Thermodynamics

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Lecture 03

Basic Concepts and definitions -Part 3

Welcome back to the thermodynamics course. In the last class, we looked at the basics of thermodynamics. We looked at what thermodynamics deals with and definitions such as state and path and process and so on.

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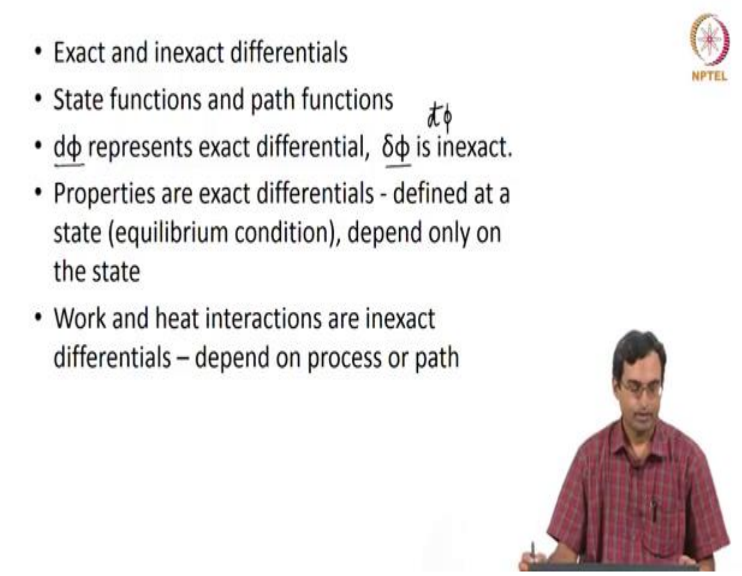

We will go on to what are called exact and inexact differentials. These are also called as state and path functions: the exact differential corresponds to a state function and the inexact once corresponds to a path function. We use different notations to represent them.

We use the alphabet d to represent an exact differential. For example, we write $d\phi$ to represent an exact differential. In contrast, for inexact differentials, we use Greek letter δ. We write $\delta\phi$ for an inexact differential. In some books, the inexact differential is also written with a đ.

The properties are exact differentials and they are only defined at a state. Of course, a state requires the system to be in equilibrium. Once you have a system in equilibrium, the properties only depend on that particular state. In contrast to that, work and heat interactions are inexact and they depend on the process or the path.

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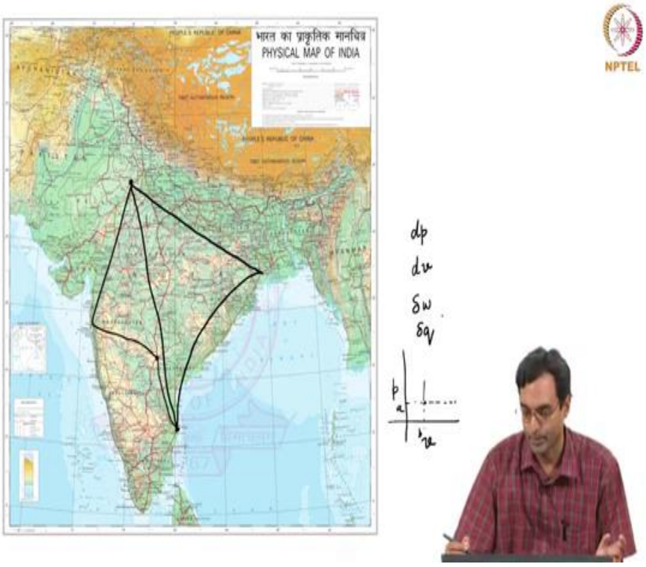

Figure 1: The map of India.

It sounds a little abstract at the moment, but we can look at it with the help of a map. As we discussed earlier, the state is something which depends on the properties, and you can plot any properties on a map. For example, Fig. 1 shows the map of India, a physical map, which shows the latitudes and the longitudes. If I want to specify what in the thermodynamics would be called a state, I can think of it as a location on a map.

