University of Mosul

College of Science

Department of Physics

Second Stage

Heat and Thermodynamic

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Lecture 7: The complete (exact)and incomplete (partial) differentiation

Preparation

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The complete (exact)and incomplete (partial) differentiation

The differential of some of the quantities depends on the path between the initial and the final states, such as work $w = \int p dv$ is called incomplete differentiation ∂

As for the differential that does not depend on the two state paths, it is called the complete differentiation (d) and since the state functions of a particular system (properties of that system such as P, V, T, ...) do not depend on the path we conclude that all the properties of the system have perfect differentials, and therefore Work is not a state function (not a system property)

If Z is a state function for each of the independent variables X, Y, then

Z= f(x,y)…………..(1)

So the total change of Z is

$$dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy \ldots\ldots\ldots (2)$$

Assume that

$$\left(\frac{\partial Z}{\partial x}\right)_y = M \qquad\qquad \left(\frac{\partial Z}{\partial y}\right)_x = N$$

$$dZ = Mdx + Ndy \ldots\ldots\ldots (3)$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \ldots\ldots\ldots\ldots (4)$$ Exact differential

$$\left(\frac{\partial M}{\partial y}\right)_x \neq \left(\frac{\partial N}{\partial x}\right)_y \ldots\ldots\ldots\ldots (5)$$ Partial differential

Example :Prove the volume of ideal gas is exact differential

If volume V is a state function then:

$V = F(T,P)$ (1)

And for one mole of gas we have:

$$V = \frac{RT}{P} \ldots\ldots\ldots\ldots..(2)$$

The total change in V as a result of a change in both P and T is dV, that is

$$\mathbf{dV} = \left(\frac{\partial V}{\partial T}\right)_P \mathbf{dT} + \left(\frac{\partial V}{\partial P}\right)_T \mathbf{dP} \ldots\ldots\ldots\ldots\ldots.(3)$$

dV= MdT +NdP……………….(4)

$$M = \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \ldots\ldots\ldots(5)$$

$$N = \left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2} \ldots\ldots\ldots(6)$$

To solve this equations if

$$\left(\frac{\partial M}{\partial P}\right)_T = -\frac{R}{P^2} \ldots\ldots\ldots\ldots\ldots..(7)$$

$$\left(\frac{\partial N}{\partial T}\right)_P = -\frac{R}{P^2} \ldots\ldots\ldots\ldots\ldots..(8)$$

Since equations 7 and 8 are equal (the condition in equation 9 is fulfilled, i.e. Exact differentiation)

$$\left(\frac{\partial M}{\partial P}\right)_T = \left(\frac{\partial N}{\partial T}\right)_P = -\frac{R}{P^2} \text{ ....(9)} \quad \text{Exact differential}$$

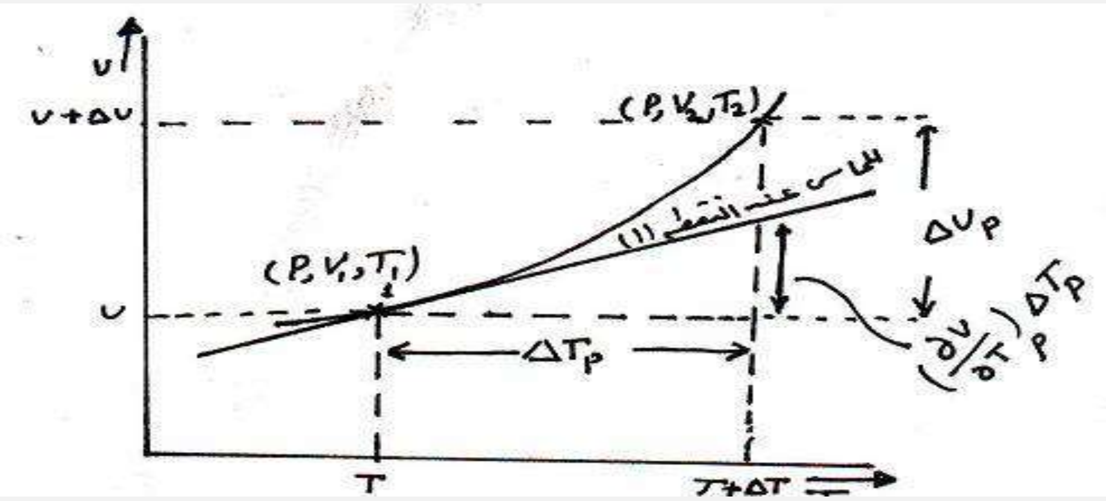
Then volume is a state function that fulfills the above condition.

partial derivatives :

the curve in fig 1 is a graph of the intersection of the surface in fig A with the plane at which the pressure has the constant value P_1. That is, it is a graph of volume (V) as a function of the temperature for the isobaric curve along which the pressure equals P_1 . the slope of this curve at any point means the slope of the tangent to the curve at the point, and this is given by the derivative of V with respect to T .however the volume V is a function of P as well as of T since P is constant along the curve, the derivative of V is called the partial derivative of V with respect to T at constant pressure.

