Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture - 9
Maxwell's relations

Welcome!

In the last class, we looked at the relationships between some of those properties, thermodynamic properties using some simple aspects of mathematics. We also saw the Gibbs-Duhem equation, which is a central equation in thermodynamics. Since, it gives the simultaneous variation with temperature, pressure and chemical potential, which are the fundamental intrinsic properties of a system. We will continue looking at useful relationships between various variable, and also I will tell you how it comes in useful in the tutorial part. The next thing that we are going to look at in the same vein is Maxwell's relations.

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Maxwell's Relations

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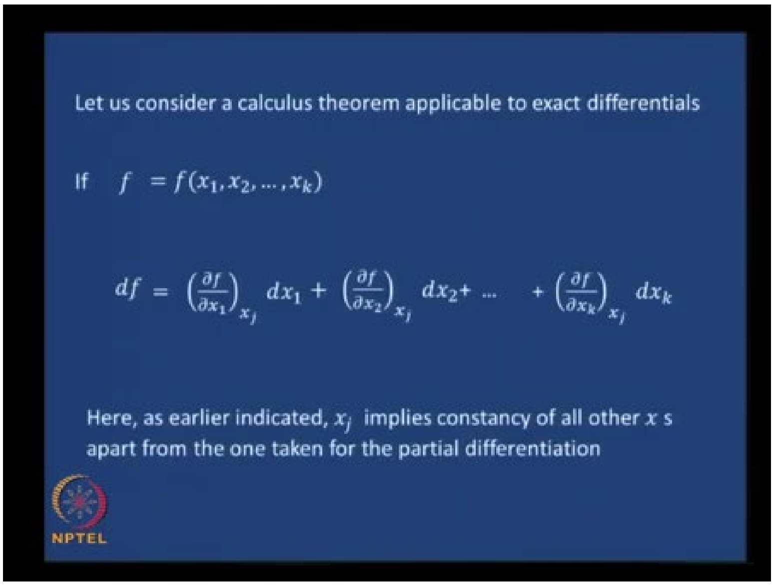

Let us consider a calculus theorem applicable to exact differentials

If $f = f(x_1, x_2, \ldots, x_k)$

$$df = \left(\frac{\partial f}{\partial x_1}\right)_{x_j} dx_1 + \left(\frac{\partial f}{\partial x_2}\right)_{x_j} dx_2 + \ldots + \left(\frac{\partial f}{\partial x_k}\right)_{x_j} dx_k$$

Here, as earlier indicated, x_j implies constancy of all other x s apart from the one taken for the partial differentiation

To get to Maxwell's relations, let us first consider a theorem and calculus that is applicable to exact differentials. We do not have to worry too much about whether we are dealing with exact different differentials or not in thermodynamics, because we deal with state functions in thermodynamics mostly, and most of those state functions can be written as exact differentials.

The theorem says if f can be considered as a function of some variables which are given here as x 1, x 2 and so on till x k,

$$f = f(x_1, x_2, \ldots, x_k)$$

then df … df being an exact differential, can be written as

$$df = \left(\frac{\partial f}{\partial x_1}\right)_{x_j} dx_1 + \left(\frac{\partial f}{\partial x_2}\right)_{x_j} dx_2 + \cdots + \left(\frac{\partial f}{\partial x_k}\right)_{x_j} dx_k$$

dou f by dou x 1 at … evaluated at all these other variables kept constant which is indicated by x j as I had mentioned earlier d x1plus dou f dou x 2 x j which means x1 x 3 and other variables … x k are held constant – that is what this x j means – dx 2 and so on until dou f by dou x k, all other x js remaining constant, dx k.

This is a fundamental theorem that is applied to … applicable to exact differentials.

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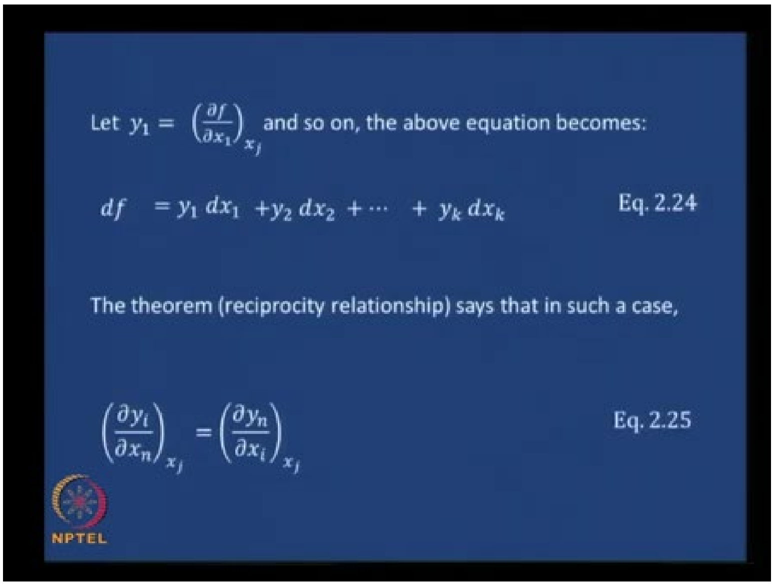

Let $y_1 = \left(\frac{\partial f}{\partial x_1}\right)_{x_j}$ and so on, the above equation becomes:

$$df = y_1\,dx_1 + y_2\,dx_2 + \cdots + y_k\,dx_k \qquad \text{Eq. 2.24}$$

The theorem (reciprocity relationship) says that in such a case,

$$\left(\frac{\partial y_i}{\partial x_n}\right)_{x_j} = \left(\frac{\partial y_n}{\partial x_i}\right)_{x_j} \qquad \text{Eq. 2.25}$$

Now, let us take those partial differentials dou f by dou x 1 at constant x j, dou f by dx 2 at constant x j, and so on and replace them with another symbol for easy manipulation. Let us say

$$y_1 = \left(\frac{\partial f}{\partial x_1}\right)_{x_j}$$

If we do that, then, we can write the previous equation as

$$df = y_1\,dx_1 + y_2\,dx_2 + \cdots + y_k\,dx_k$$

Let us call this equation 2.24.

The theorem that is also known as reciprocity relationship, says that when we can do this that is df being expressed as y1 dx 1plus y 2 dx 2 and so on till y k, dx k,

$$\left(\frac{\partial y_i}{\partial x_n}\right)_{x_j} = \left(\frac{\partial y_n}{\partial x_i}\right)_{x_j}$$

For example, if you take i to be 1 and n to be 2 dou y 1 by dou x 2 at all other x j s remaining constant equals dou y 2 by dou x 1 at all other x j s remaining constant. It is applicable for any i and any n … that is different from i. For example, it could be dou y 3 by dou x 10 at all other x j s remaining constant equals dou y 10 by dou x 3 at all other x j s remaining constant.

