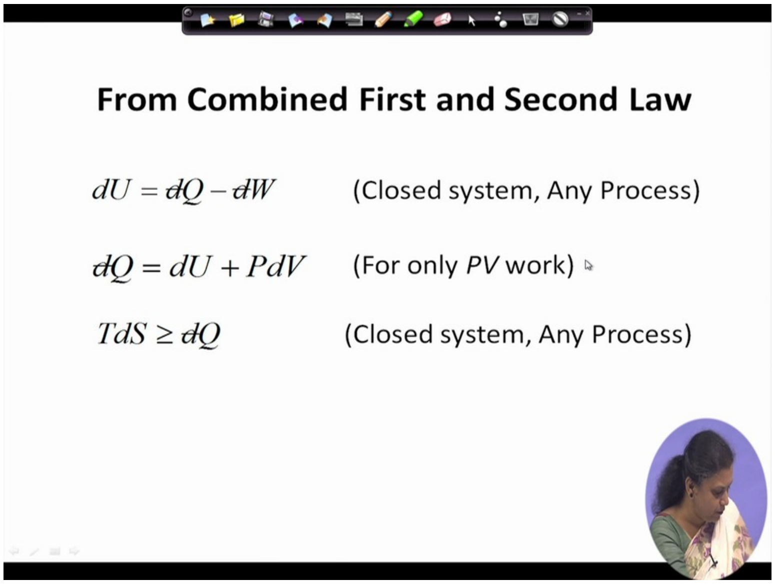
Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
Department of Chemical Engineering
Indian Institute of Technology Kharagpur
Lecture 08
Criteria Of Spontaneity (Contd.)

(Refer Slide Time: 0:25)



From Combined First and Second Law

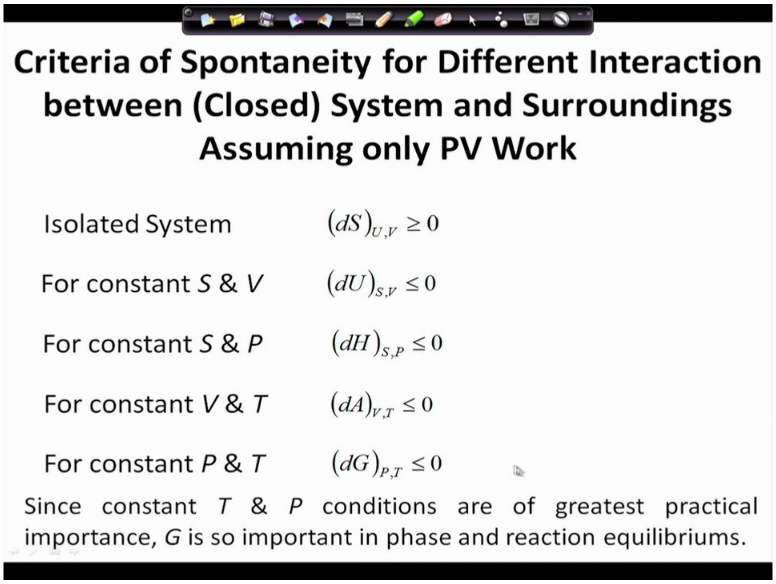
$dU = \text{đ}Q - \text{đ}W$ (Closed system, Any Process)

$\text{đ}Q = dU + PdV$ (For only PV work)

$TdS \geq \text{đ}Q$ (Closed system, Any Process)

Hello everybody, so till now we have gone through or rather we have discussed several experts of the first and second law and based on these 2 laws we found out we have developed these particular equations in this particular case. So the things which we have the different equations that we have defined the first equation was this and based on the first law this was the equation, based on second law this was the equation.

(Refer Slide Time: 1:37)



Criteria of Spontaneity for Different Interaction between (Closed) System and Surroundings Assuming only PV Work

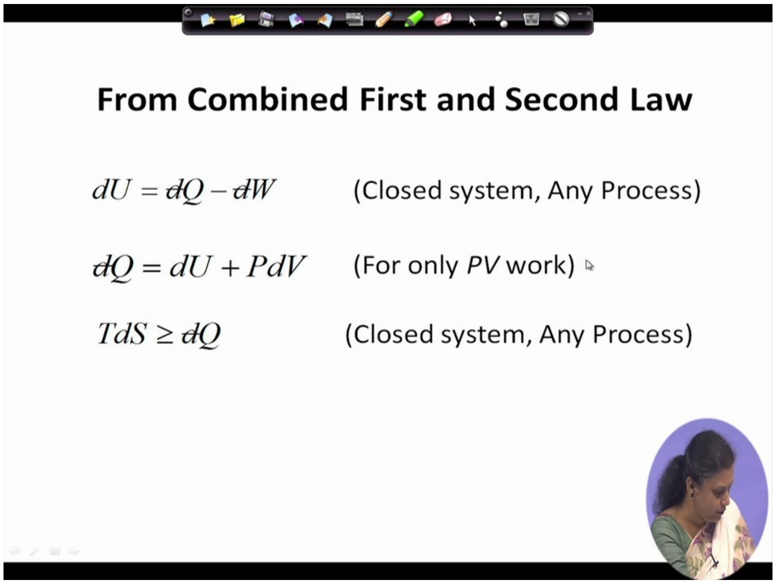
Isolated System	$(dS)_{U,V} \geq 0$
For constant *S* & *V*	$(dU)_{S,V} \leq 0$
For constant *S* & *P*	$(dH)_{S,P} \leq 0$
For constant *V* & *T*	$(dA)_{V,T} \leq 0$
For constant *P* & *T*	$(dG)_{P,T} \leq 0$

Since constant *T* & *P* conditions are of greatest practical importance, *G* is so important in phase and reaction equilibriums.