A point on a pressure-temperature diagram has pressure of a certain value and temperature of a certain value. I can think of it as equivalent to a location/point on a map. Here, pressure and temperature are analogues to a latitude and a longitude of certain values. If I give the latitude and longitude values of a particular location on a map, everybody will be able to find that particular place. Corresponding to this location, there is a certain temperature associated with it (may vary with time), there is a certain altitude associated with it, and there is a certain velocity of wind. There are a lot of other properties associated with it. So, as long as I give the latitude and longitude, everybody knows that this is the particular place we have to go to.

Instead of giving these two properties (latitude and longitude), I could give name of the place, for example, Hyderabad. Is one attribute (the name of the place in this case) enough to locate the place on the map? In this case, it may not be enough, because there is a place called Hyderabad in India which all of us are aware of. There is also a place called Hyderabad in Pakistan. Hence, I may need to tell you something else. If I go to the place called Hyderabad, which is at a latitude of around 20 degrees, then I would be able to find out that this place is in India.

So, if I told you the name of the place and one other attribute, for example, latitude, then you may be able to find out the place. In some cases, it may be sufficient to tell you only one property/attribute to locate the place, for example, Mount Everest. There is only one Mount Everest and the name itself is sufficient to find its location.

In a similar analogy, we will find later on, that under certain conditions, where if I just tell you one property, that is sufficient to identify a state in the thermodynamics sense. The variables we usually use are pressure, temperature, specific volume, etc. We may need to specify two of them or one of them or more than two of them in order to specify the state.

We can plot all of the thermodynamics properties on maps, for example, we can have a pressure versus volume map. If I have pressure which has a certain value a and volume of a certain value b and if I go to a location which has a pressure of a` and volume of b`, this new location is a distinct location which can be found.

State functions or properties are represented as exact differentials. A small infinitesimal change in pressure is represented as dp, or a small infinitesimal change in volume is represented as dv.

In contrast to these, I could ask other questions. For example, if I go from Chennai to Delhi, what is the distance I would travel? The distance of course depends on how I go. I could take a road which goes more or less a straight line. I could go first to Calcutta and then I go to Delhi. So, the distance I travel to go from one point to another would naturally depend on how I go there. Different paths imply different distances. So, these kinds of functions which depend on the path which I take are called as path functions. We will see later on that work and heat are two examples of path functions.

Path functions are represented by the alphabet δ. For example, in the case of work, infinitesimal small work is represented as δw. We will see later on that we use alphabet q to represent heat. So, a small quantity of heat which is transferred is represented as δq.

So, in the case of the state functions or the properties, we talk of a certain location on the map having a certain value, whereas in the case of path functions, we talk of a certain path being followed, when going from one location to some other location on the map.

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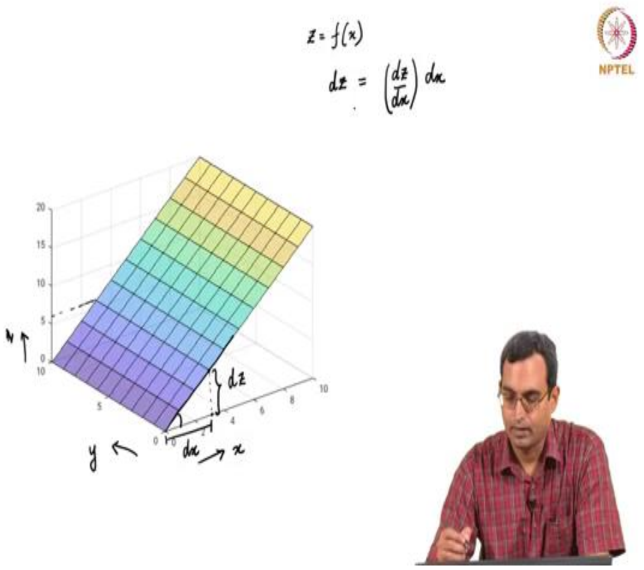

Figure 2

Let's see how to describe these things mathematically. In Fig. 2, the z value (altitude or height) is a function of x only as the slope is constant along x direction. However, it is not a function of y as it is not changing in y direction for a given x.

So, the height is varying as I go along the x direction. As I go along the y direction, the altitude values are not changing at all. Hence, z is a function of only x.

