

Chapter 4

Partial Derivatives and Their Meanings

4-1 Multivariable Functions

We introduce the function $F(x, y, z) = a$, where a is some constant and could even be 0. This function may be the trajectory of a missile in space with respect to some coordinate system, the electric potential of a charged particle or an equation of state of a system. Therefore, $F(x, y, z)$ is a multivariable function.

$F(x, y, z) = a$ is the equation of a surface in xyz space. For example, $x^2 + y^2 + z^2 = a$ is the equation of a sphere in Cartesian coordinates with radius $a^{1/2}$. The variables x , y and z may themselves be functions of time, in this case a is a variable.

In thermodynamics, $F(x, y, z) = 0$ may be an equation of state, that is, a description of a system in terms of what are called state variables. The state variables are also called thermodynamic coordinates. There may be arbitrary changes in any two of the state variables, but not all three. This is because the equation of state is a **constraint** on the values that the variables may have. That is, any one of the variables may be expressed as a function of the other two.

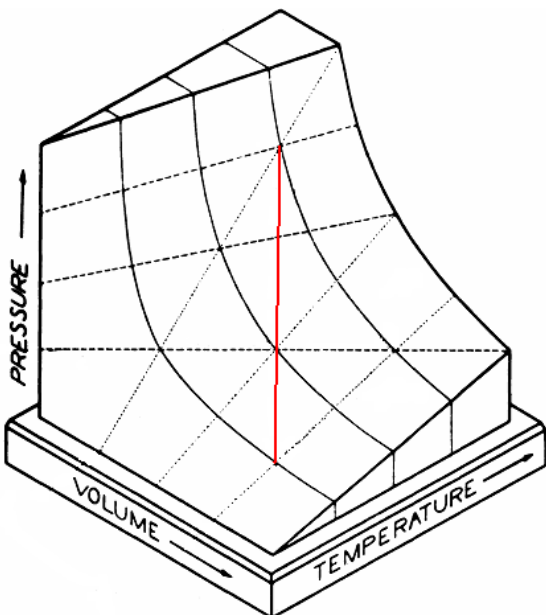
Continuing with our example from thermodynamics: $F(P,v,T) = 0$, where P , v , & T are thermodynamic coordinates describing a system. For example:

$$P = f(v,T). \quad (4-1.1)$$

P is considered the dependent variable and v and T are called the independent variables. It is important to remember what is dependent and what is independent. An example is the ideal gas law:

$$P = nRT/V \quad (4-1.2)$$

This is the equation of a surface in PVT -space



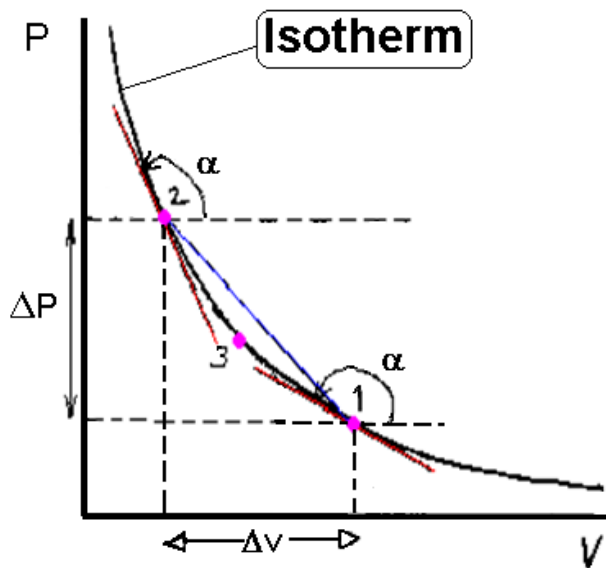
called the PVT-surface. Such a surface is schematically shown in the figure above. The curves drawn on the surface represent changes that occur in the system when one of the parameters is held constant and the other two are allowed to change. The red curve lies on the surface and represents an arbitrary change in the state of a system from one set of values of P, V, and T to another set of values. But remember, only two of the parameters may be arbitrarily changed. That is, $V = g(P,T)$ and $T = h(V,P)$.

4-2 Partial Derivatives

Now, the rate of change of P as a result of a change in V when T is held constant is called the partial derivative of P with respect to V and is written as

$$\left(\frac{\partial P}{\partial V}\right)_T = (\partial f(V,T)/\partial V)_T, \quad (4-2.1)$$

where the meaning of T as a subscript is that T is held constant when taking the derivative of the function f with respect to V.



