

Thermodynamics (Classical) for Biological Systems

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Module No. # 02

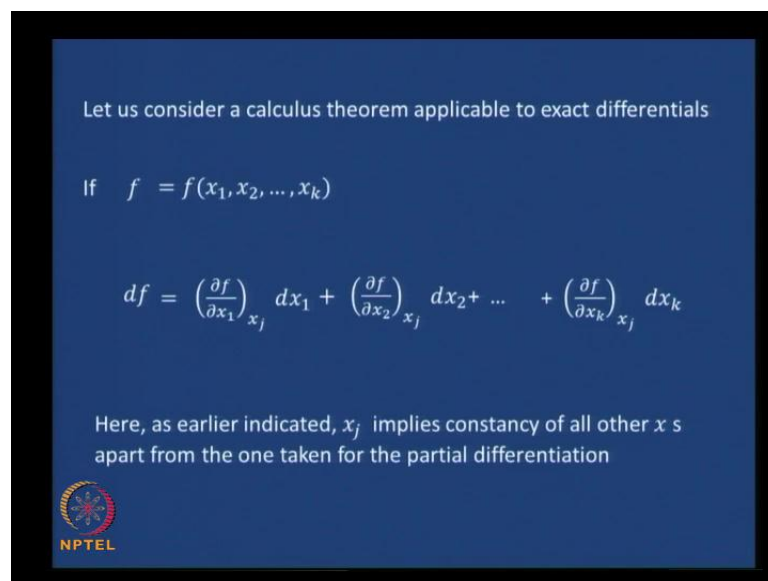
Additional Thermodynamics Functions

Lecture No. # 04

Maxwell's Relations

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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Let us consider a calculus theorem applicable to exact differentials

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

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

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 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 , then $df \dots$ df being an exact differential, can be written as $df = \left(\frac{\partial f}{\partial x_1}\right)_{x_2, \dots, x_k} dx_1 + \left(\frac{\partial f}{\partial x_2}\right)_{x_1, \dots, x_k} dx_2 + \dots + \left(\frac{\partial f}{\partial x_k}\right)_{x_1, \dots, x_{k-1}} dx_k$. This means x_1, x_2, \dots, x_k are held constant – that is what this x_j means – dx_2 and so on until $df = \left(\frac{\partial f}{\partial x_k}\right)_{x_1, \dots, x_{k-1}} dx_k$, all other x_j s remaining constant, dx_k . So, this is a fundamental theorem that is applied to ... applicable to exact differentials.


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Let $y_1 = \left(\frac{\partial f}{\partial x_1}\right)_{x_2, \dots, x_k}$ and so on, the above equation becomes:

$$df = y_1 dx_1 + y_2 dx_2 + \dots + y_k dx_k \quad \text{Eq. 2.24}$$

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

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



Now, let us take those partial differential $\left(\frac{\partial f}{\partial x_1}\right)_{x_2, \dots, x_k}$ at constant x_2, \dots, x_k , $\left(\frac{\partial f}{\partial x_2}\right)_{x_1, \dots, x_k}$ at constant x_1, \dots, x_k , and so on and replace them with another symbol for easy manipulation. Let us say that y_1 equals $\left(\frac{\partial f}{\partial x_1}\right)_{x_2, \dots, x_k}$ at constant all other x_j s. If we do that, then, we can write the previous equation as $df = y_1 dx_1 + y_2 dx_2 + \dots + y_k dx_k$. Let us call this equation 2.24. The theorem that was mentioned initially with this also known as reciprocity relationship, says that when we can do this that is df being expressed as $y_1 dx_1 + y_2 dx_2 + \dots + y_k dx_k$, $\left(\frac{\partial y_i}{\partial x_n}\right)_{x_j} = \left(\frac{\partial y_n}{\partial x_i}\right)_{x_j}$ at constant x_j equals $\left(\frac{\partial y_n}{\partial x_i}\right)_{x_j}$ at all other x_j s remaining constant. For example, if you take i to be 1 and n to be 2 $\left(\frac{\partial y_1}{\partial x_2}\right)_{x_3, \dots, x_k} = \left(\frac{\partial y_2}{\partial x_1}\right)_{x_3, \dots, x_k}$ at all other x_j s remaining

constant equals $\frac{\partial y}{\partial x}$ at all other x_j remaining constant. It is applicable for any i and any $n \dots$ that is different from i . For example, it could be $\frac{\partial y}{\partial x}$ at all other x_j remaining constant equals $\frac{\partial y}{\partial x}$ at all other x_j remaining constant.