In this case, the slope is constant in the x direction. Let's call the altitude of any point on this surface as dz (with respect to origin). To find dz, I would find the slope of this plane, which is essentially $\frac{dz}{dx}$ (which is constant), and multiply it by the distance dx. This would tell me what is dz. I can find $\frac{dz}{dx}$ as $\tan\theta$ and multiply that by dx to get the value of dz. This is a special case where the slope is constant.

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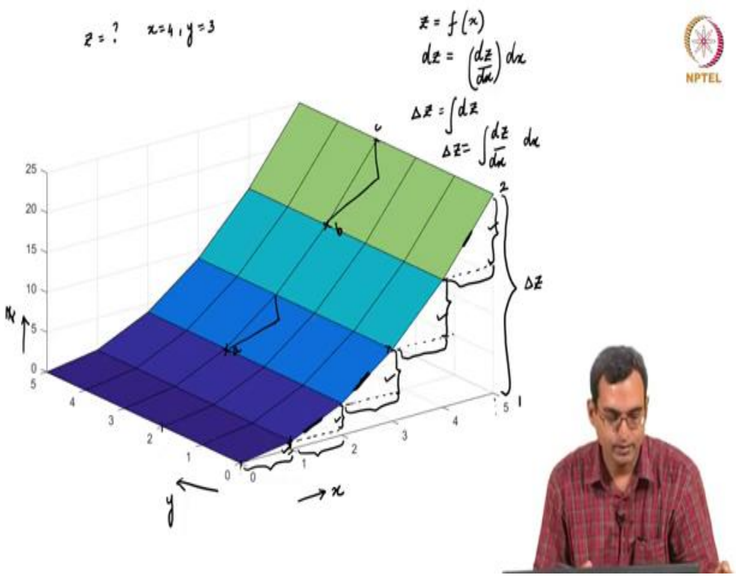

Figure 3

The more general case is where the slope, even in one direction, is changing (Fig. 3). As we go along the x direction, the value of z changes. However, as we go along the y direction (for a given x), the value of z does not change. Mathematically, we say z is a function of x. For any given value of x, if I go along the y direction, the value of z does not change.

So, z is not a function of y, but z is a function of x. Here again, it is a function of only one variable, which is x. In a similar fashion to what we wrote earlier, if I go small distances along the x-axis, I can say $dz = \frac{dz}{dx}dx$. But in this case, the slope $\left(\frac{dz}{dx}\right)$ along the x-axis itself is changing. Hence, I cannot write $dz = \frac{dz}{dx}dx$ for large distances.

In this case, I can use the expression $dz = \frac{dz}{dx}dx$ only when dx is a small distance so that $\frac{dz}{dx}$ is constant over that small dx. For a large distance, $\Delta z = \int dz = \int \frac{dz}{dx}dx$. Basically, we find a slope over a very short distance (so that the slope can be considered constant over that distance) and multiply it by that short distance to obtain local dz. We repeat the same procedure till we reach the point whose height/altitude we want to find. Then, we just add all the local $\frac{dz}{dx}dx$ i.e. we integrate. Hence, $\Delta z = \int dz = \int \frac{dz}{dx}dx$. In Fig. 3, Δz (the height of point 2 above origin) is the sum of 5 different $\frac{dz}{dx}dx$ where, in each case, dx is 1 unit long and the slope $\frac{dz}{dx}$ is constant over that 1 unit.

The height at a particular point on the graph can be found out using any path available. For example, the height of the point 2 above the origin in Fig. 3 can be found out by going along the edge of the surface (y=0) or going along x=0 till y=2, then going along x till x=5 (at y=2), and then going along y till y=0 (at x=5). There are infinitely many such paths. In all these cases, the height of the point 2 above the ground is the same.

The height/altitude of any point on such a graph/surface is a state function or a property. It is independent of the path used to calculate it.

