Chapter 3

Partial Derivatives and Their Meanings

3.1 Multivariable Functions

Let the function $F(P,v,T)= 0$ be an equation of state. The equation of state is a description of a system in terms of several thermodynamical coordinates or state variables, and therefore, it is a multivariable function.

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 function of the other two.

For example:

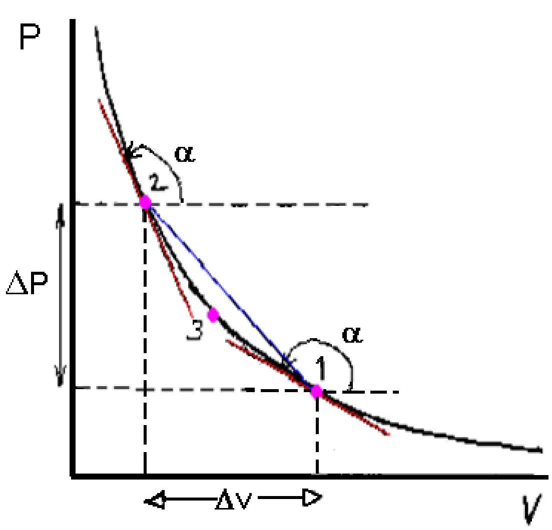
$$P = f(v,T). \tag{3.1-1}$$

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.

Similarly we have $v = g(P,T)$ and $T = h(v,P)$.

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

$$\left(\frac{\partial P}{\partial v}\right)_T = (\partial f(v,T)/\partial v)_T, \tag{3.1-2}$$



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 in the adjacent, 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,

$$(\partial P/\partial v)_T = -\tan(\alpha)$$

The partial derivatives depend on the substance via the equation of state, but not on the processes that the substance may undergo.

Now consider a change ΔP that results from a 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,

$$(\Delta P/\Delta v)_T = (\partial P/\partial v)_3$$

The subscript 3 on the partial means that the partial derivative is evaluated at point 3, while the subscript T means T is constant and has a specific value. Now let Δv approach 0 in the limit. Visualize points 1 and 2 approaching the point 3. Then:

$$\lim_{\Delta v \to 0} \left(\frac{\Delta P}{\Delta v}\right)_T = \left(\frac{dP}{dv}\right)_T \equiv \left(\frac{\partial P}{\partial v}\right)_T$$

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.

Similarly, we have $dP = \left(\frac{\partial P}{\partial T}\right)_v dT$ for an isochoric process. 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:

$$dP = \left(\frac{\partial P}{\partial v}\right)_T dv + \left(\frac{\partial P}{\partial T}\right)_v dT$$

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:

$$dT = (\partial T/\partial v)_P \, dv + (\partial T/\partial P)_v \, dp$$

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:

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

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

3.2 The Coefficients of Volumetric Expansion or Compression.

The coefficient of volumetric expansion is called the expansitivity of a substance and is represented by the symbol β. We approach the definition of β in the following way. If a finite change in temperature ΔT brings about a corresponding finite change in volume $\Delta V = V_2 - V_1$ at constant P, then the mean value for β is:

$$\bar{\beta} \equiv \left[\frac{(V_2-V_1)}{V_1(T_2-T_1)}\right]_P .$$

The quantity $\bar{\beta}$ is defined to be the mean fractional increase in volume per unit change in temperature at constant pressure. In the limit, as ΔT approaches dT and ΔV approaches dV, we have

$$\beta = \left[\frac{dV}{V_1(dT)}\right]_P = \frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_P$$

or

$$\beta = \frac{1}{v}\left[\frac{\partial v}{\partial T}\right]_P . \qquad (3.2\text{-}1)$$

The units of β are reciprocal Kelvins, (K^{-1}). Now β is not a slope in the vT plane, but $\beta v = \left[\frac{\partial v}{\partial T}\right]_P$ is. As an example, consider an ideal gas for which PV=nRT or Pv=RT. Then v=(RT/P) and

$$\beta v = \left[\frac{\partial v}{\partial T}\right]_P = \left[\frac{\partial}{\partial T}\left(\frac{RT}{P}\right)\right]_P = \frac{R}{P}\left[\frac{\partial T}{\partial T}\right]_P$$

