

Thermodynamics
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Lecture 04

Tutorial problems on exact and inexact differential

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Evaluate path independence of

$z = f(p, V)$ $z = f(x, y)$

$$dz = \left(\frac{\partial z}{\partial p}\right)_V dp + \left(\frac{\partial z}{\partial V}\right)_p dV$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$dz = M dx + N dy$$

$$\frac{\partial}{\partial V} \left(\frac{\partial z}{\partial p}\right) = 0 \quad \frac{\partial}{\partial p} \left(\frac{\partial z}{\partial V}\right) = \frac{\partial p}{\partial p} = 1 \quad \frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$$

$$\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$$

exact

$$dz = \int_1^3 pdV$$

$$\int_1^3 Vdp$$

$$dz = \int_1^3 (pdV + Vdp)$$

$$\int_1^3 (pdV - Vdp)$$

$z = f(p, V)$

$$dz = \left(\frac{\partial z}{\partial p}\right)_V dp + \left(\frac{\partial z}{\partial V}\right)_p dV$$

$$\frac{\partial V}{\partial V} = 1 \quad \frac{\partial}{\partial p} [p] = 1$$

= 1





Figure 1

If we have z as a function of x and y , we should be able to write it in the form $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$. $\left(\frac{\partial z}{\partial x}\right)_y$ represents derivative of z with respect to x keeping y constant (partial derivative of z with respect to x) and $\left(\frac{\partial z}{\partial y}\right)_x$ represents derivative of z with respect to y keeping x constant (partial derivative of z with respect to y). How do we know that dz is an exact differential or inexact differential?

Let's say we have $M = \left(\frac{\partial z}{\partial x}\right)_y$ and $N = \left(\frac{\partial z}{\partial y}\right)_x$. Now, differentiate M with respect to y and N with respect to x . Therefore, $\frac{\partial M}{\partial y} = \frac{\partial}{\partial y} \left(\frac{\partial z}{\partial x}\right)_y = \frac{\partial^2 z}{\partial y \partial x}$ and $\frac{\partial N}{\partial x} = \frac{\partial}{\partial x} \left(\frac{\partial z}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x \partial y}$. Now, compare $\frac{\partial M}{\partial y}$ and $\frac{\partial N}{\partial x}$. If $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$, dz is an exact differential. However, if they are not equal, dz is an inexact differential.

Physically, exact differentials can be used to represent points on a graph. They represent properties or state functions. Inexact differentials can be used to represent path functions.

We want to know if $\int_1^3 p dV$ is an exact or inexact differential.

Let's write it as $dz = \int_1^3 p dV$. Here, z is a function of two variables p and V .

Hence, $dz = \left(\frac{\partial z}{\partial p}\right)_V dp + \left(\frac{\partial z}{\partial V}\right)_p dV$. Let's write dz as $dz = M dp + N dV$. Here, $M=0$ as there is no dp term in the expression and $N=p$. Apply the same strategy as before.

$$\frac{\partial M}{\partial V} = \frac{\partial\left(\frac{\partial z}{\partial p}\right)}{\partial V} = 0 \text{ and } \frac{\partial N}{\partial p} = \frac{\partial\left(\frac{\partial z}{\partial V}\right)}{\partial p} = \frac{\partial p}{\partial p} = 1.$$

Hence, $\frac{\partial M}{\partial V} \neq \frac{\partial N}{\partial p}$. So, dz is not exact in this case. Hence, it is a path function.

We encourage you to do a similar exercise with the expression $\int_1^3 V dp$. This is also an inexact differential.

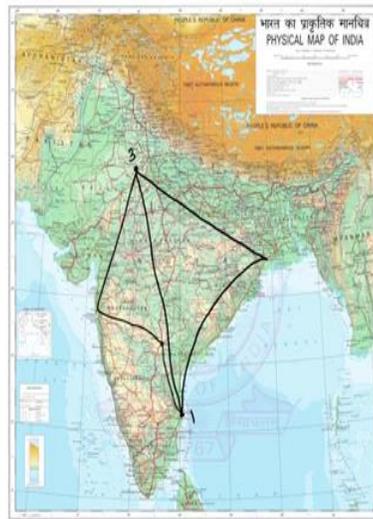
We will see if the third expression $\int_1^3 p dV + V dp$ is an exact or inexact differential. Let's follow the same steps. Here again, z is a function of two variable p and V . So, $dz = \left(\frac{\partial z}{\partial p}\right)_V dp + \left(\frac{\partial z}{\partial V}\right)_p dV$.

Therefore, $M = \left(\frac{\partial z}{\partial p}\right)_V = V$ and $N = \left(\frac{\partial z}{\partial V}\right)_p = p$. Now, $\frac{\partial M}{\partial V} = \frac{\partial V}{\partial V} = 1$ and $\frac{\partial N}{\partial p} = \frac{\partial p}{\partial p} = 1$. Hence,

$\frac{\partial M}{\partial V} = \frac{\partial N}{\partial p} = 1$. Therefore, dz is an exact differential. z represents a property or a state function.

The value of $p dV + V dp$ does not depend on the path followed by a system. It depends only on the state of the system. In this case, the integral depends only on the values of $p dV + V dp$ at states 1 and 3. It does not depend on how you go from 1 to 3.

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$$\begin{matrix} dp \\ dv \\ \delta w \\ \delta q \\ \int_a^b \\ \int_{x_1}^{x_2} \end{matrix}$$



Figure 2: The map of India

Evaluate path independence of $z = f(p, V)$

$$dz = \left(\frac{\partial z}{\partial p}\right)_V dp + \left(\frac{\partial z}{\partial V}\right)_p dV$$

$$dz = M dp + N dV$$

Exact $\int_1^3 pdV$

Exact $\int_1^3 Vdp$

Exact $dz = \int_1^3 (pdV + Vdp)$

Exact $dz = \int_1^3 (pdV - Vdp)$

$$\frac{\partial}{\partial V} \left(\frac{\partial z}{\partial p}\right) = 0 \quad \frac{\partial}{\partial p} \left(\frac{\partial z}{\partial V}\right) = 1$$

$$\frac{\partial M}{\partial V} = \frac{\partial N}{\partial p}$$

$$\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$$

exact

$$\frac{\partial V}{\partial V} = \frac{\partial}{\partial p} [p]$$

$$1 = 1$$



Figure 3

If we were to look at the map of India again (Fig. 2), the difference in pressure and density at two different locations at a particular time does not depend on the path followed in going from one location to another because density and pressure are state functions.

I request you to find out if the expression $\int_1^3 pdV - Vdp$ represent an exact or inexact differential. This differential is inexact.

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If $\delta\phi = f(T) dT + \left(\frac{RT}{V}\right) dV$ *for an ideal gas*
is ϕ a property?
If not, suggest what changes in the
function can make ϕ a property



Figure 4

In Fig. 4, we have a function $\delta\phi = f(T)dT + \left(\frac{RT}{V}\right) dV$. Let's say this expression was written for an ideal gas. We want to find out whether ϕ is a property or not. If it is not a property, make changes in the expression such that ϕ becomes a property. Here, R is a constant (gas constant). Apply the same procedure as we applied in the earlier problems. There are many ways ϕ could be made a property.