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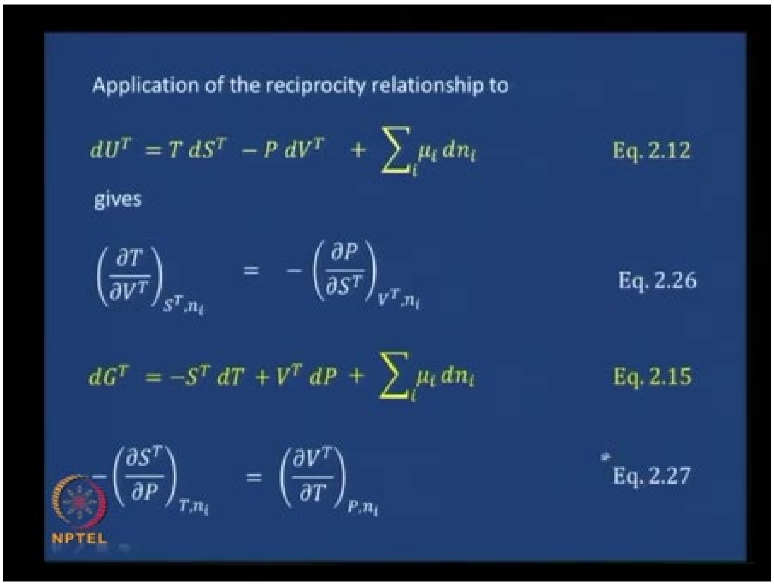

Application of the reciprocity relationship to

$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\, dn_i$ Eq. 2.12

gives

$\left(\frac{\partial T}{\partial V^T}\right)_{S^T,n_i} = -\left(\frac{\partial P}{\partial S^T}\right)_{V^T,n_i}$ Eq. 2.26

$dG^T = -S^T\,dT + V^T\,dP + \sum_i \mu_i\, dn_i$ Eq. 2.15

$-\left(\frac{\partial S^T}{\partial P}\right)_{T,n_i} = \left(\frac{\partial V^T}{\partial T}\right)_{P,n_i}$ Eq. 2.27

If we apply this theorem, also called the reciprocity relationship, to our basic equations that we had given earlier, basic differentials that we had given earlier … If you recall equation 2.12 which is also given here

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\, dn_i$$

Remember that this consists of many different terms that are given by the sum sign. If we apply the reciprocity relationship here it will give us dou T by – let us choose this be other variable – dou V T, at all other things remaining constants such as S T and all n is remaining constant, this equals

$$\left(\frac{\partial T}{\partial V^T}\right)_{S^T,\, n_i} = -\left(\frac{\partial P}{\partial S^T}\right)_{V^T,\, n_i}$$

This gives a nice relationship between the thermodynamic variables just by using the reciprocity relationship of writing differentials.

We will call this equation 2.26. Let me show this a few more times so, that it becomes simpler to remember. Let us consider the next relationship

$$dG^T = -S^T\, dT + V^T\, dP + \sum_i \mu_i\, dn_i$$

as we have already seen in equation 2.15. If we utilize the reciprocity relationship here,

$$-\left(\frac{\partial S^T}{\partial P}\right)_{T,\, n_i} = \left(\frac{\partial V^T}{\partial T}\right)_{P,\, n_i}$$

By now, you must be getting comfortable with writing reciprocity relationships from total differentials. Let us call this equation 2.27

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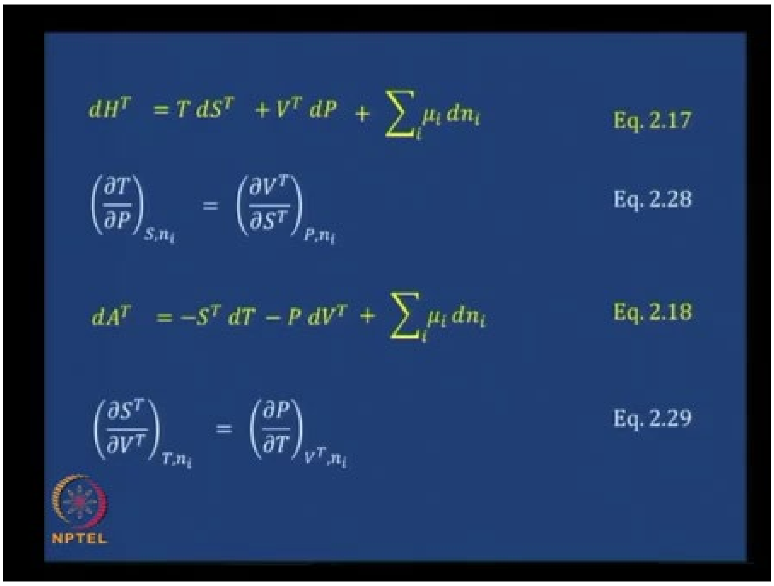

$$dH^T = T\, dS^T + V^T\, dP + \sum_i \mu_i\, dn_i \qquad \text{Eq. 2.17}$$

$$\left(\frac{\partial T}{\partial P}\right)_{S,n_i} = \left(\frac{\partial V^T}{\partial S^T}\right)_{P,n_i} \qquad \text{Eq. 2.28}$$

$$dA^T = -S^T\, dT - P\, dV^T + \sum_i \mu_i\, dn_i \qquad \text{Eq. 2.18}$$

$$\left(\frac{\partial S^T}{\partial V^T}\right)_{T,n_i} = \left(\frac{\partial P}{\partial T}\right)_{V^T,n_i} \qquad \text{Eq. 2.29}$$

Let us take another example. I will give you all four or … more than four in the first case.

$$dH^T = T\, dS^T + V^T\, dP + \sum_i \mu_i\, dn_i$$

this was equation 2.17 before. If we write … or apply the reciprocity relationship here

$$\left(\frac{\partial T}{\partial P}\right)_{S,\, n_i} = \left(\frac{\partial V^T}{\partial S^T}\right)_{P,\, n_i}$$

equation 2.28.

Let us consider d A T now. We already have equation 2.18 as

$$dA^T = -S^T\,dT - P\,dV^T + \sum_i \mu_i\,dn_i$$

note – both are minuses here. So, you do not have to worry about it, if you take these two.

$$\left(\frac{\partial S^T}{\partial V^T}\right)_{T,\,n_i} = \left(\frac{\partial P}{\partial T}\right)_{V^T,\,n_i}$$

We will call this equation 2.29.