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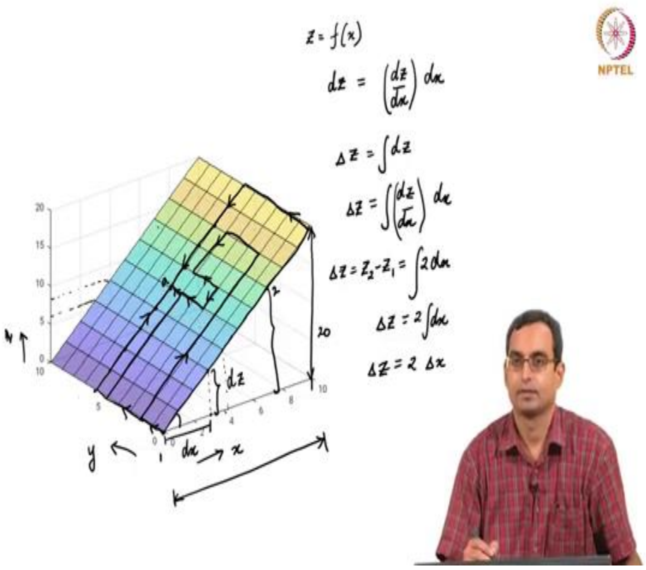

Figure 4

In the previous graph (Fig. 4), since the slope $\left(\frac{dz}{dx}\right)$ is constant, it can be taken out of the integral in the general expression $\Delta z = \int dz = \int \frac{dz}{dx} dx$.

So, the height of any point a on such surfaces can be found with respect to any other point b provided that b’s height is known with respect to the ground or it can be calculated using the same procedure mentioned before.

However, while calculating the height of a point with respect to the origin for example, the distance travelled depends on the path taken from the origin to the point, to calculate the height. This is an example of a path function, because it depends on the path I travel by.

Similarly, when we go by a car from one location to another by different routes (assuming car characteristics are the same all the time), the amount of petrol needed depends on the distance travelled. Hence, the amount of petrol needed is a path function.

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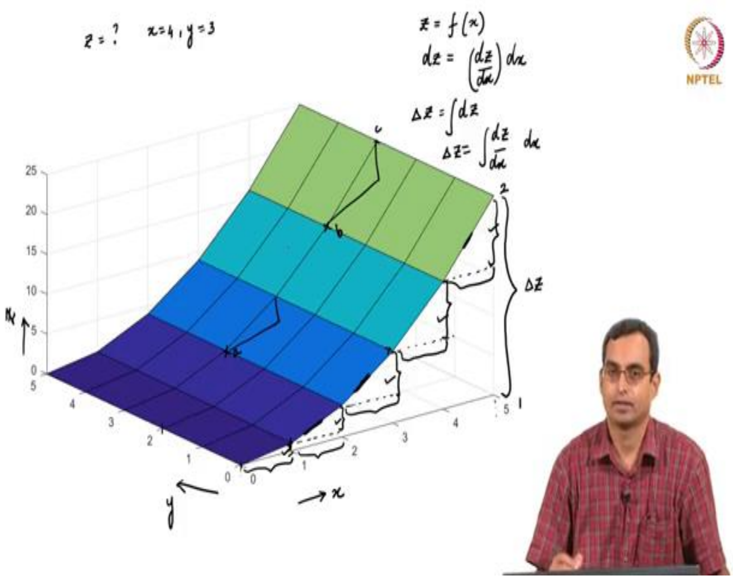

Figure 5

In Figs. 4 and 5, for a given x, if I move along y, z does not change. So, these are the cases where z is a function of only one variable.

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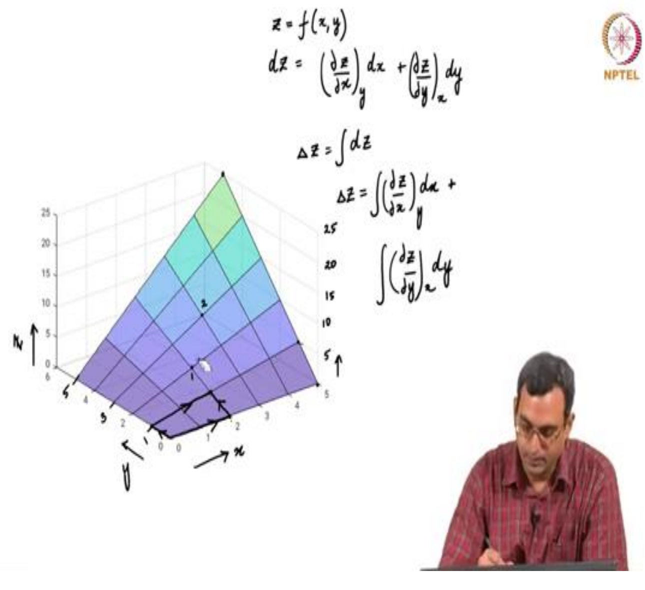

Figure 6

A more general case would be, where z changes, if I go along x and/or y as shown in Fig. 6. For y=1, if I go along x from 0 to 5, the z value keeps changing. Similarly, for x=1, if I go along y from 0 to 5, the z value keeps changing.