Now if you observe this equations we will found that as a consequence of the first and second law we have defined 2 new properties from first law defines dU and the second law defines dS and if you observe closely you will find that both these properties have been defined as differences and not as absolute values which implies or rather from this we find that all the other equations that we have suggested for example the different criteria of spontaneity that we have selected you find that all of these they are defined in the terms of difference quantities.

And let me tell you this is the greatest or rather this makes phase equilibrium thermodynamics much more difficult, why? Because since we defined all the properties as difference properties, so as a result of which the specification or the definition of standard states become very difficult and it is also very important that when you have a big or rather when you have a equation comprising of different properties it is important to ensure that the standard states for all the properties are taken or they are the same. So these particular small small aspects as we shall see while proceeding towards in the succeeding classes we will see, these are the things which made this subject slightly more difficult and it is very important that a student concentrates on this aspects when he is dealing with this particular subject.

(Refer Slide Time: 2:41)



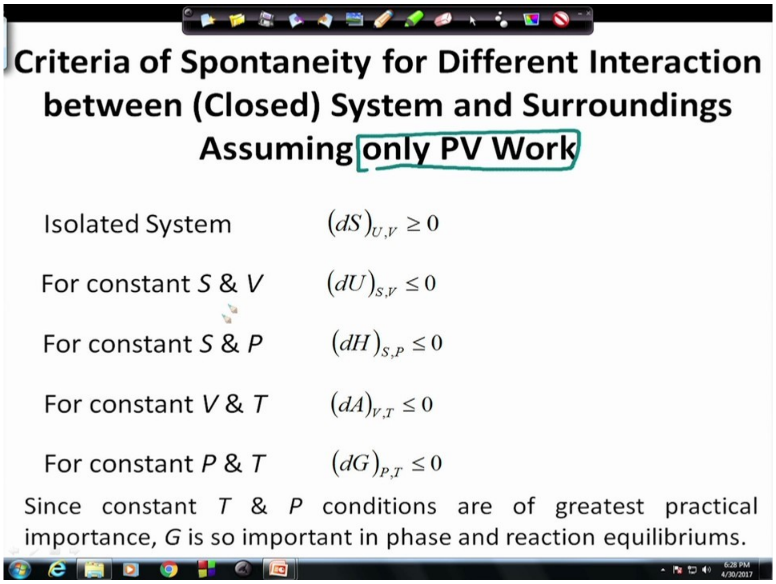
From Combined First and Second Law

$dU = \text{đ}Q - \text{đ}W$ (Closed system, Any Process)

$\text{đ}Q = dU + PdV$ (For only *PV* work)

$TdS \geq \text{đ}Q$ (Closed system, Any Process)

(Refer Slide Time: 3:16)



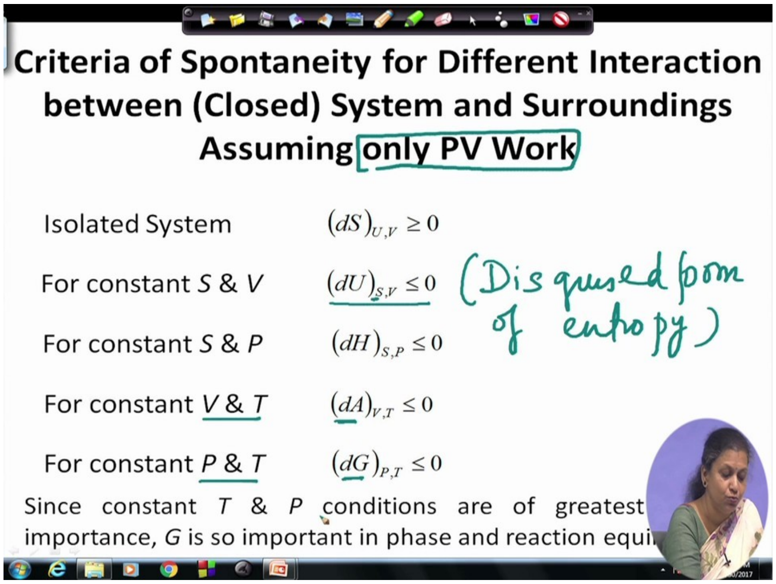
Criteria of Spontaneity for Different Interaction between (Closed) System and Surroundings Assuming only PV Work

Isolated System	$(dS)_{U,V} \geq 0$
For constant *S* & *V*	$(dU)_{S,V} \leq 0$
For constant *S* & *P*	$(dH)_{S,P} \leq 0$
For constant *V* & *T*	$(dA)_{V,T} \leq 0$
For constant *P* & *T*	$(dG)_{P,T} \leq 0$

Since constant *T* & *P* conditions are of greatest practical importance, *G* is so important in phase and reaction equilibriums.

So based on the equations we find that these are different criteria of spontaneity for different interactions between a system and the surrounding, now let me remind you once more that we have done this only for assuming that we are dealing with just Pv type of work. We all of us we know for isolated system it's the entropy maximization principle and which gives us the energy minimization principle and the enthalpy minimization principle for constant S and V and S and P.

(Refer Slide Time: 3:23)



Criteria of Spontaneity for Different Interaction between (Closed) System and Surroundings Assuming only PV Work

Isolated System	$(dS)_{U,V} \ge 0$
For constant S & V	$\underline{(dU)_{S,V}} \le 0$ (Disguised form of entropy)
For constant S & P	$(dH)_{S,P} \le 0$
For constant V & T	$(dA)_{V,T} \le 0$
For constant P & T	$(dG)_{P,T} \le 0$