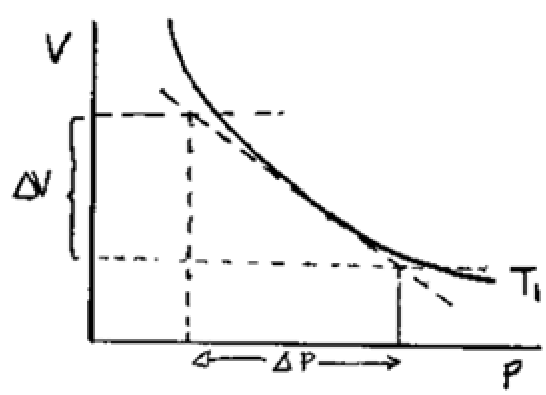
So βv = R/P = slope of line tangent to PvT surface, which is constant since R and P are constant. This means that an isobaric process in PvT-space is a straight line (Charles' Law). Also,

$$\beta = (R/Pv) = (R/RT) = 1/T$$

In general, the slope of an isobar depends on the both P and T. How it varies depends on the substance. So β = β(P, T).

Isothermal Compressibility, κ:

Now consider a change in volume of a material as a result of a change in P, while T is held constant. This is illustrated in the adjacent diagram. The slope of the tangent line at a point is:



$$\left(\frac{\partial V}{\partial P}\right)_T = \text{slope of tangent line}$$

Then $\Delta V_T = \text{slope} \times \Delta P_T = \left(\frac{\partial V}{\partial P}\right)_T \Delta P_T$. As we saw before, in the limit as ΔP approaches zero,

$$dV_T = \left(\frac{\partial V}{\partial P}\right)_T dP_T$$

We now define κ as

$$\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{3.2-2}$$

The negative sign here indicates that volume decreases with increasing pressure at constant temperature. That is , $(\partial V/\partial P)_T$ is negative. As an example, consider an ideal gas again. In this case, V = nRT/P, so

$$\left(\frac{\partial V}{\partial P}\right)_T = nRT\left(\frac{\partial}{\partial P}\right)\frac{1}{P} = -nRT/P^2$$

So,
$$\kappa = -\frac{1}{V}\left(-\frac{nRT}{P^2}\right) = \frac{1}{nRT/P}\left(-\frac{nRT}{P^2}\right) = \frac{1}{P}$$

The mean compressibility for finite changes in V and P is

$$\bar{\kappa} = \frac{1}{V}\left(\frac{\Delta V_T}{\Delta P_T}\right)$$

Kappa is usually a function of both T and P.

So far, we have discussed isothermal and isobaric processes. Now consider some general process that takes a system from one state to another, such as indicated by the green curve in the following diagram. In general, $\Delta V = V_3 - V_1$. That is, the volume difference between state 3 and state 1, does not depend on the path we took on the PvT-surface to get there. Hence, we have the following very important concept or principle:

The volume difference between two equilibrium states is independent of the process.

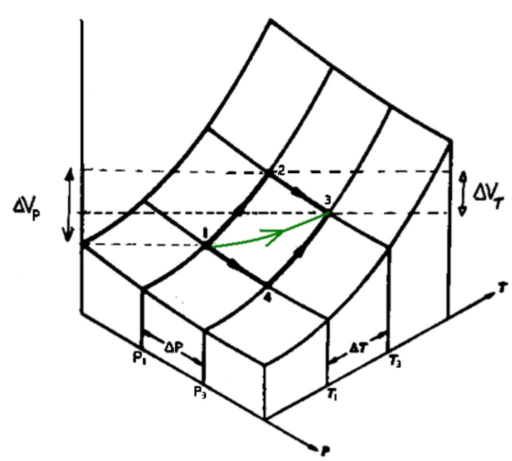


Fig. 3-3. Examples of processes on the PVT-surface for a substance. The change in the state of the substance is independent of the path.

This permits us to replace the original process with two others, as shown in the figure above. First we go from state 1 to state 2 by an isobaric process. Then from state 2 to state 3 by an isothermal process. Hence:

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

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

$$dV = dV_P + dV_T$$

Now, if V is a function of T and P, we may write:

$$\mathbf{dV = (\partial V/\partial T)_P \Delta T + (\partial V/\partial P)_T \Delta P} \qquad (3.2\text{-}3)$$

This is the total differential of V.