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Application of the reciprocity relationship to

$$dU^T = T dS^T - P dV^T + \sum_i \mu_i dn_i \quad \text{Eq. 2.12}$$

gives

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

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

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


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 $\frac{\partial T}{\partial V^T}$ by – let us chose this be other variable – $\frac{\partial P}{\partial S^T}$, at all other things remaining constants such as S^T and all n_i remaining constant, this equals minus $\frac{\partial P}{\partial S^T}$ which is related to V^T earlier $\frac{\partial P}{\partial S^T}$ at V^T and all other n_i remaining constant. So, 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, one of them, then, minus comes from here –

minus of $\left(\frac{\partial S^T}{\partial P}\right)_{T, n_i}$ equals $\left(\frac{\partial V^T}{\partial T}\right)_{P, n_i}$ at constant T and all other 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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$$dH^T = T dS^T + V^T dP + \sum_i \mu_i dn_i \quad \text{Eq. 2.17}$$

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

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

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

Let us take another example. I will give you all four or ... more than four in the first case. dH^T , we have seen, is $T dS^T + V^T dP + \sum \mu_i dn_i$ and this was equation 2.17 before. If we write ... or apply the reciprocity relationship here $\left(\frac{\partial S^T}{\partial P}\right)_{S, n_i} = \left(\frac{\partial V^T}{\partial S^T}\right)_{P, n_i}$ by $\left(\frac{\partial S^T}{\partial P}\right)_{S, n_i}$ equals $\left(\frac{\partial V^T}{\partial S^T}\right)_{P, n_i}$ at constant S all other n_i equals $\left(\frac{\partial V^T}{\partial S^T}\right)_{P, n_i}$ at constant P all other n_i – equation 2.28. Let us consider dA^T now. We already have equation 2.18 as dA^T equals $-S^T dT - P dV^T + \sum \mu_i dn_i$. That must become second nature to you. $\left(\frac{\partial S^T}{\partial V^T}\right)_{T, n_i}$ note – both are minuses here. So, you do not have to worry about it, if you take these two. $\left(\frac{\partial S^T}{\partial V^T}\right)_{T, n_i}$ at constant T all other n_i equals $\left(\frac{\partial P}{\partial T}\right)_{V^T, n_i}$ at constant V^T all other n_i . We will call this equation 2.29.

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The slide contains the following content:

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

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

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

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

 NPTEL

Let us consider equation 2.15 again. Earlier for all the four equations ... for a close 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 ... $\left(\frac{\partial \mu_i}{\partial T}\right)_{P, n_i}$ equals minus $\left(\frac{\partial S^T}{\partial n_i}\right)_{T, P, n_j}$ at constant T, P and all n_j s apart from this n_i. Let me repeat this $\left(\frac{\partial \mu_i}{\partial T}\right)_{P, n_i}$ equals, minus – minus here – $\left(\frac{\partial S^T}{\partial n_i}\right)_{T, P, n_j}$ 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.

$\left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_i}$ equals $\left(\frac{\partial V^T}{\partial n_i}\right)_{T, P, n_j}$ at constant T, P, all n_j s different from n_i remaining constant. 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 actually use dG^T 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 equations. 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.

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Application of the reciprocity relationship to

$$dU^T = T dS^T - P dV^T + \sum_i \mu_i dn_i \quad \text{Eq. 2.12}$$

gives

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

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

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


The equations 2.26 to 2.31 let me go back and show you 2.26 just for recall; 2.27... 2.26 was $\left(\frac{\partial T}{\partial V^T} \right)_{S^T, n_i} = - \left(\frac{\partial P}{\partial S^T} \right)_{V^T, n_i}$. 2.27, $\left(\frac{\partial S^T}{\partial P} \right)_{T, n_i} = \left(\frac{\partial V^T}{\partial T} \right)_{P, n_i}$. Equation 2.28, $\left(\frac{\partial \mu_i}{\partial T} \right)_{P, n_j} = - \left(\frac{\partial S^T}{\partial n_i} \right)_{T, P, n_j}$. Equation 2.29, $\left(\frac{\partial \mu_i}{\partial P} \right)_{T, n_j} = \left(\frac{\partial V^T}{\partial n_i} \right)_{T, P, n_j}$. And, as we spent some extra time here $\left(\frac{\partial \mu_i}{\partial T} \right)_{P, n_j} = - \left(\frac{\partial S^T}{\partial n_i} \right)_{T, P, n_j}$ and $\left(\frac{\partial \mu_i}{\partial P} \right)_{T, n_j} = \left(\frac{\partial V^T}{\partial n_i} \right)_{T, P, n_j}$.