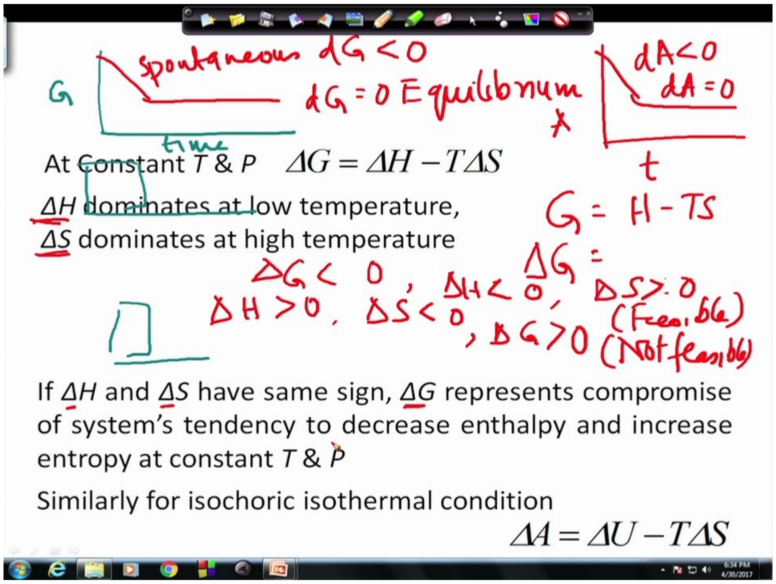
Since constant T & P conditions are of greatest importance, G is so important in phase and reaction equi

Now before I proceed I would just like to ask you one thing if you look at this particular equation, what does it show? It shows that for a spontaneous process the energy has to keep on decreasing, does it mean that the spontaneous process will only proceed when the energy of a system keeps on decreasing or does it mean that energy of the system has to keep on decreasing for a spontaneous process and finally the energy will or the system will sync into your 0 energy sort of a sync?

It is not that, this particular statement is basically a disguised statement about entropy. This basically means that for a constant entropy process, if a process has to be spontaneous and it is occurring under constant entropy conditions that the internal energy has to decrease at the expense of energy moving from the system to the surroundings or in other words it means that if the entropy of a system is maintained constant then in that case heat has to flow or rather energy has to flow from the system to the surroundings for a spontaneous process to occur.

So this is in reality a disguised statement about entropy and from these 2 in the last class we had defined that for constant volume and temperature conditions it is the Helmholtz free energy which is important for constant pressure and temperature conditions it is the Gibbs free energy which is important and it is important for you to know that usually in your practical applications we deal with constant temperature and pressure conditions and therefore Gibbs free energy you will find that is going to be our companion throughout this particular course on phase equilibrium thermodynamics it is also important for reaction equilibrium.

(Refer Slide Time: 6:04)



At Constant T & P $\Delta G = \Delta H - T\Delta S$

ΔH dominates at low temperature,

ΔS dominates at high temperature

If ΔH and ΔS have same sign, ΔG represents compromise of system's tendency to decrease enthalpy and increase entropy at constant T & P

Similarly for isochoric isothermal condition

$$\Delta A = \Delta U - T\Delta S$$

Now after this, what do we get? So from there what does it imply? It implies from this particular equation it implies that more or less we find out that from this particular equation we find out that suppose we are plotting say G, suppose spontaneous reaction occurs and in that particular spontaneous reaction we are plotting the Gibbs free energy versus time what do we observe? We observe that initially the Gibbs free energy it keeps on decreasing, right?

This is the time where the spontaneous reaction is occurring and after a while when equilibrium has achieved then we find the dG becomes equal to 0 and this signifies the equilibrium condition for this particular case it was dG less than 0, for this particular case it is dG equal to 0. Same way if you would like to plot the Helmholtz free energy as a function of time for a constant volume and constant temperature conditions we find that while this spontaneous reaction is occurring that Helmholtz free energy keeps on decreasing and finally when equilibrium has achieved dA becomes equal to 0, right?

So therefore if we observe suppose at constant temperature and pressure Gibbs free energy I have said this is equal to G minus TS, so at constant temperature suppose we would like to plot or rather we would like to find the change in Gibbs free energy when the process occurs this can very well be written down the way I have written it down, Delta G equals to Delta S minus T

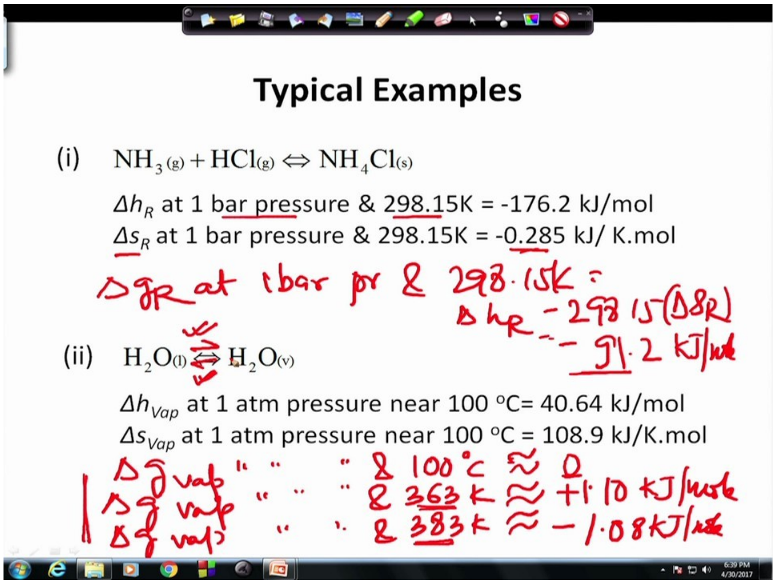
Delta S. From here what is the first thing that you observe? You observe that enthalpy dominates at low-temperature and entropy dominates at high-temperature, right?

So therefore when we know that a spontaneous process has to occur for that particular condition Delta G is less than 0, how can Delta G be less than 0? When then Delta H is less than 0 and Delta S is greater than 0. We know that for such a situation the process it is a feasible process or in other words the process is spontaneous.

Again suppose we find that for any particular equation Delta H is greater than 0 and Delta S greater than 0. So for this particular situation we definitely know that for this situation Delta G will be greater than 0 as a result this process is not feasible but it will be feasible in the reverse direction, right?

