial differential

$$\left(\frac{\partial P}{\partial \bar{V}}\right)_T \tag{9.1.2}$$

In this case molar volume is the variable 'x' and the pressure is the function $f(x)$, the rest is just constants, so Equation 9.1.1 can be rewritten in the form

$$f(x) = \frac{c}{x - b} - \frac{a}{x^2} \tag{9.1.3}$$

When calculating

$$\left(\frac{\partial P}{\partial T}\right)_{\bar{V}} \tag{9.1.4}$$

should look at Equation 9.1.1 as:

$$f(x) = cx - d \tag{9.1.5}$$

The active variable 'x' is now the temperature T and all the rest is just constants. It is useful to train your eye to pick out the one active one from all the inactive ones. Use highlighters, underline, rewrite, do whatever helps you best.