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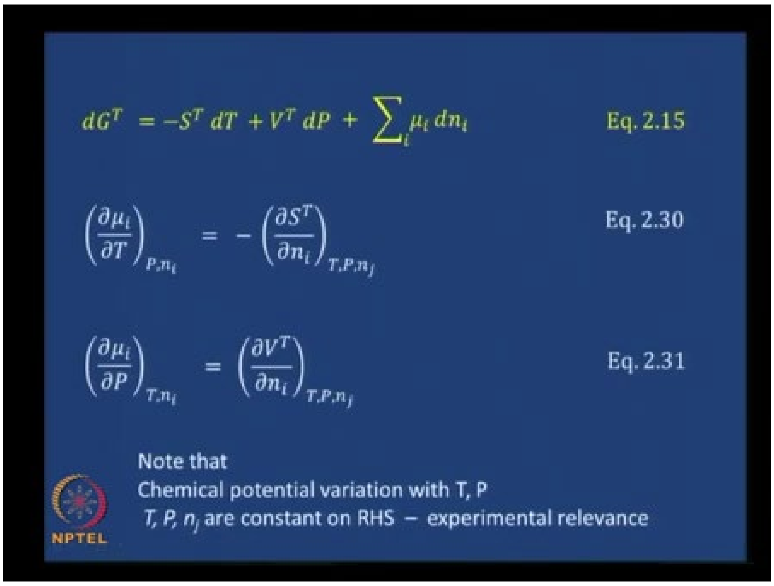


$$dG^T = -S^T\,dT + V^T\,dP + \sum_i \mu_i\,dn_i$$ Eq. 2.15

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i} = -\left(\frac{\partial S^T}{\partial n_i}\right)_{T,P,n_j}$$ Eq. 2.30

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i} = \left(\frac{\partial V^T}{\partial n_i}\right)_{T,P,n_j}$$ Eq. 2.31

Note that
Chemical potential variation with T, P
T, P, n_j are constant on RHS – experimental relevance

Let us consider equation 2.15 again.

$$dG^T = -S^T\,dT + V^T\,dP + \sum_i \mu_i\,dn_i$$

Earlier for all the four equations … for a closed system, we looked at just the first two terms for writing the reciprocity relationship. Now let us look at the third term also. Note that this consists of the sum. So, each one is different here. So, let us take one of those …

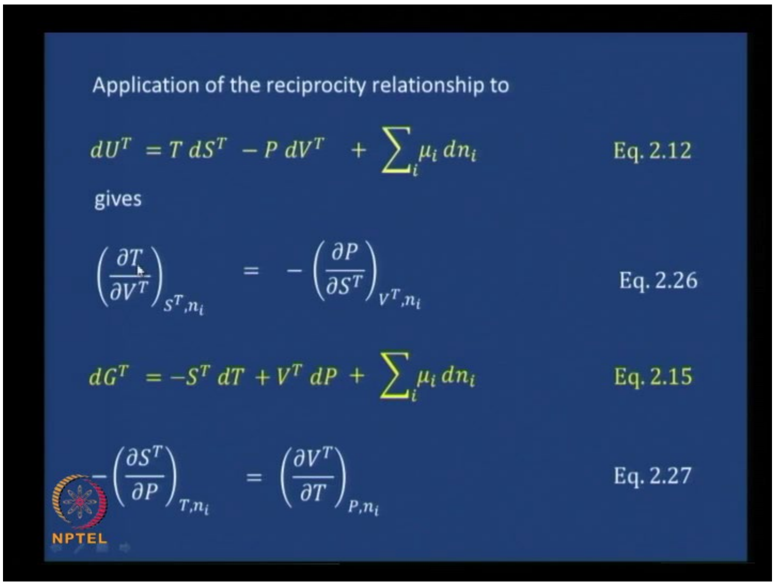
$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,\ n_i} = -\left(\frac{\partial S^T}{\partial n_i}\right)_{T,P,n_j}$$

Let me repeat this dou mu i dou T at constant P all other n i equals, minus – minuses here – dou S T dou n i constant T, P, all other n j s … which are different from i. Let us do this once again to get other useful relationships. Before that, let's call this equation 2.30.

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,\ n_i} = \left(\frac{\partial V^T}{\partial n_i}\right)_{T,P,n_j}$$

We had considered these two terms while this equation. Let us call this equation 2.31. There was a reason why we chose to compare these two and these two and actually use d j 2 to do it. If you recall we have dG T with variation of T P and n i. So, which are easily measurable variables? If they are easily measurable then we can do experiments with them quietly easily. This gives the variation of chemical potential with temperature which is a very useful relationship to have when the pressure and the number of moles of all species are held constant which can be done experimentally.

This gives the variation of chemical potential with pressure when the temperature and all moles are held constant which can be again done in an experiment. And this is given in terms of the other thermodynamic variables which may be easier to determine. So, that is going to be some sort of a theme in this particular module. That is expression of difficult to measure thermodynamic variables in terms of easy to measure thermodynamic variables. That is a way we are going to use these equation. These equations are valid for anything that you want to do. These relationships are there for anything that you want to do. We are going to do one small aspect or one aspect of the many different things that you can do with these relationships.



Application of the reciprocity relationship to

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gives

$$\left(\frac{\partial T}{\partial V^T}\right)_{S^T,n_i} = -\left(\frac{\partial P}{\partial S^T}\right)_{V^T,n_i} \qquad \text{Eq. 2.26}$$

$$dG^T = -S^T\,dT + V^T\,dP + \sum_i \mu_i\,dn_i \qquad \text{Eq. 2.15}$$

$$-\left(\frac{\partial S^T}{\partial P}\right)_{T,n_i} = \left(\frac{\partial V^T}{\partial T}\right)_{P,n_i} \qquad \text{Eq. 2.27}$$

The equations 2.26 to 2.31 let me go back and show you 2.26 just for recall; 2.27… 2.26 was dou T dou V T constant S T n i equals minus dou P dou S T constant V T n i. 2.27, minus dou S T dou P at constant T n i equals dou V T dou T at constant P n i equation 2.27. 2.28, was dou P dou T constant S n i equals dou V T dou S T constant P n i. Equation 2.29 was dou S T dou V T constant T n i equals dou P dou T at constant V T n i. And, as we spent some extra time here dou mu i dou T at constant P n i equals minus dou S T dou n i at constant T P all other n j s and dou mu i dou P at constant T n i equals dou V T dou n i at constant T P all other n j s.