The problem starts when Delta H and then Delta S they have the same sign which means that both of them are positive or both of them are negative under that condition the change in Gibbs free energy represents a compromise of the system’s tendency to decrease enthalpy and increase entropy under constant temperature and pressure conditions.

(Refer Slide Time: 9:42)



Typical Examples

(i) $NH_{3(g)} + HCl_{(g)} \Leftrightarrow NH_4Cl_{(s)}$

Δh_R at 1 bar pressure & 298.15K = -176.2 kJ/mol

Δs_R at 1 bar pressure & 298.15K = -0.285 kJ/ K.mol

Δg_R at 1bar pr & 298.15K = $\Delta h_R - 298.15(\Delta s_R)$ = -91.2 kJ/mole

(ii) $H_2O_{(l)} \Leftrightarrow H_2O_{(v)}$

Δh_{Vap} at 1 atm pressure near 100 °C= 40.64 kJ/mol

Δs_{Vap} at 1 atm pressure near 100 °C = 108.9 kJ/K.mol

Δg_{vap} " " " & 100 °C ≈ 0

Δg_{vap} " " " & 363 K ≈ +1.10 kJ/mole

Δg_{vap} " " & 383 K ≈ −1.08 kJ/mole

Let us state a definite example in this particular aspect. Suppose we take a definite example here what do we find? We find that the very typical example of say ammonia and HCl reacting to find NH4Cl. We know that for this particular reaction the heat of reaction is known to us as well as the Delta sR is known to us both of them are negative, just if you observe the entropy change of this particular reaction what will you get?

You are going to find that the entropy change it is negative. Just if you are not aware enough it will immediately appear to you that this reaction should not occur in the forward direction but the reverse reaction is possible but in order to find this out since this particular reaction occurs under constant temperature and constant pressure conditions it is important to find out Delta gR at the same conditions of 1 bar pressure and 298.15 Kelvin it is not difficult you can just find it out by plotting or rather by calculating Delta hR minus298.15 Calvin into Delta sR.

What is the value that that you get under this condition? We find that the value is minus 91.2kilo joules per mole under this condition. Immediately from the value of delta gR that this reaction is spontaneous which is the actual case under normal circumstances. Same way suppose I take another very common example vaporization of water although this is a physical process I have denoted it in the form of a in the form of a reaction.

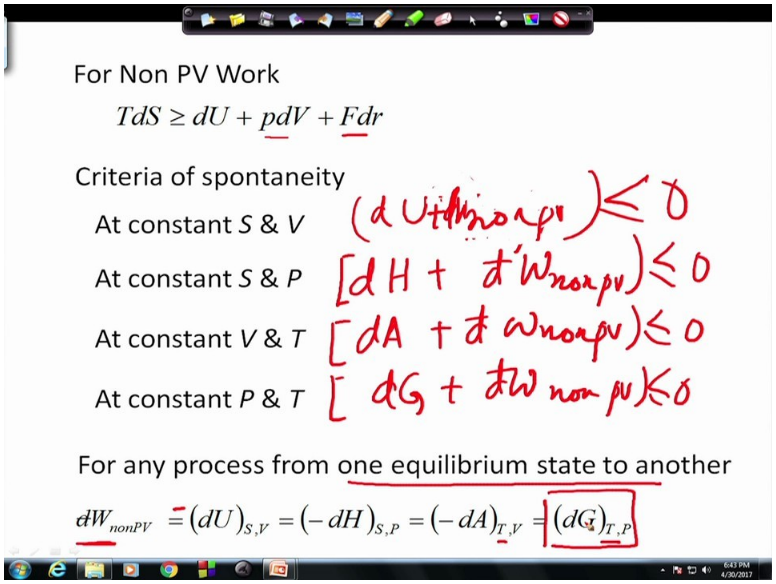
We know the standard enthalpy of vaporization and the entropy of vaporization of water at 1 atmospheric pressure around 100 degrees centigrade, let us calculate Delta g vaporization at 1 atmosphere pressure and exactly at 100 degrees centigrade that is 373 degree Kelvin. Just calculate it and you are going to find that this will almost be equal to 0, now repeat the calculation for 1 atmosphere pressure and say 363 degree Kelvin or 90 degrees centigrade, just calculate it and you are going to find that it is going to be plus 1.10 kilo Joules per mole.

And suppose you calculate this for 383 degree Kelvin what do you find? You find this is about 1.0 this is around minus 1.08 kilo joules per mole. So immediately from these particular values of delta g vaporization, immediately you have got the answer that why water vaporizes at 100 degrees centigrade and steam condenses at 100 degrees centigrade since Delta g vaporization is almost 0 at that temperature therefore this process at 100 degrees centigrade is reversible and it is feasible in both directions.

And this also gives you the answer that why your condensation of steam to water is spontaneous at 363 degree Kelvin because Delta g vaporization is positive, so naturally the reverse reaction is spontaneous and at 383 degree Kelvin we find that the reaction it is spontaneous in the forward direction.

So therefore just by calculating the delta g vaporization values we know that the reaction can occur in both ways for 100 degrees centigrade and this particular direction it is spontaneous for 383 degree Kelvin and this particular reaction is spontaneous for 363 degree Kelvin. We can take up several other examples as well but anyhow these are the 2 typical examples which I have shown so that you can appreciate the importance of calculating Delta g vaporization.

