Chemical and Biological Thermodynamics: Principles to Applications
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Lecture –14
Further discussion on properties of Gibbs energy

Let us now discuss the pressure dependence of Gibbs energy. Just the way the temperature dependence of Gibbs energy can provide a lot of information, similarly the pressure dependence of Gibbs energy can provide a lot of information.

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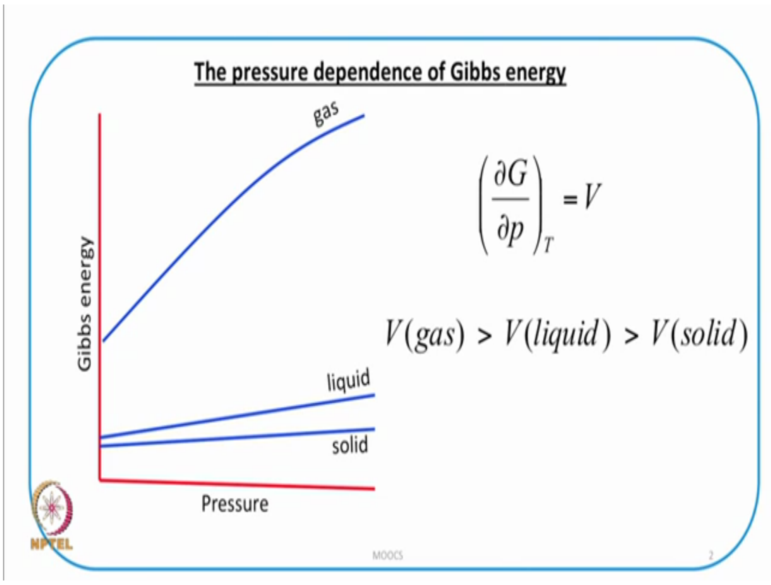

The pressure dependence of Gibbs energy

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

$$V(gas) > V(liquid) > V(solid)$$

If Gibbs energy of a system is plotted against pressure, this is the type of variation is that we generally observe. The dependence on gas is large whereas, there is not significant variation for liquid or for salt. What could be the reason for a relatively stronger pressure dependence for gas and weaker pressure dependence for liquid and salt? For this we will again have to go back to discuss the properties of Gibbs free energy in terms of its definition and then, you remember that we derived an equation d G is equal to V d p minus S d t. From that equation we derived this formula. This partial derivative we showed that is equal to volume dou G by dou p at constant temperature is equal to volume and since, the volume of gas in general is larger than the volume of liquid which is larger than the volume of solid and this is the reason you have the dependence is maximum for gas followed by liquid and that for the solid. Here lies the origin of that.

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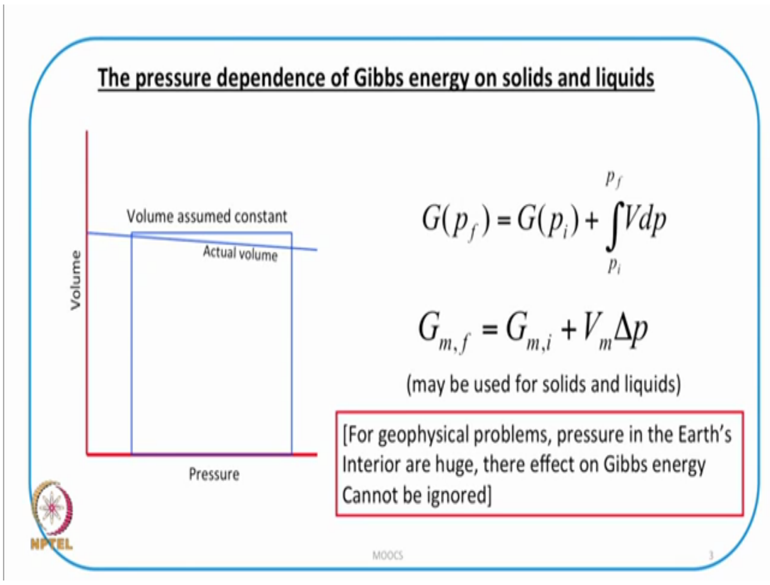

The pressure dependence of Gibbs energy on solids and liquids

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp$$

$$G_{m,f} = G_{m,i} + V_m \Delta p$$

(may be used for solids and liquids)

[For geophysical problems, pressure in the Earth's Interior are huge, there effect on Gibbs energy Cannot be ignored]

Let us now go a little more into the details of pressure dependence of Gibbs energy on solids and liquid we have.

