Consider a function *f* which depends upon the values of two independent variables *x* and *y*. If one thinks about this in graphical terms, as shown in Figure 1, we can see that each point *(x,y)* in the xy plane maps into a value *f(x,y)*, and the set of points *f(x,y)* then describes a surface in the 3D plot frame. The question we will now try to answer is the following: Suppose we start at a point $f(x_1,y_1)$ and change both x and y by small amounts *dx* and *dy*. What is the resulting change df in the function *f*? We will show that the answer is given by the equation:

$$df = \left(\frac{\partial f}{\partial x}\right)dx + \left(\frac{\partial f}{\partial y}\right)dy \qquad (1)$$

The proof is geometric in nature: Suppose we start at $f(x_1,y_1)$ and change from y_1 to y_2, a change of Δy. In Figure 1 this corresponds to changing along the plane where *x* is constant and equal to x_1. The slope (derivative) of *f* along this constant-*x* plane is designated as $\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial f}{\partial y}\right) = \frac{\partial f}{\partial y}\Big) = \frac{\partial f}{\partial y}$. (Four common alternative ways of writing this are shown.) The funny derivative symbol always implies that <u>only one</u> of the independent variables is being allowed to change. The change in *f* which results from this small change in *y* is then given by: $\delta f_2 = \frac{\partial f}{\partial y}\Big)\Delta y$ (see Fig. 1). If *x* is now allowed to change, so that we are going from $f(x_1,y_2)$ to $f(x_2,y_2)$, there is a corresponding additional change in f given by: $\delta f_1 = \frac{\partial f}{\partial x}\Big)\Delta x$. The total change in *f* from changing both *x* and *y* is the sum: $df = \delta f_1 + \delta f_2$ (see boxed formula in Fig. 1) and in the limit as Δx and Δy approach 0, this gives equation (1) above.