(Refer Slide Time: 14:46)



For Non PV Work

$$TdS \geq dU + \underline{p}dV + \underline{F}dr$$

Criteria of spontaneity

At constant S & V $(dU + đW_{non\,pv}) \leq 0$

At constant S & P $[dH + đ'W_{non\,pv}) \leq 0$

At constant V & T $[dA + đW_{non\,pv}) \leq 0$

At constant P & T $[dG + đW_{non\,pv}) \leq 0$

For any process from one equilibrium state to another

$$\underline{đW}_{nonPV} = (dU)_{S,V} = (-dH)_{S,P} = (-dA)_{T,V} = \boxed{(dG)_{T,P}}$$

Well, so far as I have already mentioned that we have just considered a closed system with just Pv type of work this I have been repeatedly mentioning you. What happens if suppose there is some amount of non-pv work also performed by this particular system any particular closed system? Let the system be closed but it performs some non-pv type of work. Naturally along with pdV then what do we have? Along with pdV then we have 1 Fdr term as well, isn't it?

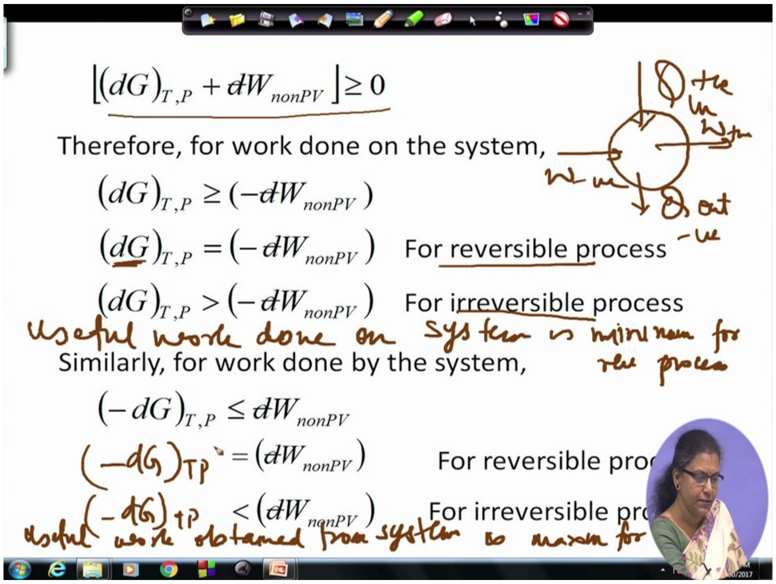
Where F is the thermodynamic driving force and r is the thermodynamic displacement, under this condition do the same criteria of spontaneity hold? For constant S and V what was the criteria of spontaneity? The criteria of spontaneity was dv less than equal to 0, do you expect the same criteria to hold in this particular case? No, if we just substitute the equations at constant S and V you find that the criteria dU S,V less than equal to 0 does not hold for constant S and V conditions.

On the contrary what should happen under this particular condition? Under this particular condition we find that dU plus dW non-pv this particular term should be less than 0. In the same way for constant S and P what should be the conditions of spontaneity? It should be dH plus dW non-pv is less than equal to 0 same way if we continue we will find that for constant volume temperature conditions this is the equation and for constant pressure temperature conditions this is going to be the equations.

So therefore from here what are the things that that we have found out? We have found out that when there is some amount of non-pv type of work under that condition, we find that whenever there is some non-pv type of work under that condition the amount of useful work or the non-PV work that we can get from a system or that has to be performed on a system when it moves from one equilibrium state to another is equal to the decrease in the internal energy of the system at constant entropy volume conditions if the process occurs under constant entropy pressure conditions then it is a decrease of the enthalpy and usually what we find?

We find the reactions occurring or the processes occurring for constant temperature volume or constant temperature pressure conditions and under these conditions we find that the amount of non-pv work that can be obtained from a system is equal to the decrease in the Helmholtz free energy or the Gibbs free energy of the system. Again I would like to remind you that since we are mostly concerned and interested with constant temperature and pressure conditions, so therefore dG T, P is going to be of interest to us, right?

(Refer Slide Time: 18:16)



$$\left[(dG)_{T,P} + \text{đ}W_{nonPV}\right] \geq 0$$

Therefore, for work done on the system,

$$(dG)_{T,P} \geq (-\text{đ}W_{nonPV})$$

$$(dG)_{T,P} = (-\text{đ}W_{nonPV})$$ For reversible process

$$(dG)_{T,P} > (-\text{đ}W_{nonPV})$$ For irreversible process

useful work done on system is minimum for rev process

Similarly, for work done by the system,

$$(-dG)_{T,P} \leq \text{đ}W_{nonPV}$$

$$(-dG)_{TP} = (\text{đ}W_{nonPV})$$ For reversible proc

$$(-dG)_{TP} < (\text{đ}W_{nonPV})$$ For irreversible pro

useful work obtained from system is maxm for

So therefore for non-pv type of work we will find that more or less. Well, so from the last slide let me just write down this equation once more, what does this equation show? This is the equation which I have derived in the last line, right? Now from this particular equation if you observe this equation we can write it two particular ways, the first thing is we can write it down as dG T, P is greater than equal to minus dW non-PV.

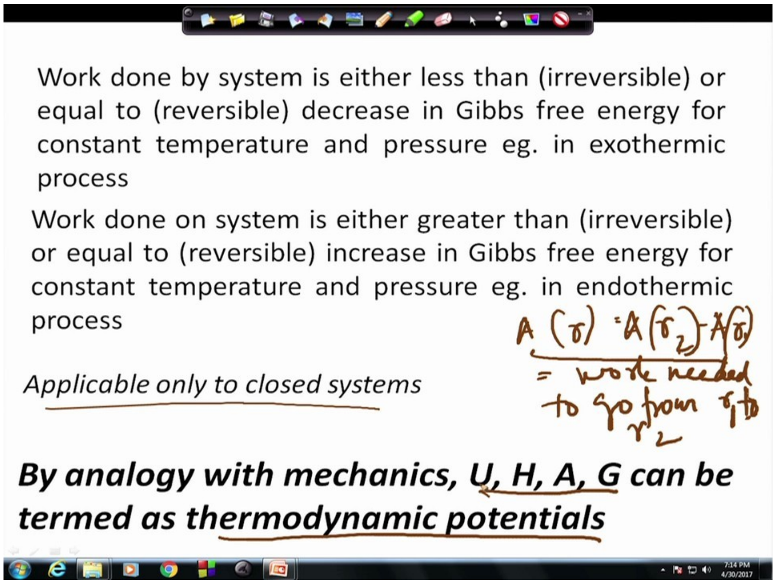
What is minus dW non-PV? If you remember these the sign convention which we are using this is Q in is positive and the Q out that is negative, work done by the system is positive, work done on the system is negative, so therefore minus dW non-pv is a work done on the system. So we find out that the work which has to be done on the system in order to bring or rather to affect some amount of change in the Gibbs free energy.