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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

NPTEL

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**

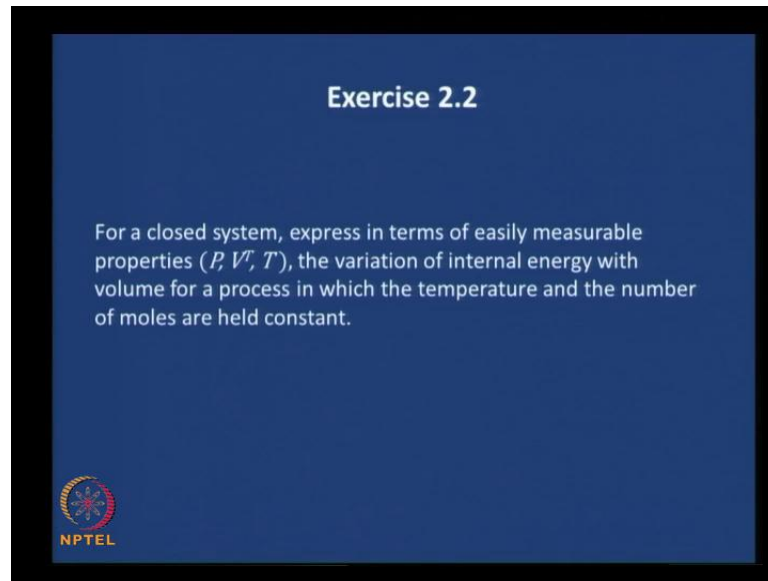
This is normally found in the textbooks as Maxwell's relations

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


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. $\left(\frac{\partial T}{\partial V}\right)_S$ equals minus $\left(\frac{\partial P}{\partial S}\right)_V$. This was obtained by applying the reciprocity relationship to the total differential written for one mole of the substance. $\left(\frac{\partial T}{\partial V}\right)_S$ equals minus $\left(\frac{\partial P}{\partial S}\right)_V$; minus $\left(\frac{\partial S}{\partial P}\right)_T$ equals $\left(\frac{\partial V}{\partial T}\right)_P$; $\left(\frac{\partial T}{\partial P}\right)_S$ equals $\left(\frac{\partial V}{\partial S}\right)_P$; and $\left(\frac{\partial S}{\partial V}\right)_T$ equals $\left(\frac{\partial P}{\partial T}\right)_V$.


You may want to compare these expressions ... I would like to do that ... I do not want to go back now. I would like to do that. 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 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.

 NPTEL

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 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 $\left(\frac{\partial U}{\partial V}\right)_T$, the variation of internal energy, with volume. So, $\left(\frac{\partial U}{\partial V}\right)_T$ at constant temperature and n . Please go ahead you have about 10 minutes. I will come back in some time in present part of the solution.

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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 U , 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. Because this has the relationship for dU^T and these would be $\left(\frac{\partial U^T}{\partial V^T}\right)_{T, n_i}$ and so on. $\left(\frac{\partial U^T}{\partial V^T}\right)_{T, n_i}$ variation. We know that dU^T equals $T dS^T$ minus $P dV^T$ plus some overall terms $\sum_i \mu_i dn_i$. The partial derivative of U at constant T and n_i can be written as $\left(\frac{\partial U^T}{\partial V^T}\right)_{T, n_i} = T \left(\frac{\partial S^T}{\partial V^T}\right)_{T, n_i} - P \left(\frac{\partial V^T}{\partial V^T}\right)_{T, n_i} + \sum_i \mu_i \left(\frac{\partial n_i}{\partial V^T}\right)_{T, n_i}$ at constant T and n_i . To continue further ... we are looking at $\left(\frac{\partial U^T}{\partial V^T}\right)_{T, n_i}$. 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 $\left(\frac{\partial S^T}{\partial V^T}\right)_{T,n_i} = \left(\frac{\partial P}{\partial T}\right)_{V^T,n_i}$