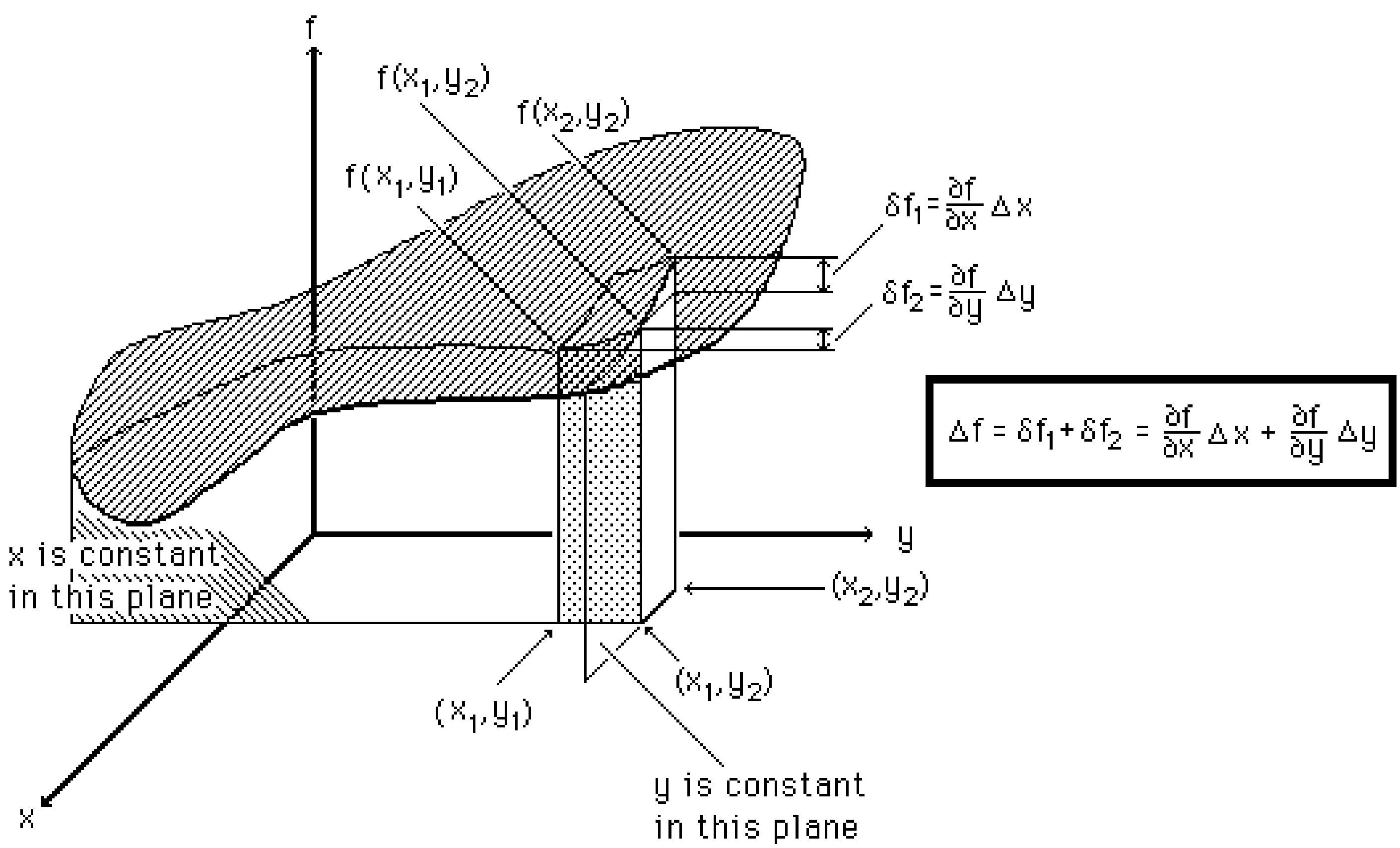

Figure 1.

Beginning Applications of Partial Derivatives in Thermodynamics

I. Ideal Gas behavior

Starting with $P = nRT/V$, we can write $dP = \left.\frac{\partial P}{\partial T}\right)_V dT + \left.\frac{\partial P}{\partial V}\right)_T dV$ Furthermore, $\left.\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$ and $\left.\frac{\partial P}{\partial V}\right)_T = \frac{-nRT}{V^2}$ so that $dP = \frac{nR}{V}dT - \frac{nRT}{V^2}dV$ is an expression which describes how small changes in T and in V will affect the pressure. Note that a positive dT will *increase* the pressure, and a positive dV will *decrease* the pressure as expected.

II. Internal Energy (U) as a function of T and V

If we consider U to be defined for a system once the state of the system is described by T and V values, we can say:

$$dU = dU(T,V) = \left.\frac{\partial U}{\partial T}\right)_V dT + \left.\frac{\partial U}{\partial V}\right)_T dV .$$

One useful special case of this equation occurs when $dV = 0$, *i.e.* a constant volume process. In this case,

$$dU = dU(T,V) = \left.\frac{\partial U}{\partial T}\right)_V dT + \left.\frac{\partial U}{\partial V}\right)_T dV = \left.\frac{\partial U}{\partial T}\right)_V dT + 0 = dq - PdV = dq_V + 0 .$$

Rearranging, we find that $\left.\frac{\partial U}{\partial T}\right)_V = \frac{dq_V}{dT} = C_V$ where C_V is the constant-volume heat capacity of a system. It is also worth noting that $\left.\frac{\partial U}{\partial V}\right)_T = 0$ for an ideal gas (the ideal gas energy depends only upon T, not on intermolecular spacing) and that this term is small even for real gases.

III. Enthalpy (H) as a function of T and P

Parallel to the previous example, we write: $dH = dH(T,P) = \left.\frac{\partial H}{\partial T}\right)_P dT + \left.\frac{\partial H}{\partial P}\right)_T dP$ From the definition of $H = U + PV$, we can also write $dH = dU + PdV + VdP = dq - PdV + PdV + VdP = dq + VdP$

At constant P, this gives $dH = dq_P = \left.\frac{\partial H}{\partial T}\right)_P dT$, leading to a definition of a constant-pressure heat capacity: $\left.\frac{\partial H}{\partial T}\right)_P = \frac{dq_P}{dT} = C_P$

In a further parallel to the previous case, $\left.\frac{\partial H}{\partial P}\right)_T = 0$ for an ideal gas, and is close to 0 for real gases. Finally, we can easily get a relationship between the constant P and constant V molar heat capacities for an ideal gas as follows: First assume we are talking about 1 mole of gas. Then

$$C_{P,m} = \left.\frac{\partial H_m}{\partial T}\right)_P = \left.\frac{\partial U_m + PV}{\partial T}\right)_P = \left.\frac{\partial U_m + RT}{\partial T}\right)_P = \left.\frac{\partial U_m}{\partial T}\right) = C_{V,m} + R \qquad i.e., \qquad \boxed{C_{P,m} = C_{V,m} + R}$$

There is a little bit of sleight-of-hand in this derivation because I have assumed that $\left.\frac{\partial U_m}{\partial T}\right)_P = \left.\frac{\partial U_m}{\partial T}\right)_V = C_{V,m}$ In fact the two partial derivatives, one at constant P and the other at constant V, are not necessarily equal for all systems, but since we have already seen that energy (U) depends *only* on T for an ideal gas, the derivative will be the same for both constant P and constant V in this case.