It is for a reversible process we will find that dG T, P equals to minus dW non-pv and you will find that for an irreversible process we find that the useful work which is done on the system is minimum for the reversible process. So from these 2 things what do we deduce? We deduce that useful work done on the system it is minimum for reversible process.

And similarly we can also write it down in this particular case if a system has to perform work on the surroundings then that has to be accompanied by a decrease in the Gibbs free energy we find that the decrease in the Gibbs free energy is equal to the non-pv work for reversible process and this is less than the non-pv work for the irreversible process. So from here what do we find? We find that the useful work obtained from system that is maximum for reversible process, right?

So therefore what can be deduced from here? We can write the equation in 2 particular modes one shows that the decrease in Gibbs free energy is equal to the useful work done by the system and we find that the maximum work that can be extracted from the system is obtained for reversible process and whatever useful work we can obtain for the system for an irreversible process is less than useful work that can be obtained for a reversible process in the same way if you have perform work on the system then we find that the minimum work that has to be done on a system in order to effect some particular change in the Gibbs free energy that is minimum for a reversible process for any particular irreversible process the work which we have to perform is will be much greater in that particular case.

(Refer Slide Time: 21:54)



Work done by system is either less than (irreversible) or equal to (reversible) decrease in Gibbs free energy for constant temperature and pressure eg. in exothermic process

Work done on system is either greater than (irreversible) or equal to (reversible) increase in Gibbs free energy for constant temperature and pressure eg. in endothermic process

$\underline{A(r) = A(r_2) - A(r_1)}$

= work needed to go from r_1 to r_2

Applicable only to closed systems

By analogy with mechanics, U, H, A, G can be termed as thermodynamic potentials

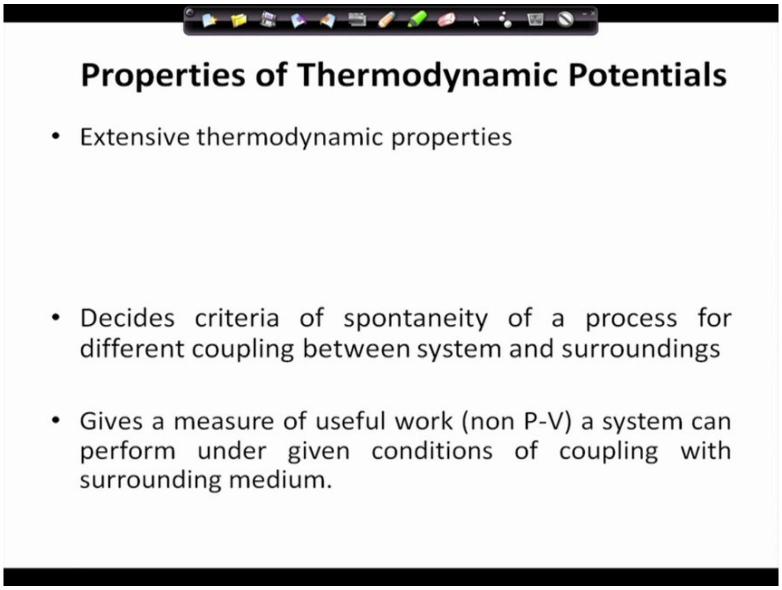
Or in a nutshell suppose we would like to tell this is a nutshell, so therefore we can say it as that the work done by a system is either less than or equal to the decrease in Gibbs free energy for constant temperature and pressure conditions for example in an exothermic process. And the work done on the system is either greater than or equal to increase in Gibbs free energy for constant temperature and pressure for example in an endothermic process where it is important to remember that this is applicable only to a closed system.

Now when we relate these particular terms with the useful work which can be obtained from a system of the useful work done on this system does this tell you or does this suggest any particular similarity with any term which you had studied earlier? If you recall you will find that in mechanics of potential A(r) was defined as A(r2) minus A(r1) and that was equal to the work needed to go from r1 to r2. If you remember this thing, so therefore in mechanics a potential was defined as the work needed to go from r1 to r2 and that was equal to the difference A(r2) minus A(r1).

The decisive point in this particular case was that Ar it did not depend on the particular way it was chosen to go from 1 to 2 as long as the acting forces were given as the derivative of the potential with respect to the coordinates if you compare we will find that in this case also U, H, A and G their differences give us a measure of the amount of work needed from going in going from state 1 to 2 and they are independent on the particular way that we have chosen in going from 1 to 2.

So therefore by analogy with mechanics all these 4 terms can be termed as thermodynamic potentials and they can be related to the work or rather useful work attained or performed on a on a system for different coupling of the system and surroundings I repeat dU gives you the non-pv or the amount of useful work that can be obtained under constant entropy volume conditions, H for constant entropy pressure conditions, A for constant temperature volumes conditions and G for constant temperature and pressure conditions.