Using the definitions for β and κ , we can transform (3.2-3) to:

$$\mathbf{dV = \beta V dT - \kappa V dP} \qquad \mathbf{(3.2\text{-}4)}$$

This equation may be integrated to find the change in volume for a change in T and P. This requires knowing β, κ, and V as functions of the variables of integration.

To integrate, use what is called the Method of Separation of Variables:

$$dV/V = \beta dT - \kappa dP \qquad (3.2\text{-}5)$$

But this is only valid if P and T are both changing simultaneously, that is, V has the same value in both of the above terms. Integrating this we obtain:

$$\ln V = \int_{T1}^{T2} \beta dT - \int_{P1}^{P2} \kappa dP \qquad (3.2\text{-}6)$$

In reality, the integration of (3.2-4) is not done this way. Instead, we first do an isobaric process such that dP = 0. The first term in (3.2-4) (not 3.2-5) gives us a change in v, Δv, as a result of the change in T. We then do an isothermal process. That is we do the integral in the 2^{nd} term with dT=0. This gives us the change in v due to the change in temperaure. We then add together the two changes in v to get the total change. This is equivalent of first going from state 1 to state 4 in Fig. 3-3, and then going from state 4 to state 3. We should get the same result if went from state 1 to state 2 first, and then state 2 to state 3.

For a solid or real substance, β and κ may only be known in terms of a graph or table. In this case the integrals must be replaced by summations. That is

$$\Delta v = \sum_{T_1}^{T_2} \beta v \, \Delta T - \sum_{P_1}^{P_2} v \kappa \, \Delta P \qquad (3.2\text{-}7)$$

3.3 Exact Differentials

As we have just illustrated, the volumn difference between 2 equilibrium states of a system is independent of the path, that is, the nature of the process in getting from one state to the other.

On the PvT surface, a process is always represented by a curve, drawn on the surface, connecting the two states. Now consider the change in volume moving along the path in Fig. 3-3 from point 1 to point 2 along an isobar and then from point 2 to point 3 along an isotherm. Then

$$\Delta V_{1\text{-}2\text{-}3} = (\partial V/\partial T)_{P_1}\Delta T + (\partial V/\partial P)_{T_2}\Delta P \qquad (3.3\text{-}1)$$

Now move from point 1 to point 4 along an isotherm and then from point 4 to point 3 along and isobar to get

$$\Delta V_{1\text{-}4\text{-}3} = (\partial V/\partial P)_{T_1}\Delta P + (\partial V/\partial T)_{P_4}\Delta T \qquad (3.3\text{-}2)$$

Now since $\Delta V_{1\text{-}2\text{-}3} = \Delta V_{1\text{-}4\text{-}3}$, we may equate the right sides of the above two expressions and collect the coefficients of ΔP and ΔT:

$$[(\partial V/\partial T)_{P_1} - (\partial V/\partial T)_{P_4}]\Delta T = [(\partial V/\partial P)_{T_1} - (\partial V/\partial P)_{T_2}]\Delta P \qquad (3.3\text{-}3)$$

Now divide both sides by $\Delta P\Delta T$:

$$[(\partial V/\partial T)_{P_1} - (\partial V/\partial T)_{P_4}]/ \Delta P = [(\partial V/\partial P)_{T_1} - (\partial V/\partial P)_{T_2}]/\Delta T \qquad (3.3\text{-}4)$$

The difference in the partials at constant pressures on the left is found at the same temperature, T_1 and the difference in the partials at constant temperatures on the right is found at the same pressure, P_3. This may be visualized in Fig. 3-3. Hence, we may write:

$$[(\partial V/\partial T)_{P_1} - (\partial V/\partial T)_{P_4}]_T/ \Delta P = [(\partial V/\partial P)_{T_1} - (\partial V/\partial P)_{T_2}]_P/\Delta T,$$

Or

$$[\Delta(\partial V/\partial T)_P]_T/\Delta P = [\Delta(\partial V/\partial P)_T]_P/\Delta T.$$

We are not saying that $(\partial V/\partial T)_{P_1} = (\partial V/\partial T)_{P_4}$ but that the partials are done at constant P. A similar remark is to be made for $(\partial V/\partial P)_T$.