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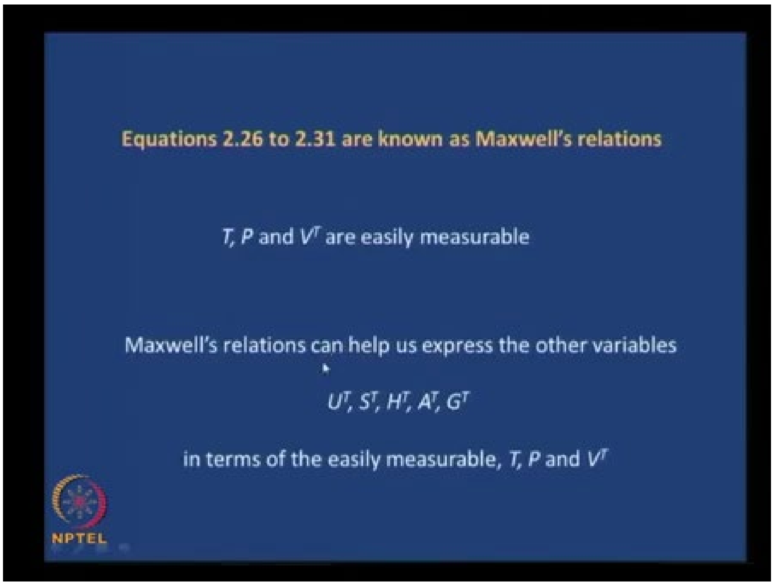

Equations 2.26 to 2.31 are known as Maxwell's relations

T, P and V^T are easily measurable

Maxwell's relations can help us express the other variables

U^T, S^T, H^T, A^T, G^T

in terms of the easily measurable, T, P and V^T

So, these equations are called Maxwell's relations. Very useful. As I had already mentioned its worth mentioning again: Temperature, pressure and the total volume are easily measurable. Maxwell's relations can help us that is one of the things they do you can do many other things with them can help us express the other variables such as U T, internal energy, S T, enthalpy total enthalpy – all these are total quantities since that are more than one mole of the substance … of the pure substance that way considering here – H T is enthalpy … total enthalpy, A T is total Helmholtz free energy, and G T is total Gibbs free energy.

All these can be written in terms of easily measurable T P and total volume and therefore, by these measurements under suitable conditions we can estimate these thermodynamic variables U T, S T, H T, A T and G T.

We started with a slightly more general set of relations. The Maxwell's relations that we have written down so far are valid for any system, any pure substance, irrespective of the size of the system or the number of the moles in the system. Whereas, in many different books including your text book, initially when this is introduced, you would find the Maxwell's relations written for one mole. Which means, the mu i d n i terms any d n i related terms n i related terms will not be there because you have only one mole and that is held constant.

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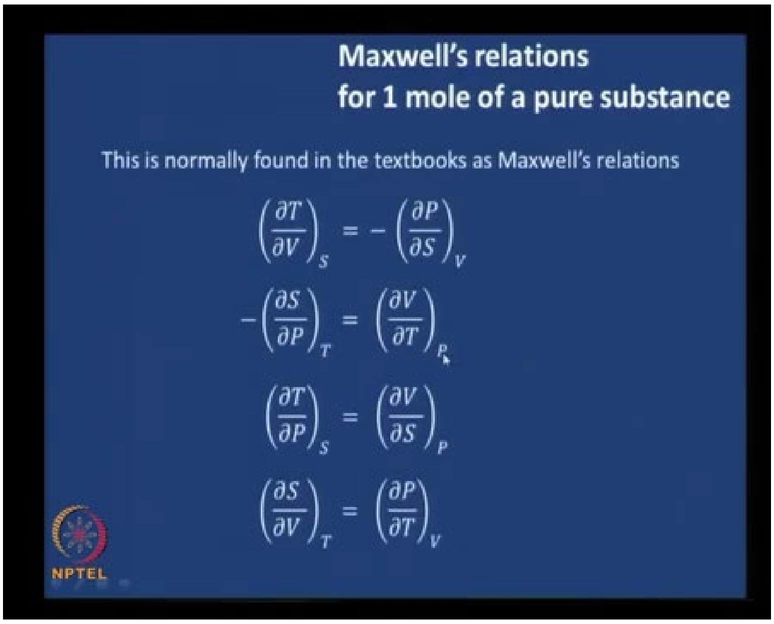

Maxwell's relations
for 1 mole of a pure substance

This is normally found in the textbooks as Maxwell's relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Let us look at these relationships for completeness because you can directly use these relationships under such conditions where you have one mole of the substance.

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

You may want to compare these expressions … I would like you to do that … I do not want to go back now. If you just compare this expression with the earlier Maxwell's relations that we have written, you would see that these are exactly the same as the first four Maxwell's relations that we had written except that you do not have any n i s occurring because we have one mole of the substance. These would come in handy in some of your problems in the university exams and so on.

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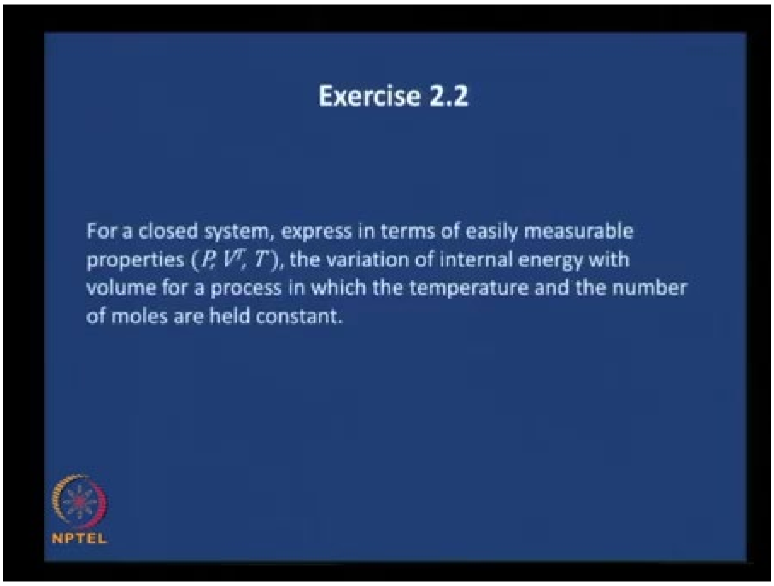

Exercise 2.2

For a closed system, express in terms of easily measurable properties (P, V, T), the variation of internal energy with volume for a process in which the temperature and the number of moles are held constant.

OK, now, we are going to do some tutorial work. I am going to present this problem to you, and then I will give you some time to work it out, because you will understand the application of these equations and get comfortable with the applications of these equations only by working out problems. And you need to work them out first – that would be the most effective. So, you will work them out. I will give you time, may be about 10 minutes. And may be after some time, I will present a part of the solution so that you can start working at a faster pace if that hint or part of the solution is going to help you.

Later I will give you the entire solution. This exercise essentially shows a way to use some of the relationships that we have a developed so far. The question is, for a closed system express in terms of easily measurable properties, pressure, total volume and temperature the variation of internal energy with volume for a process in which the temperature and the number of moles are held constant. Essentially we are looking for dou U T, the variation of internal energy, with volume. So, dou U T dou V T at constant temperature and n i. Please go ahead you have about 10 minutes.