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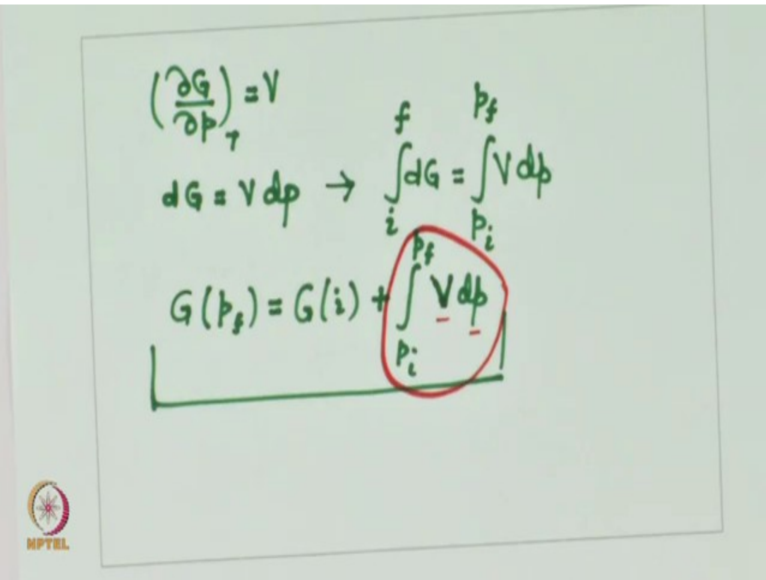

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

$$dG = V dp \rightarrow \int_i^f dG = \int_{p_i}^{p_f} V dp$$

$$G(p_f) = G(i) + \boxed{\int_{p_i}^{p_f} \underline{V} \underline{d}p}$$

This definition now dou G by dou p at constant temperature is equal to volume. This allows me to write d G is equal to V d p. Of course, the temperature is constant and i can use this to write for a finite change for initial state to final state corresponding to pressures P i change into P f. This I can write G at a final pressure is equal to G at initial pressure plus integration P i to p f V d p. This equation allows me to understand the pressure dependence of Gibbs free energy. What we need is volume. How the volume changes with pressure and if you remember earlier when we discussed the work, we can solve for this integral either numerically or by graphical method. Graphical method means we need to plot volume against pressure and then, calculate the area under the curve or under the line.

Let us also realize that the volume of solid and liquid in general does not depend significantly on pressure; does not change significantly with pressure. So, for solid and liquid we can conveniently consider volume to be not depending upon pressure and take it out of the integral. So, let us go back to the slide and as I just discussed if I take volume out of the integral because for solid and liquid as I said volume does not depends significantly on pressures; if you treat it as a constant quantity and then, convert everything into a molar quantity, then final molar Gibbs free energy is equal to initial molar Gibbs free energy plus V m into delta p.

We can also calculate evaluate this integral by the indicator type of diagram. If you assume volume constant, you are just taking this horizontal line, but in fact the actual volume does depend slightly on pressure. This is how the actual volume changes. In that case if you really want to be very exact, you have to substitute the expression for volume, here volume dependent on pressure and then, solve this integral and if you assume constant, then you can simply use this equation G m final is equal to G m initial plus V m into delta, ok.

When we are talking about geophysical problems that means we are talking about the interior of the earth and then, the pressure in the earth’s interior are huge. Pressure is very huge in the interior of the earth. There we cannot ignore this volume dependent on pressure, we cannot. In that case we have to really worry about the pressure and volume dependent upon both pressure and temperature.

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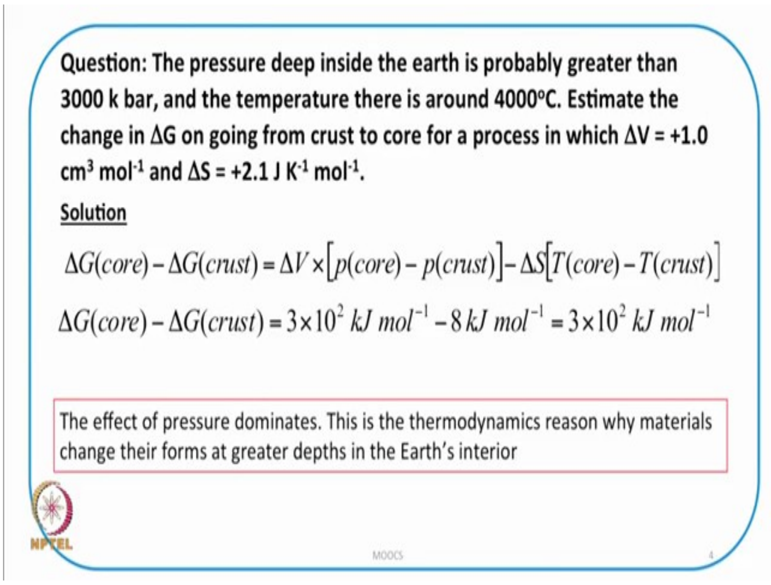

Question: The pressure deep inside the earth is probably greater than 3000 k bar, and the temperature there is around 4000°C. Estimate the change in ΔG on going from crust to core for a process in which ΔV = +1.0 cm^3 mol^{-1} and ΔS = +2.1 J K^{-1} mol^{-1}.