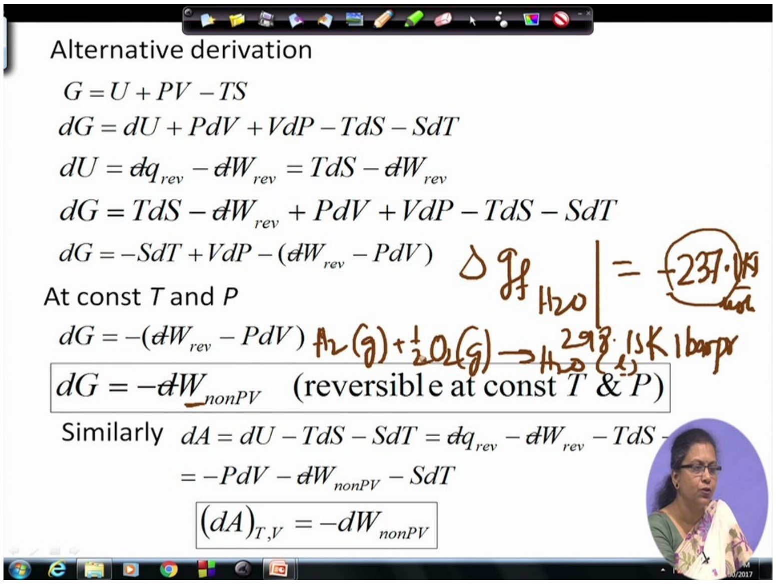
(Refer Slide Time: 24:52)



Properties of Thermodynamic Potentials

- Extensive thermodynamic properties
- Decides criteria of spontaneity of a process for different coupling between system and surroundings
- Gives a measure of useful work (non P-V) a system can perform under given conditions of coupling with surrounding medium.

(Refer Slide Time: 25:04)



Alternative derivation

$$G = U + PV - TS$$

$$dG = dU + PdV + VdP - TdS - SdT$$

$$dU = \text{đ}q_{rev} - \text{đ}W_{rev} = TdS - \text{đ}W_{rev}$$

$$dG = TdS - \text{đ}W_{rev} + PdV + VdP - TdS - SdT$$

$$dG = -SdT + VdP - (\text{đ}W_{rev} - PdV)$$

$$\Delta g_{f}\Big|_{H_2O} = -\boxed{237.1\ \text{kJ/mol}}$$

At const T and P

$$dG = -(\text{đ}W_{rev} - PdV)$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad 298.15\,K \ 1\,\text{bar pr}$$

$$\boxed{dG = -\underline{\text{đ}W}_{nonPV} \quad (\text{reversible at const } T \ \& \ P)}$$

Similarly $dA = dU - TdS - SdT = \text{đ}q_{rev} - \text{đ}W_{rev} - TdS -$

$$= -PdV - \text{đ}W_{nonPV} - SdT$$

$$\boxed{(dA)_{T,V} = -dW_{nonPV}}$$

From here therefore in a nutshell, we can go to the properties of thermodynamic potentials but before we do this I would just like to present an alternative derivation of decrease in Gibbs free energy being equal to the non-pv type of work I have done an alternative derivation for both dG as well as dA. I would like to remind you that since both of them are thermodynamic properties, so therefore in whatever way we do the derivation we are supposed to arrive at the same results provided initial and final states are the same.

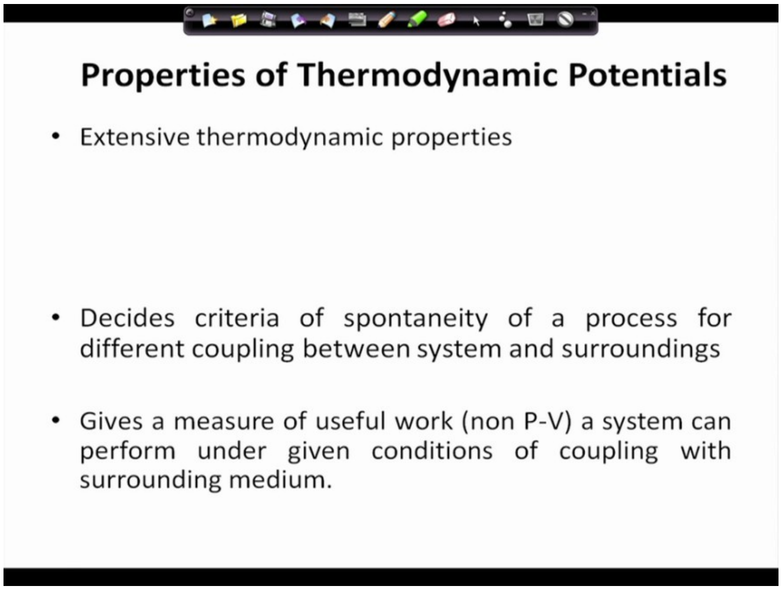
So in this particular case what I have done? I have started from the basic definitions and I have defined dU from the first law and for and then at constant temperature and pressure I find that dG is equals to the reversible work which can be performed by a system and minus the PdV work which is there because Pv work is anyhow in that particular case it is there.

So from here can you tell me that suppose I give you an statement say that suppose a statement is given to you say for example I state Delta gf the Gibbs free energy of formation of water at say some particular condition say delta gf water at say 298.15 Kelvin and 1 bar pressure this is equal to say I tell you it is equal to minus 237.1 kilo joules per mole, can you tell me what this particular statement means?

If I tell you Delta gf water is equal to at 298.15 Kelvin and 1 bar pressure equals to minus 237.1 kilojoules per mole. Well, this means that suppose we perform some particular reaction say water hydrogen at gas plus half O_2 gas to give you H_2O liquid and for this particular condition hydrogen is at 1 bar pressure 298.15 Kelvin, oxygen is at 1 bar pressure 298.15 Kelvin and water formed is also at 1 bar pressure and 298.15 Kelvin. So therefore from this particular forward reaction we can actually get 237.1 kilo joules of energy we can get from here.

It also means that if we have to decompose water into its constituents we have to provide 237.1 kilojoules per mole of energy provided the reaction takes place reversibly, right? So therefore the non-pv type of work in this particular case was the electrical work which has to be provided or rather which is obtained in a galvanic cell where hydrogen and oxygen react to form water or minus or this much amount of energy is necessary to decompose water to obtain its constituent elements.