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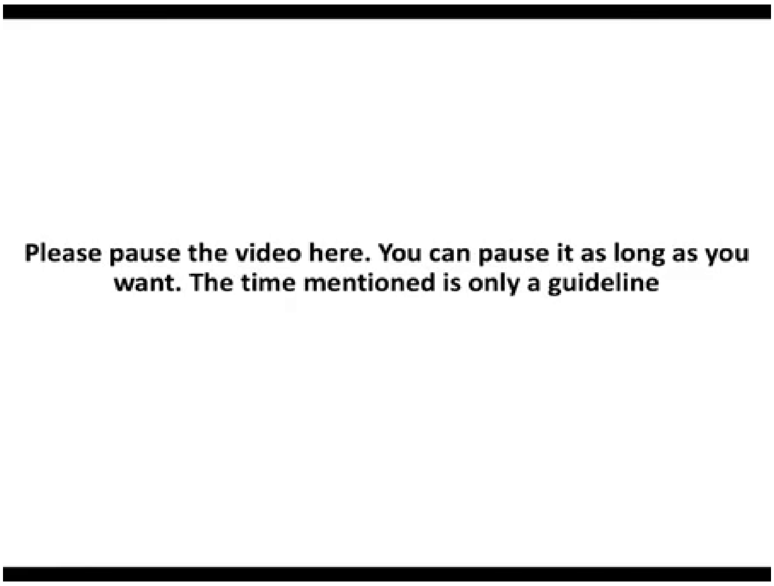

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Let us look at the part of the solution now.

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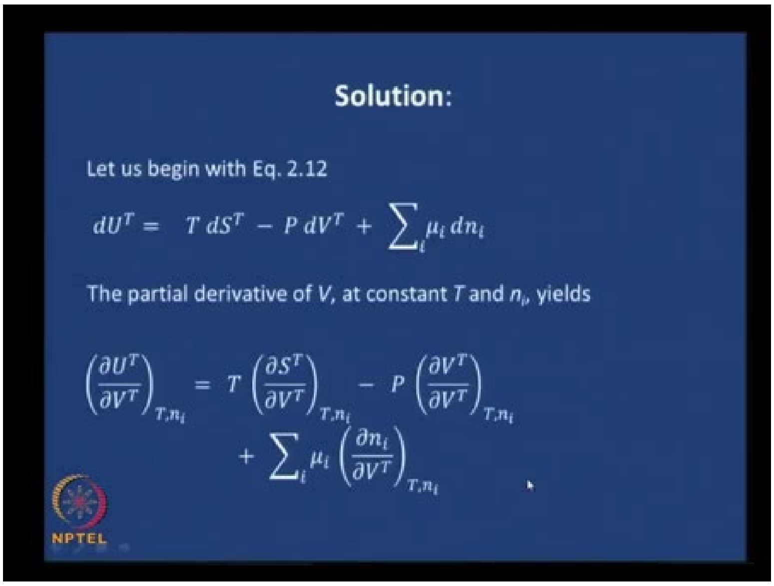

Solution:

Let us begin with Eq. 2.12

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i$$

The partial derivative of V, at constant T and n_i, yields

$$\left(\frac{\partial U^T}{\partial V^T}\right)_{T,n_i} = T\left(\frac{\partial S^T}{\partial V^T}\right)_{T,n_i} - P\left(\frac{\partial V^T}{\partial V^T}\right)_{T,n_i} + \sum_i \mu_i\left(\frac{\partial n_i}{\partial V^T}\right)_{T,n_i}$$

Let us look at a part of the solution now. To do this, you know that we are looking for

$$\left(\frac{\partial U^T}{\partial V^T}\right)_{T,\,n_i}$$

Let us begin with equation 2.12.

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i$$

Because this has the relationship for dU T and these would be dou U T and so on. dou U T variation. The partial derivative of VT at constant T and n i can be written as

$$\left(\frac{\partial U^T}{\partial V^T}\right)_{T,\,n_i} = T\left(\frac{\partial S^T}{\partial V^T}\right)_{T,\,n_i} - P\left(\frac{\partial V^T}{\partial V^T}\right)_{T,\,n_i} + \sum_i \mu_i\left(\frac{\partial n_i}{\partial V^T}\right)_{T,\,n_i}$$

To continue further … we are looking at dou U T dou V T at constant T n i. Look at these terms here and see what you could do to get it in terms of measurable quantities. Take another five minutes or so.

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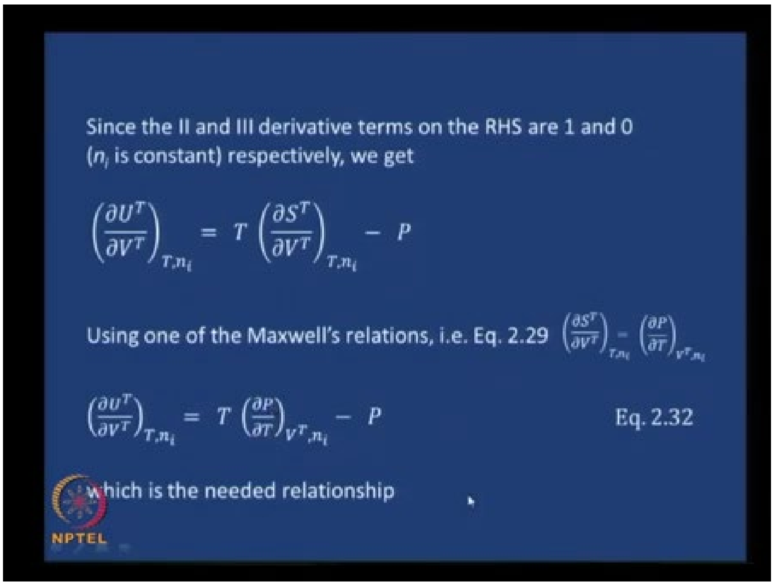

Since the II and III derivative terms on the RHS are 1 and 0 (n_i is constant) respectively, we get

$$\left(\frac{\partial U^T}{\partial V^T}\right)_{T,n_i} = T\left(\frac{\partial S^T}{\partial V^T}\right)_{T,n_i} - P$$

Using one of the Maxwell's relations, i.e. Eq. 2.29 $\left(\frac{\partial S^T}{\partial V^T}\right)_{T,n_i} = \left(\frac{\partial P}{\partial T}\right)_{V^T,n_i}$

$$\left(\frac{\partial U^T}{\partial V^T}\right)_{T,n_i} = T\left(\frac{\partial P}{\partial T}\right)_{V^T,n_i} - P \qquad \text{Eq. 2.32}$$

which is the needed relationship

Let us continue with the solution. Look at the second and third terms on the right hand side here … P dou V T dou V T T n i plus summation of mu i dou n i dou V T at constant T n i. The second and third derivative terms on the right hand side are 1 and 0. 1 because dou V T dou V T. So, that goes to 1 and 0 because n i is a constant. So, any variation with n i would be 0. Therefore, what remains of that equation is dou U T dou V T at constant T n I; this was the initial left hand side. The first term remains: equals T dou S T S dou V T at constant T n i, and since this is gone to one whatever accompany P here we just have a P remaining minus p.