So, z is a function of x and y, which is to say z varies if I go along x and/or y. For measuring a change in z, I need to account for changes in z along both the directions. In such a case, the change in altitude/height i.e. Δz is expressed as $\Delta z = \int \left(\frac{\partial z}{\partial x}\right)_y dx + \int \left(\frac{\partial z}{\partial y}\right)_x dy$, where $\left(\frac{\partial z}{\partial x}\right)_y$ represents a change in z with respect to x when y is kept constant (partial derivative of z with respect to x) and $\left(\frac{\partial z}{\partial y}\right)_x$ represents a change in z when with respect to y when x is kept constant (partial derivative of z with respect to y).

I want to go to a point (x=2, y=2) from (x=0, y=0) on the surface shown in Fig. 6. There are many ways to do that. Let's discuss two of those. I can go from x=0 to x=2 along y=0, and then from y=0 to y=2 along x=2. In this case, $\int_{x=0}^{x=2} \left(\frac{\partial z}{\partial x}\right)_y dx = 0$ as the slope is 0 and $\int_{y=0}^{y=2} \left(\frac{\partial z}{\partial y}\right)_x dy$ has some value. Another way that I can go to a point (x=2, y=2) from (x=0, y=0) is to go from y=0 to y=2 along x=0, and then from x=0 to x=2 along y=2. In this case, $\int_{y=0}^{y=2} \left(\frac{\partial z}{\partial y}\right)_x dy = 0$ as the slope is 0, while $\int_{x=0}^{x=2} \left(\frac{\partial z}{\partial x}\right)_y dx$ has some value. However, in both the cases, the height of the point (x=2, y=2) with respect to (x=0, y=0) would be the same. There are ways where both the terms, $\int_{x_1}^{x_2} \left(\frac{\partial z}{\partial x}\right)_y dx$ and $\int_{y_1}^{y_2} \left(\frac{\partial z}{\partial y}\right)_x dy$, are not 0. In all these cases, these integrals can be calculated as discussed before. It is also possible that we know the functional form of z = f(x,y). In such a case, finding derivatives and integrations become easier.

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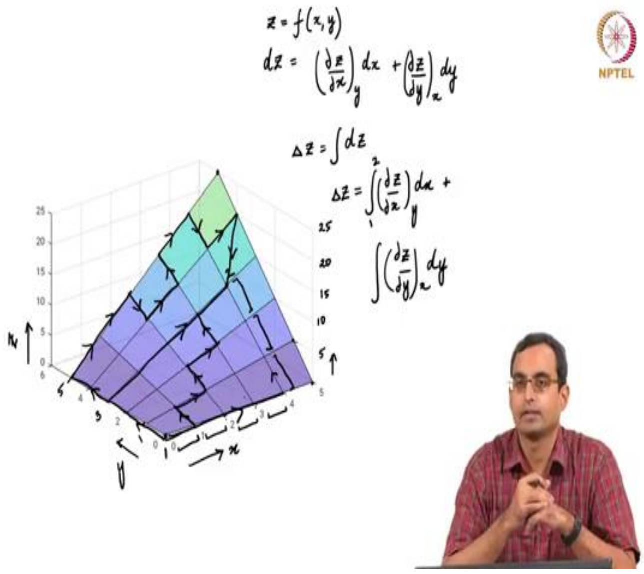

Figure 7

Finding Δz between any two points on the surface in Fig. 7 can be done in multiple ways. However, no matter what path you take, Δz would be the same between those two points.

Again, the distance travelled between any two points depends on the path taken. It is a path function. We don’t have the expression for distance travelled as we have for the height difference between two points.