

## 32.8: 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:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \quad (32.8.1)$$

Suppose we must compute the partial differential

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

In this case molar volume is the variable ' $x$ ' and the pressure is the function  $f(x)$ , the rest is just constants, so Equation 32.8.1 can be rewritten in the form

$$f(x) = \frac{c}{x - b} - \frac{a}{x^2} \quad (32.8.2)$$

When calculating

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

should look at Equation 32.8.1 as:

$$f(x) = cx - d$$

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.

### Cross Derivatives

As shown in Equations H.5 and H.6 there are also higher order partial derivatives versus  $T$  and versus  $V$ . A very interesting derivative of second order and one that is used extensively in thermodynamics is the [mixed second order derivative](#).

$$\left( \frac{\partial^2 P}{\partial T \partial \bar{V}} \right) = \left( \frac{\partial^2 P}{\partial \bar{V} \partial T} \right) \quad (32.8.3)$$

Of course here the 'active' variable is first  $T$ , then  $V$ . The interesting thing about it is that it does not matter whether you first take  $T$  and then  $V$  or the other way around.

Example H-2 shows an example of how mixed derivatives can be used to translate one quantity into the other. This trick is used over and over again in thermodynamics because it allows you to replace a quantity that is really hard to measure by one (or more) that are much easier to get good experimental values for.

For example:

$$\left( \frac{\partial S}{\partial \bar{V}} \right)_T = \left( \frac{\partial P}{\partial T} \right)_{\bar{V}}$$

This expression is not obvious at all. It tells you that if you study the pressure  $P$  when heating up while keeping the volume the same (which is doable) you're measuring how the entropy changes with volume under isothermal conditions. Entropy will be

discussed later, suffice it to say that nobody has ever constructed a working 'entropometer'! So that is an impossible quantity to measure directly.

## The Decomposition of Changes

A very important result of multivariate calculus is that if a quantity  $Q$  is a function of more than one variable, say  $A$  and  $B$  that we can decompose any infinitesimal change  $dQ$  into infinitesimal changes in  $A$  and  $B$  in a very simple linear way:

$$dQ = \alpha dA + \beta dB \quad (32.8.4)$$

$dq$  is sometimes referred to as the total differential. The coefficients  $\alpha$  and  $\beta$  are the partial derivatives of first order versus  $A$  and  $B$ . This mathematical fact is something we will be using over and over.

## Exact and Inexact differentials: State and path functions

### The car trip

Suppose you drive your car up and down a mountain. You perform two measurements: you have a barometer that measures the air pressure and you keep an eye on your gas gage. Even though the barometer will show lower values on top of the mountain, its value will return to its initial value when you return home (barring weather changes). You might wish the same would hold for your gas gage particularly at current gas prices!

Pressure is a good example of a **state function** (it returns to its old value if you go back to a previous state). The other (the gas gage) is a path function. (Make a detour and your bank account will tell you difference!).

The difference between state and path functions has its roots deep in mathematics and it comes in as soon as a function has two of more variables.

The gas law is a good example. The pressure depends on both temperature  $T$  and (molar) volume  $V$ . When changing the pressure a little bit, say by  $dP$  we can show that we can write that out in the two possible components  $dT$  and  $dV$  as:

$$dP = p dT + q dV \quad (32.8.5)$$

$$= \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV \quad (32.8.6)$$

At first, I wrote arbitrary coefficients  $p$  and  $q$  in Equation 32.8.5, but as you can see they are really partial derivatives (Equation 32.8.6). This is another way that thermodynamics exploits multivariate calculus: it shows how total changes can be built up of various contributions.

The interesting thing is that **if** the function  $P$  is a **state** function (and your barometer will testify to that) then Equation 32.8.3 **must** hold. However, if the function is a **path** function, then this equality does **not** hold.

Thermodynamics is largely based upon exploiting the above facts:

- It tries to define state functions to describe energy changes
- It tries to decompose changes into well-defined contributions
- It uses partial differentials to link known quantities to unknown ones

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