(Refer Slide Time: 28:42)



Properties of Thermodynamic Potentials

- Extensive thermodynamic properties
- Decides criteria of spontaneity of a process for different coupling between system and surroundings
- Gives a measure of useful work (non P-V) a system can perform under given conditions of coupling with surrounding medium.

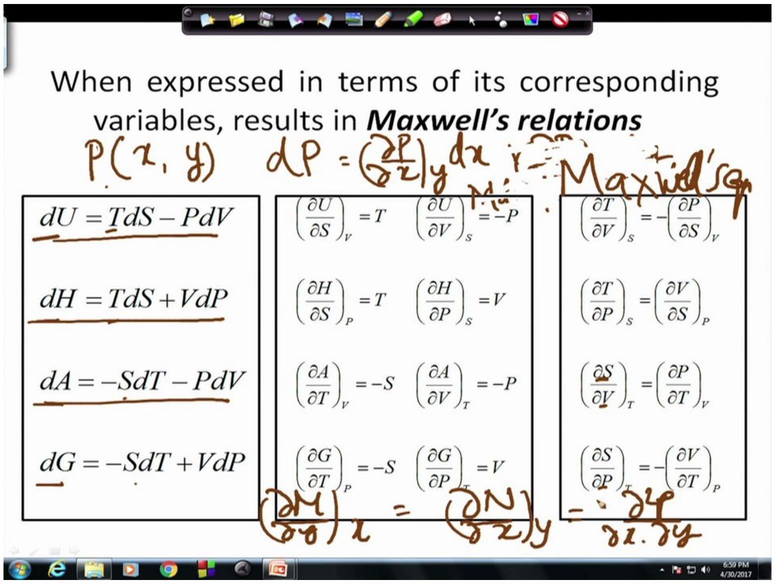
So therefore after this in a nutshell we would like to discuss the properties of the thermodynamic potentials, what are the properties of the thermodynamic potentials? We all of us know that they all of them are the thermodynamic potentials are thermodynamic properties and all of them are extensive properties, what does it mean? It means that U should be equal it should be number of moles into the molar internal energy, same way the total enthalpy of the system is the number of moles into the molar enthalpy of the system, your total Helmholtz free energy should be equal to the number of moles into the molar Helmholtz free energy of the system and Gibbs free energy should be the number of moles times the molar Gibbs free energy of the system and just like the total properties here also we know that the molar Gibbs free energy is nothing but H minus TS the same way a would be equal to U minus TS.

Now here I would very categorically like to mention something which you should be remembering throughout the entire course of phase equilibrium thermodynamics. Since we are dealing with a large number of properties here, so therefore all total properties will be defined in terms of capital letters and all molar properties will be defined in terms of small case letters, we would be maintaining this particular nomenclature throughout our class or rather throughout this particular course on phase equilibrium thermodynamics.

So therefore coming back to the properties of thermodynamic potentials all of them are extensive thermodynamic properties they decide the criteria of spontaneity of a process for different coupling between system and surroundings I need not repeat, you decide the criteria for constant S and V, H for constant S and P, A for constant T and V, A for constant T and V, G for constant T and P.

The other thing is it gives a measure of the useful work of the non-PV work to be specific because we have found out that it is W non-PV minus PdV. So therefore it gives the measure of useful work a system can perform under given conditions of coupling with the surrounding medium.

(Refer Slide Time: 31:34)



When expressed in terms of its corresponding variables, results in ***Maxwell's relations***

$P(x, y) \quad dP = \left(\frac{\partial P}{\partial x}\right)_y dx$ Maxwell's eq

$$dU = TdS - PdV \qquad \left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$dH = TdS + VdP \qquad \left(\frac{\partial H}{\partial S}\right)_P = T \quad \left(\frac{\partial H}{\partial P}\right)_S = V \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$dA = -SdT - PdV \qquad \left(\frac{\partial A}{\partial T}\right)_V = -S \quad \left(\frac{\partial A}{\partial V}\right)_T = -P \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$dG = -SdT + VdP \qquad \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial G}{\partial P}\right)_T = V \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 P}{\partial x . \partial y}$$

Well, the most important property of the thermodynamic potentials with which we will be primarily interested is that if you observe each and every of this particular properties if you observe this property these the different particular equations we will find this was the combined first and second law that we have already discussed. From here we have come here, just substituting A equals to U minus TS we get this equation substituting G equals to H minus T is you get this equation, so for each thermodynamic potential you have got one set of differential equations number 1.

Number 2 is, we already know that all of them are properties of the system, so therefore they have exact or rather they are exact differentials, what are the properties of exact differentials? If you remember suppose d is an exact differential, so therefore in that particular case suppose P is an exact differential and it is a function of say x, y then in that case I can write down dP is equal to del P del x at constant y dx plus del P del y at constant x dy this can also be written down as Mdx plus Ndy, isn't it?

And under that particular condition I can also write down delM del y at constant x is equal to del N del x at constant y because both of them are equal to del2p del x del y, since P is a property so therefore it hardly matters which differentiation I perform first and based on this where all these terms have been differentiated I have simply written down these properties in this particular form and then I have performed this particular equality and from here we get something which is very important and we get a set of equations which are extremely important and these equations are known as the Maxwell's equation.

Just observe the Maxwell's equations what do you get? You find that the Maxwell's equation they give us the variation of entropy with pressure the variation of entropy with volume with pressure and these are related to the PVT properties of the different substances. So therefore we find from the differential equations of the different thermodynamic potentials we come across a set of Maxwell's equations and these Maxwell's equations are very important because they relate the non-measurable properties with the measurable properties.

So therefore in the next class we are going to continue and find out how Maxwell's equation can be used to relate measurable with non-measurable properties? Thank you very much.