In the limit, as ΔP and ΔT approach zero these differences become differentials so we have

$$[d(\partial V/\partial T)_P]_T/dP = [d(\partial V/\partial P)_T]_P/dT.$$

Now the derivative of a partial at constant T or P must itself be a partial derivative and so we may write the above as

$$[\partial(\partial V/\partial T)_P/\partial P]_T = [\partial(\partial V/\partial P)_T/\partial T]_P,$$

The subscripts in the above expression, indicating that P and T are held constant, may be dropped since they are redundant with regard to the definition of a partial derivative. Hence, the above may now be written as:

$$\frac{\partial^2 V}{\partial T \partial P} = \frac{\partial^2 V}{\partial P \partial T}$$

The right and left hand sides of the above equation are called mixed second partial derivatives. This expression indicates that the value of the mixed second order partial derivative is independ of the order of differentiation.

The above is valid only if ΔV is the same for all processes between the initial and final states. In this case, dV is called an exact differential.

We now state that a quantity whose differential is not exact, that is, it is path dependent, is not a thermodynamic property or coordinate. For an exact differential, $\oint dx = 0$. Work and heat are have inexact differentials. That is

$$d\text{Q} \neq \left(\frac{\partial Q}{\partial P}\right) dP + \left(\frac{\partial Q}{\partial T}\right) dT,$$

and similarly for work.

3.4 Relation Between Partials

Start with the total differential of P for an ideal gas:

$$dP = \left(\frac{\partial P}{\partial v}\right)_T dv + \left(\frac{\partial P}{\partial T}\right)_v dT \qquad (3.4\text{-}1)$$

What are we assuming here about P? Now the total differential for v is:

$$dv = \left(\frac{\partial v}{\partial P}\right)_T dP + \left(\frac{\partial v}{\partial T}\right)_P dT \qquad (3.4\text{-}2)$$

Now use (3.4-2) to eliminate dv in (3.4-1) and we get

$$dP = \left(\frac{\partial P}{\partial v}\right)_T \left[\left(\frac{\partial v}{\partial P}\right)_T dP + \left(\frac{\partial v}{\partial T}\right)_P dT\right] + \left(\frac{\partial P}{\partial T}\right)_v dT \qquad (3.4\text{-}3)$$

Now collect and separate the coefficient of dP and dT to opposite sides of the equal sign:

$$\left[1 - \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial P}\right)_T\right] dP = \left[\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P + \left(\frac{\partial P}{\partial T}\right)_v\right] dT \qquad (3.4\text{-}4)$$

This relation must be valid for any two neighboring states, even when ΔT =0. Then (3.4-4) leads to the following

$$\left[1 - \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial P}\right)_T\right] dP = 0$$

Or

$$\left[1 - \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial P}\right)_T\right] = 0$$

And hence,

$$\left(\frac{\partial P}{\partial v}\right)_T = 1/\left(\frac{\partial v}{\partial P}\right)_T \qquad (3.4\text{-}5)$$

This is true in genera, even when ΔT is not zero. This may be generalized to :

$$\left(\frac{\partial x}{\partial y}\right)_z = 1/\left(\frac{\partial y}{\partial x}\right)_z$$

This is valid for any permutation of x, y, & z, the latter being surogates for P, v, & T.

We can find another relationship by taking dP = 0 in (3.4-4). This leads to

$$\left[\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P + \left(\frac{\partial P}{\partial T}\right)_v\right] dT = 0.$$

Or

$$\left[\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P + \left(\frac{\partial P}{\partial T}\right)_v\right] = 0$$

And therefore,

$$\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_v \qquad (3.4\text{-}6)$$

But from the generalized form of (3.4-5), $\left(\frac{\partial P}{\partial T}\right)_v = 1/\left(\frac{\partial T}{\partial P}\right)_v$. Substitute this in (3.4-6) and we get:

$$\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P = -1/\left(\frac{\partial T}{\partial P}\right)_v.$$

Or:

$$\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_v = -1. \qquad (3.4\text{-}7)$$

This may be generalized to

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \qquad (3.4\text{-}8)$$

Again, this is valid for any permutation of x, y, & z, the latter being surogates for P, v, & T.

End of Chapter 3.