The geometric meaning of a partial derivative, such as $(\partial P/\partial V)_T$, is shown to the left, in a diagram of the PV plane. The curve (an isotherm) is formed by the intersection of a plane perpendicular to the T-axis with the PVT surface. The partial derivative is the slope of the curve at a given point. That is,

$$\left(\frac{\partial P}{\partial V}\right)_T = -\tan(\alpha) \quad (4-2.2)$$

Now consider a finite change ΔP that results from a finite change in V, ΔV , at constant T, as indicated in the above diagram. Then $(\Delta P/\Delta V)_T$ is the slope of the blue straight line between the points numbered 1 and 2 in the above diagram. This line is also parallel to the slope of the curve at the point numbered 3, and the latter line is the mean slope of the curve between points 1 and 2. That is,

$$(\Delta P/\Delta V)_T = (\partial P/\partial V)_3 \quad (4-2.3)$$

The subscript 3 on the partial means that the partial derivative is evaluated at point 3, while the subscript T is assumed. Now let ΔV approach 0 in the limit. Visualize points 1 and 2 approaching the point 3. Then:

$$\lim_{\Delta V \rightarrow 0} \left(\frac{\Delta P}{\Delta V}\right)_T = \left(\frac{dP}{dV}\right)_T \equiv \left(\frac{\partial P}{\partial V}\right)_T \quad (4-1.5)$$

Or, $dP = \left(\frac{\partial P}{\partial V}\right)_T dV$, for any point in general along the isotherm. This is actually a differential equation that expresses the change in P for an isothermal process. It is also referred to as a process equation.

4-3 Total Differentials

Similarly, we have $dP = \left(\frac{\partial P}{\partial T}\right)_V dT$ for an isochoric process (constant volume). If we move on the PVT surface along an arbitrary path, both V and T vary for a given ΔP . Hence, the total change in P is the sum of the changes that result from a change in V and a change in T. That is:

$$dP = \left(\frac{\partial P}{\partial v}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT \quad (4-3.1)$$

This is called the **total differential** of P. It is the total differential because P depends only on T and V and not on any other variable. The 1st term is the change in P as a result of a change in V only. The 2nd term is the change in P resulting from only a change in T.

Similarly:

$$dT = (\partial T/\partial V)_P dV + (\partial T/\partial P)_V dp \quad (4-3.2)$$

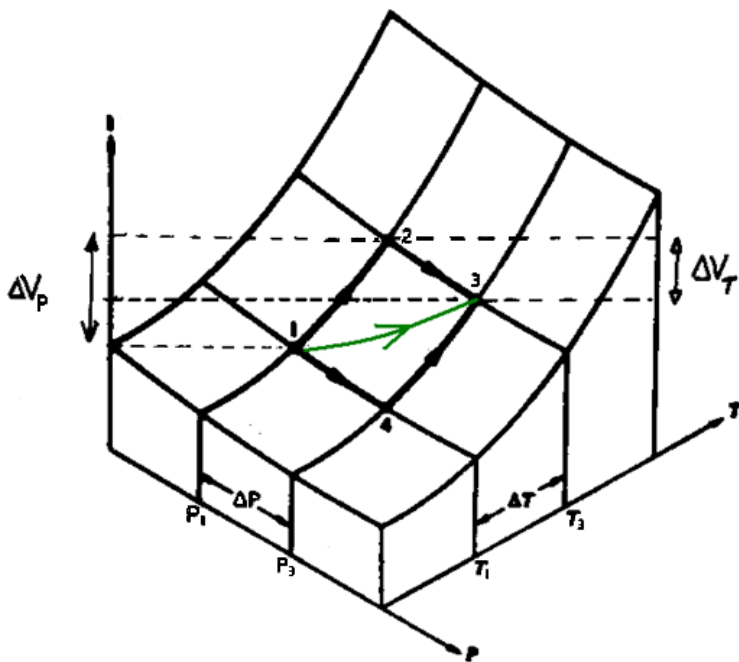
is the total differential of T. The 1st term is the change in T as a result of a change in V only and the 2nd term is the change in T resulting from only a change in P. Each of these changes is independent of the other and their sum is the total differential change in T, dT.

In general, for a given multivariable function $F = F(x, y, z)$, the total differential is:

$$dF = \left(\frac{\partial F}{\partial x}\right)_{yz} dx + \left(\frac{\partial F}{\partial y}\right)_{xz} dy + \left(\frac{\partial F}{\partial z}\right)_{xy} dz \quad (4-3.2)$$

Often, the subscripts on the partials are left off and understood.

As an example for visualizing the total differential of V , consider a system that consists of an ideal gas that undergoes a process by which it is taken from state 1 to state 3 as shown by the green curve in the adjacent diagram.



To calculate the change in V , ΔV_{13} , that takes place during this process, we may replace the original process with two others that are more readily calculated. We first go from state 1 to state 2 by an isobaric process, thereby calculating $(\Delta V_{12})_P$. We then go from state 2 to state 3 by an isothermal process, thereby calculating $(\Delta V_{23})_T$. This permits us to replace the original process with two others so that:

$$\Delta V_{13} = (\Delta V_{12})_P + (\Delta V_{23})_T$$

Now in the limit as ΔP_T and ΔT_P approach 0, $\Delta V \rightarrow dV$, where

$$dV = dV_P + dV_T$$

Hence, we may write:

$$dV = (\partial V / \partial T)_P \Delta T + (\partial V / \partial P)_T \Delta P,$$

which is the total differential of V .

Notice also, that we could just as well have first gone from state 1 to state 4 and then from state 4 to state 3. In both cases, the change in V would be the same, since we end up at the same point on the PVT-surface. **In other words, the change that takes place in going from one state to another is independent of the path we take in PVT space. Such systems are said to be “conservative systems.”** In a conservative system, energy is conserved.