$$\left(\frac{\partial U^T}{\partial V^T}\right)_{T,n_i} = T\left(\frac{\partial S^T}{\partial V^T}\right)_{T,n_i} - P$$

Now if we use one of the Maxwell's relations which is equation 2.29 here,

$$\left(\frac{\partial S^T}{\partial V^T}\right)_{T,\ n_i}$$

this we know is a little difficult to measure. So, let us try to write this in terms of easily measurable quantities.

$$\left(\frac{\partial S^T}{\partial V^T}\right)_{T,\ n_i} = \left(\frac{\partial P}{\partial T}\right)_{V^T,\ n_i}$$

In this case P, T are all easily measurable. If we do that then you can write

$$\left(\frac{\partial U^T}{\partial V^T}\right)_{T,n_i} = T\left(\frac{\partial P}{\partial T}\right)_{V^T,n_i} - P$$

Which is what we need.

Let me call this equation 2.32 because it will come in useful later. You have gotten this in terms of all easily measurable thermodynamic variables T, P, V T, n i and so on.

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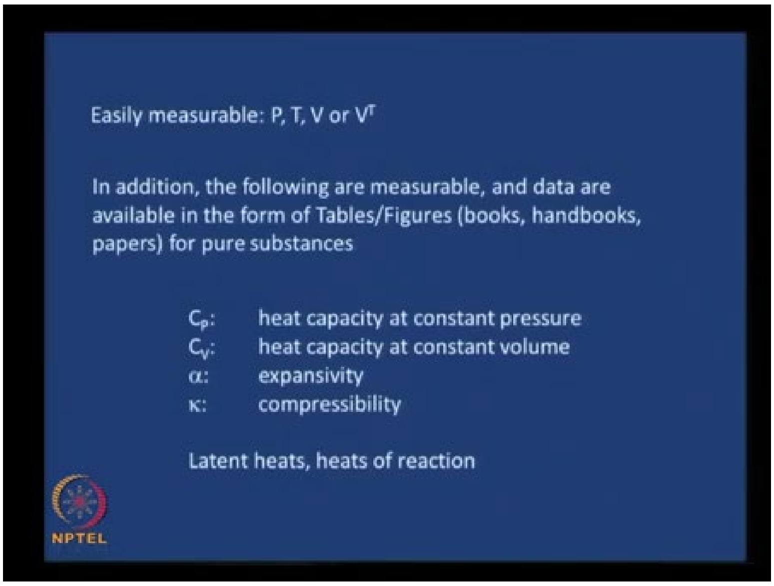

Easily measurable: P, T, V or V^T

In addition, the following are measurable, and data are available in the form of Tables/Figures (books, handbooks, papers) for pure substances

C_P: heat capacity at constant pressure
C_V: heat capacity at constant volume
α: expansivity
κ: compressibility

Latent heats, heats of reaction

To recapitulate the easily measurable ones are P, T, V the molar volume or V T the total volume. In addition, the following are measurable, and the data is available in the form of tables or figures in books, handbooks or papers for pure substances. Some of these are available at the back of your text book Smith VanNess and Abbott. C P, heat capacity at constant pressure, this is available … the data is available. C V heat capacity at constant volume, the data is available, alpha which is expansivity. I will go into details of this in a little while, and kappa the compressibility are all available. So, if they are available we might as well make use of them to estimate the difficult to measure thermodynamic variables. In addition to these the latent heats are available as well as the heats of reaction are available. Let us look these in a little more detail … other measurable thermodynamic variables.

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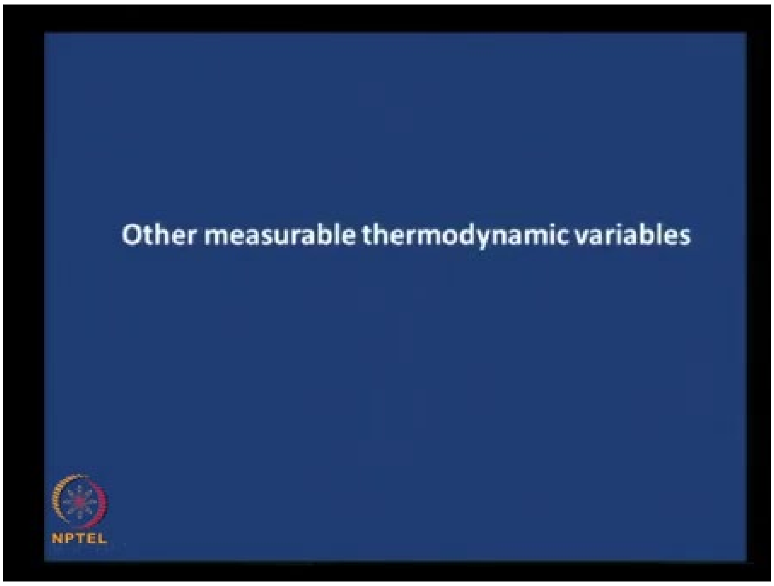

Other measurable thermodynamic variables

Other measurable thermodynamic variables:

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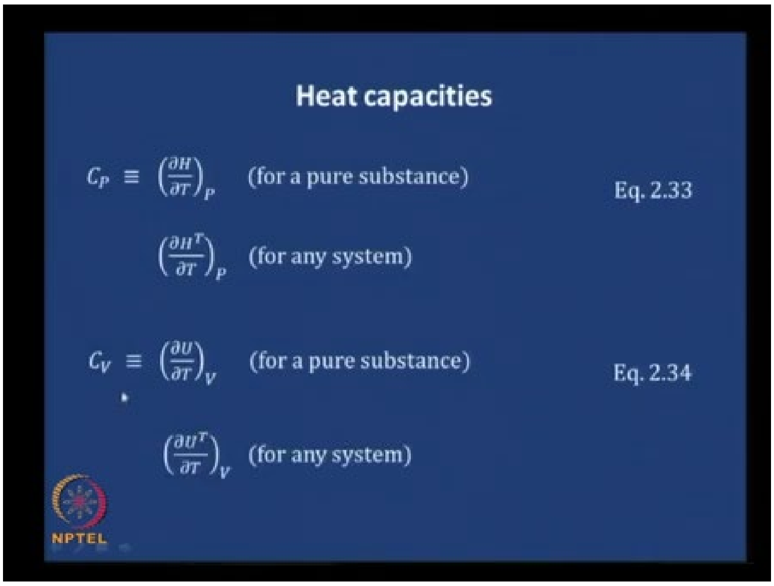


Heat capacities

$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P$ (for a pure substance) Eq. 2.33

$\left(\frac{\partial H^T}{\partial T}\right)_P$ (for any system)

$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V$ (for a pure substance) Eq. 2.34

$\left(\frac{\partial U^T}{\partial T}\right)_V$ (for any system)

Heat capacity C P is defined as

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P$$

This is for a pure substance. We will call this equation 2.33.