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

which is the needed relationship




Let us continue with the solution. Look at the second and third terms on the right hand side here ... $P \text{ d}V^T \text{ d}V^T \text{ d}T \text{ d}n_i$ plus summation of $\mu_i \text{ d}n_i \text{ d}V^T$ at constant $T \text{ d}n_i$. The second and third derivative terms on the right hand side are 1 and 0. 1 because $\text{d}V^T \text{ d}V^T$. 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 $\text{d}U^T \text{ d}V^T$ at constant $T \text{ d}n_i$; this was the initial left hand side. The first term remains: equals $T \text{ d}S^T \text{ d}V^T$ at constant $T \text{ d}n_i$, and since this is gone to one whatever accompany P here we just have a P remaining minus p .

So, $\text{d}U^T \text{ d}V^T$ at constant $T \text{ d}n_i$ equals $T \text{ d}S^T \text{ d}V^T$ constant $T \text{ d}n_i$ minus P . Now if we use one of the Maxwell's relations which is equation 2.29 here, $\text{d}S^T \text{ d}V^T$... this we know is a little difficult to measure. So, let us try to write this in terms of easily measurable quantities. $\text{d}S^T \text{ d}V^T$ at constant $T \text{ d}n_i$ equals $\text{d}P \text{ d}T$ at constant $V^T \text{ d}n_i$. In this case $P \text{ d}T$ is all easily measurable. If we do that then you can write $\text{d}U^T \text{ d}V^T$ at constant $T \text{ d}n_i$, which is what we need, equals $T \text{ d}P \text{ d}T$ at constant $V^T \text{ d}n_i$ minus P ;

This we are going to replace with this $\text{d}P \text{ d}T$ at constant $V^T \text{ d}n_i$ minus P ; equation 2.32. Let me call this equation 2.32 because it will come in useful later, which is actually the needed relationship. 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, α which is expansivity. I will go into details of this in a little while, and κ 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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Heat capacities

$$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_P \quad (\text{for a pure substance}) \quad \text{Eq. 2.33}$$
$$\left(\frac{\partial H^T}{\partial T}\right)_P \quad (\text{for any system})$$
$$C_v \equiv \left(\frac{\partial U}{\partial T}\right)_V \quad (\text{for a pure substance}) \quad \text{Eq. 2.34}$$
$$\left(\frac{\partial U^T}{\partial T}\right)_V \quad (\text{for any system})$$

NPTEL

Heat capacity C_p is defined as $\left(\frac{\partial H}{\partial T}\right)_P$ at constant P . This is for a pure substance. We will call this equation 2.33. For any system C_p is defined as $\left(\frac{\partial H^T}{\partial T}\right)_P$ at constant P . This is for one mole of a pure substance this is for any system. Now C_v is defined as $\left(\frac{\partial U}{\partial T}\right)_V$, C_p was $\left(\frac{\partial H}{\partial T}\right)_P$ – enthalpy – $\left(\frac{\partial H}{\partial T}\right)_P$, C_v is $\left(\frac{\partial U}{\partial T}\right)_V$ (internal energy) $\left(\frac{\partial U}{\partial T}\right)_V$ at constant volume. Since this is V at constant volume we call it C_v is specific heat 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 $\left(\frac{\partial U^T}{\partial T}\right)_V$ at constant V .

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Expression of the not-so-easy to measure
thermodynamic properties

in terms of

the measurable thermodynamic properties

helps in the estimation of the not-so-easy to measure ones

NPTEL

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. Now, using that exercise, let us ... those relations ... the definitions for C_P and C_V and so on; let us do a problem; let me probably post the problem now; and let you work on that we still have about 5, 6 minutes left in this lecture. Please take that as a tutorial part of this lecture; please work that out, and when we meet in the next class, I will give you the solution.

The problem is as follows: For a closed system consisting of one mole of the pure substance – makes things easier; one mole of the pure substance express in terms of more easily measurable properties. The variation of enthalpy and entropy with temperature and pressure, respectively. What I mean is $\left(\frac{\partial H}{\partial T}\right)_P$... enthalpy with temperature at constant pressure $\left(\frac{\partial S}{\partial T}\right)_P$ at constant pressure and variation of entropy with temperature at constant pressure, variation of enthalpy with pressure at constant temperature, just the vice versa, and the variation of entropy with pressure at constant temperature. Please go ahead and do this. We will start with the hints in the next class.