Coefficient of volume expansion (Expansivity β)

Making use of the relationship diagram form Fig A between the thermodynamic variables we take a section of the surface (abcd) when the pressure is constant between the thermodynamic variables. So we get the following form



$V = V_1$, $V+\Delta V = V_2$, $T=T_1$, $T+\Delta T = T_2$

The slope of the curve at any point is the slope of the tangent to the curve at that point, so if we choose point number1) The slope of the tangent is

slop of tangent = $\left(\frac{\partial V}{\partial T}\right)_P$

The slope of the chord connecting points 1 and 2 is the magnitude of The change in volume divided by the amount of change in temperature between the two points when the pressure is constant and be

slope of chord = $\frac{V_2 - V_1}{T_2 - T_1} = \frac{\Delta V_P}{\Delta T_P}$

The slope of the tangent (the slope of the curve at point 1) does not equal the slope of the cutter (chord)

$\left(\frac{\partial V}{\partial T}\right)_P \neq \frac{\Delta V_P}{\Delta T_P} \ldots\ldots\ldots\ldots..(1)$ But it can be equal when (2) approaches (1) or when (2) is about to converge to 1, that is, ΔT_P approaches zero, which means that.

$$\lim_{\Delta T_P \to 0} \frac{\Delta V_P}{\Delta T_P} = \left(\frac{\partial V}{\partial T}\right)_P \ldots\ldots\ldots.(2)$$

If we consider dv the boundary value of ΔV and dT the boundary value of ΔT and ΔT_P approaches zero we get

$$\frac{dV_P}{dT_P} = \left(\frac{\partial V}{\partial T}\right)_P \ldots\ldots\ldots\ldots\ldots.(3)$$

As we knew earlier, $\left(\frac{\partial V}{\partial T}\right)_P$ it is the slope of the simultaneous curve

at any point when the change in T and V is very small and P is constant. But if we look at the relationship curve (Fig. 1) between volume and temperature, we notice that the slope of the curve changes from one point to another depending on the value of the volume, and therefore the slope at a certain point will be related to the value of the volume at that point for a new definition, which is Coefficient of volume expansion (Expansivity β) according to the following mathematical definition : -

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \ldots\ldots\ldots\ldots(4)$$

The compressibility or coefficient of volume compression K:

consider the change in volume of a material when the pressure is changed at a constant temperature for example when the state of the system in fig A is changed from point 2 to point 3 , along the isothermal curve at temperature T_2 . the slope of the tangent line to an isothermal curve at any point is given by :

Now we take the relationship between volume and pressure with constant temperature as shown in Figure 2

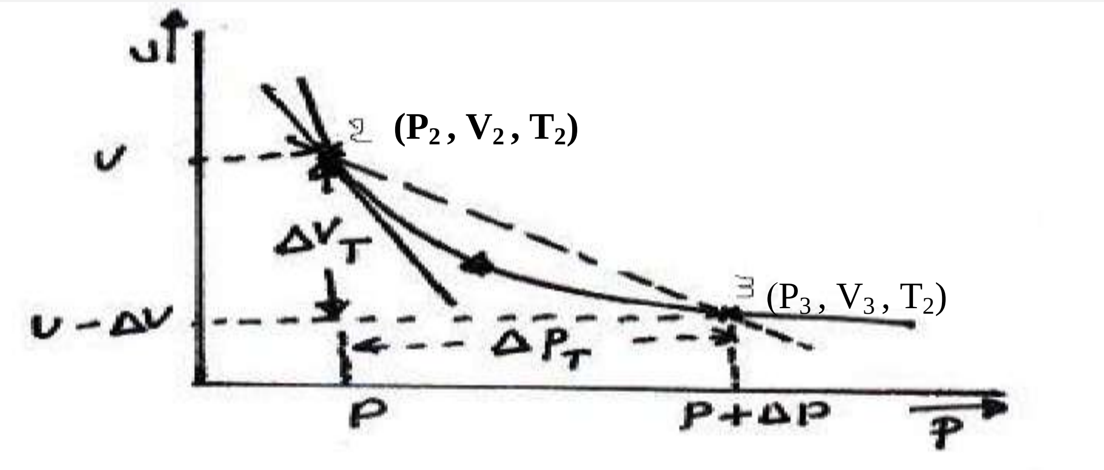


Fig. 2

On this curve, both equilibrium states 2 and 3 are at the same temperature T_2 ,The first case (2) is indicated by the values(P_2, V_2, T_2) and The second case (3) is indicated by the values(P_3, V_3, T_2)

The difference in pressure between the two cases $\Delta P_T = P_3 - P_2$

The difference in volume between the two cases $-\Delta V_T = V_3 - V_2$

As in the case of extensibility the slope of the tangent line to an isothermal curve at any point is given by :

slop of tangent at point 2= $-\left(\frac{\partial V}{\partial P}\right)_T$

The negative sign means that the volume decreases when the pressure increases

The slope of the intersection connecting points 2 and 3

Slope of chord = $\frac{\Delta V_T}{\Delta P_T}$

When point 3 approaches point 2 the slope of the intersection between the two points approaches the slope of the tangent at point 2, and when the amount of change in pressure ΔP_T approaches zero, the slope is equal and we get the relationship

$$\lim_{\Delta P \to 0} \frac{\Delta V_T}{\Delta P_T} = \left(\frac{\partial V}{\partial P}\right)_T$$

If they represent the boundary values of the change in volume and the change in pressure, respectively, of constant temperature, we get

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

The slope of the tangent changes from one point to another along the curve, and therefore we will take the value of the slope at a certain point in relation between the slope and the volume at that point and this ratio gives a definition of compressibility under a constant temperature and is symbolized by K

$$K= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

The thermal compressibility (k) of a material is defined in the same way as it is expansivity , namely ,as $\left(\frac{\partial V}{\partial P}\right)_T$

K: the slope of an isothermal curve at any point $\left(\frac{\partial V}{\partial T}\right)_P$, divided by the volume at the same point.

β : the slope of an isobaric curve at any point , divided by the volume at the same point .

and K is defined as the negative change in volume to the unit of volumes over the change by pressure and is defined K is the isothermal contraction factor .