For any system C P is defined as $\left(\frac{\partial H^T}{\partial T}\right)_P$

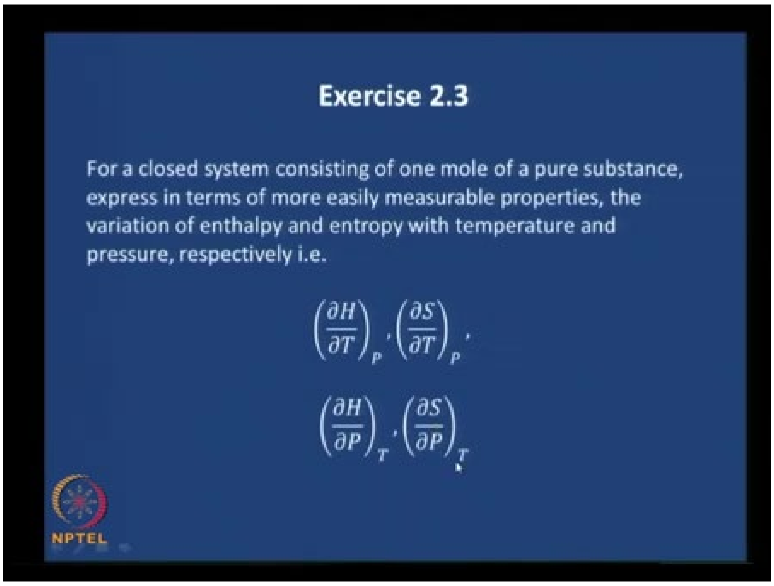
This is for one mole of a pure substance this is for any system.

Now C V is defined as

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V$$

C P was dou H – enthalpy – dou T, C V is dou (internal energy) dou T at constant volume. Since this is V at constant volume we call it C V is specific heated constant volume. This is for a pure substance we will call equation 2.34 and for any system you can write you can define C V as

$$\left(\frac{\partial U^T}{\partial T}\right)_V$$



Exercise 2.3

For a closed system consisting of one mole of a pure substance, express in terms of more easily measurable properties, the variation of enthalpy and entropy with temperature and pressure, respectively i.e.

$$\left(\frac{\partial H}{\partial T}\right)_P, \left(\frac{\partial S}{\partial T}\right)_P,$$

$$\left(\frac{\partial H}{\partial P}\right)_T, \left(\frac{\partial S}{\partial P}\right)_T$$

Expression of the not-so-easy to measure thermodynamic properties in terms of measurable thermodynamic properties helps in estimation of the not-so-easy to measure ones. I am just repeating this, so that it gets across better.

For a closed system consisting of 1 mole of a pure substance, express in terms of more easily measurable properties, the variation of enthalpy and entropy with temperature and pressure, respectively. In other words,

$$\left(\frac{\partial H}{\partial T}\right)_P, \left(\frac{\partial S}{\partial T}\right)_P, \left(\frac{\partial H}{\partial P}\right)_T, \left(\frac{\partial S}{\partial P}\right)_T$$

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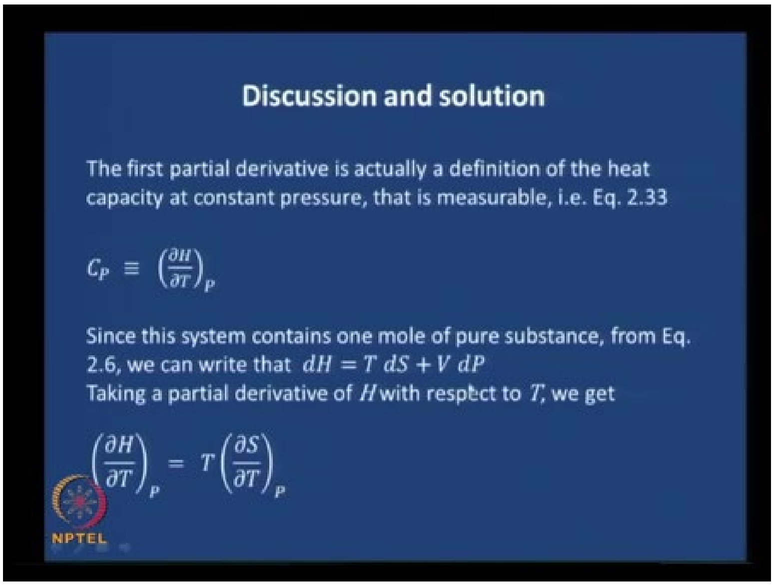

Discussion and solution

The first partial derivative is actually a definition of the heat capacity at constant pressure, that is measurable, i.e. Eq. 2.33

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P$$

Since this system contains one mole of pure substance, from Eq. 2.6, we can write that $dH = T\,dS + V\,dP$

Taking a partial derivative of H with respect to T, we get

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

The way to go about this would be as follows. The 1st partial derivative was

$$\left(\frac{\partial H}{\partial T}\right)_P$$

If you go back into your notes or into the earlier slides of this lecture, you would actually find, that this is the definition of C P, which is a measured quantity, which is … the data of which is available. So, we do not have to do anything further, $\left(\frac{\partial H}{\partial T}\right)_P$ is itself a measured quantity.

Since the system consists of 1 mole of pure substance, if you look at the equation 2.6, that we had written earlier, we can write the same equation 2.6 given here,

$$dH = T\,dS + V\,dP$$

it is for a closed system consisting of 1 mole of a pure substance.

Now, if we take the partial derivative of H with respect to T at constant P, the 2nd term is going to vanish here because we are forcing P to remain constant. Therefore, d P will go to 0 and this term would vanish. Therefore,

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

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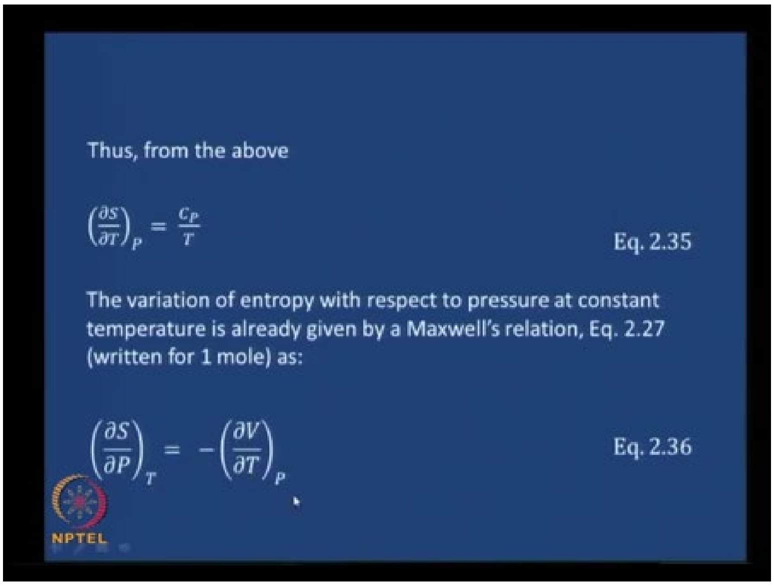

Thus, from the above

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \qquad \text{Eq. 2.35}$$

The variation of entropy with respect to pressure at constant temperature is already given by a Maxwell's relation, Eq. 2.27 (written for 1 mole) as:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{Eq. 2.36}$$

Proceeding further,

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

This, you get by comparing the previous equations. Let us go back a little bit, this is dow H dow T at constant P equals C P. dow H dow T at constant P … we had gotten this as T dow S dow T at constant P, you equate this to this, C P is easily measurable, and therefore, we get dow S dow T at constant P equals C P by T. So, we have handled this also. We will call this equation 2.35.

So, we have some more remaining. The variation of entropy S with respect to pressure at constant temperature, dow S dow P with T remaining constant, is actually given by Maxwell's relation. You go back to your … we had written all four equations for 1 mole of a pure substance; you can go back and look at that. Actually, equation 2.27, written for 1 mole was

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Let us call this as equation 2.36 here; and therefore, that takes care of three different parts of the question.

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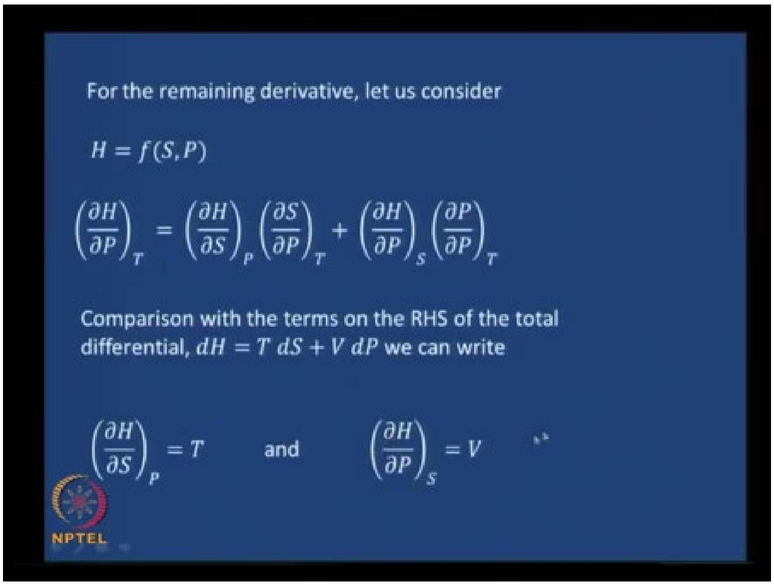

For the remaining derivative, let us consider

$H = f(S,P)$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial H}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T + \left(\frac{\partial H}{\partial P}\right)_S \left(\frac{\partial P}{\partial P}\right)_T$$

Comparison with the terms on the RHS of the total differential, $dH = T\,dS + V\,dP$ we can write

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \text{and} \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

There is one more part that is remaining. For that, let us consider

$$H = f(S,P)$$

You can consider whatever is needed – as function of the relevant variables. In this case, let us consider enthalpy as a function of entropy and pressure. If you do this, dH, you know, can be written as dow H dow S at constant P dS, dow H dow P at constant S dP.

Now, if you take the partial of that … with respect to P at constant temperature,

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial H}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T + \left(\frac{\partial H}{\partial P}\right)_S \left(\frac{\partial P}{\partial P}\right)_T$$

dow H dow P at constant T, this is the quantity that we need … dow H dow S at constant P, which is a 1st term, that came from the previous total differential writing and of course, dow S dow P at constant T, and this again comes from the partial differential writing, the total differential expansion dow H dow P at constant S. And here, dP would be there, you take the partial derivative dow P dow P at constant T; very easy to see that this goes to 1.

Now, comparison with the terms on the right hand side of the total differential,

$$dH = T\,dS + V\,dP$$

we can write,

$$\left(\frac{\partial H}{\partial S}\right)_P = T$$

$$\left(\frac{\partial H}{\partial P}\right)_S = V$$

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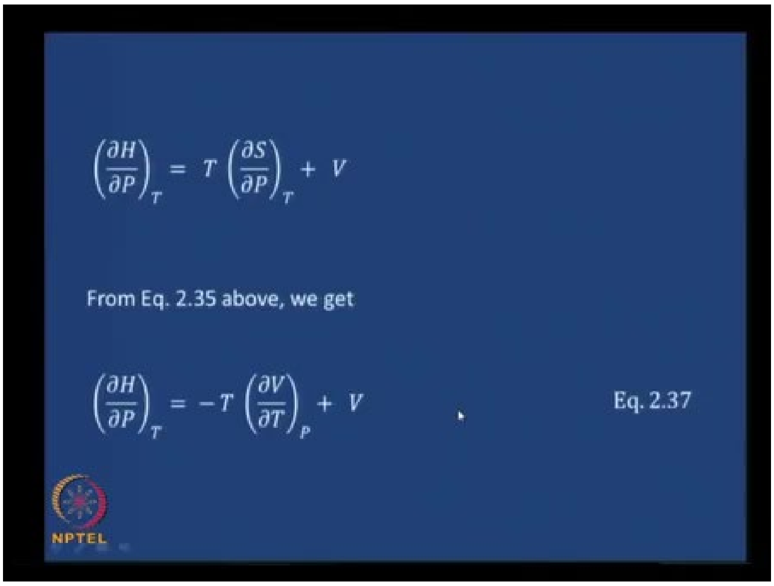

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

From Eq. 2.35 above, we get

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V \qquad \text{Eq. 2.37}$$

Therefore, dow H dow P at constant T, which is the one that we require – it is nothing but

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

So, we have gotten all four quantities, that we were required to get. If you look at it, it is essentially, manipulation, appropriate manipulation of the mathematical relationships to get whatever we needed. This is still in terms of dow S dow P at constant T and this is not completely in terms of easily measurable variables, but using the relationship between dow S dow P at constant T, that we had given in equation 2.35 earlier. You can look at equation 2.35, we have numbered that … yeah, dow S dow T at constant P as CP by T. We can write

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

This is the other relationship, which brings dow S dow P at constant T in terms of V, T and P. We will call this equation 2.37.

See you in the next class.