Solution

$$\Delta G(core) - \Delta G(crust) = \Delta V \times \left[p(core) - p(crust)\right] - \Delta S\left[T(core) - T(crust)\right]$$

$$\Delta G(core) - \Delta G(crust) = 3\times10^{2}\ kJ\ mol^{-1} - 8\ kJ\ mol^{-1} = 3\times10^{2}\ kJ\ mol^{-1}$$

The effect of pressure dominates. This is the thermodynamics reason why materials change their forms at greater depths in the Earth's interior

Let us take a look at this numerical problem. The pressure deep inside the earth is probably greater than 3000 kilo bar and the temperature there is around 4000 degree centigrade. The question is estimate the change in delta G on going from crust to core for a process in which delta V is plus 1 centimeter cube per mol and delta S is plus 2.1 joules per Kelvin per mol. See the pressures which are given to us are for deep inside the earth. That means, we are talking about the code and the temperature there is about 4000 degrees centigrade, the pressure and temperature. Then, at the curst we can simply take to be very less or negligible compared to these values given how do we approach solving this question.

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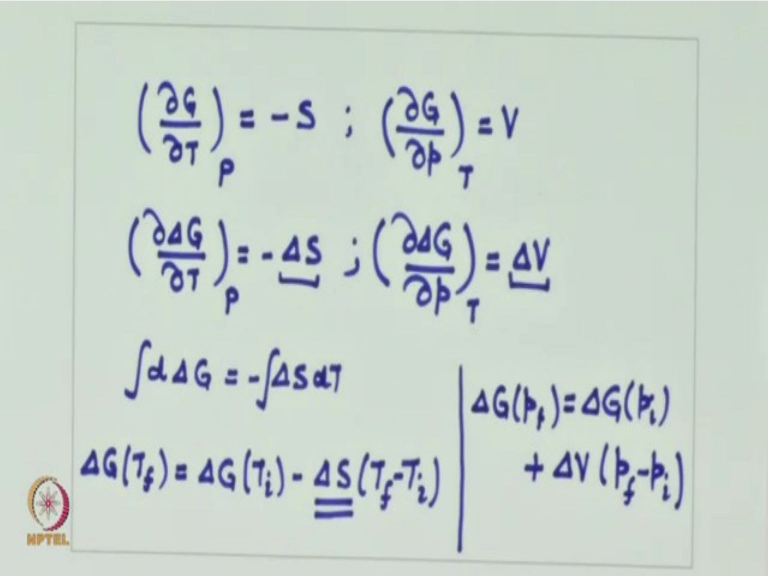

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \; ; \; \left(\frac{\partial G}{\partial p}\right)_T = V$$

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\underline{\Delta S} \; ; \; \left(\frac{\partial \Delta G}{\partial p}\right)_T = \underline{\Delta V}$$

$$\int d\Delta G = -\int \Delta S \, dT$$

$$\Delta G(T_f) = \Delta G(T_i) - \underline{\underline{\Delta S}}(T_f - T_i)$$

$$\Delta G(p_f) = \Delta G(p_i) + \Delta V(p_f - p_i)$$

We have just discussed that dou G by dou T at constant pressure is equal to minus S and the other equation that we just discussed dou G by dou p at constant temperature is equal to volume. In other word, if I write these four changes, I can write dou delta G by dou T at constant pressure is equal to minus delta S and dou delta G by dou p at constant temperature is equal to delta v. Thus from the knowledge of delta S and the knowledge of delta v, I can talk about the delta G which depends or which changes with the change in temperature and delta G which changes with the change in pressure. I can calculate those numbers. So, if I calculate these delta gs based on these two equations and then add up, that will be the answer that I am looking for.

So, by using this equation I write d delta G is equal to minus delta S into d T and then, I can integrate within the limits. This gives me delta G at some final temperature is equal to delta G at the chosen initial temperature minus delta S T f minus T i. If I assume that the entropy is actually not changing much with this small change in temperature, this is one equation and from this a similar equation can be derived. Delta G at some final pressure is equal to delta G at some initial pressure plus delta V into p f minus p i. These equations can be derived.

Let us go back to the slide. So, by using the equations that we just derived, I can get delta G core minus delta G curst is equal to change in volume into p final minus p initial and the second contribution is from the temperature dependence. This is equal to minus delta

S times T core minus T crust if p core minus p crust. I simply use approximately 3000 kilo bar and T core minus T crust. I approximately use 4000 degree centigrade, then I can get of the value of 3 into 10 raise to the power 2 kilojoules per mol. That is the answer that we are getting and please remember that the numbers here that we are putting in are approximate number. I am not really going into the decimal points and in these two, see the cont. This first one is contribution due to the pressure; second one 8 kilojoules per mol is the contribution due to the temperature and obviously, the effect of pressure is 300 kilojoules per mol effect of temperature is 8 kilojoule per mol. So, that is why this comment is made that the effect of pressure dominates and this is the thermodynamic reason why materials change their forms at greater depths in the earths interior.

Now, how about for gases? As we discussed earlier, obviously the effect of pressure on Gibbs free energy is expected to be larger for the gases because the volume of the gas is more than the volume of a substance in its liquid or in its solid form. Thus, as we discussed earlier that G at a final pressure is equal to G at initial pressure plus P i to p f V d p and if this volume does depend upon pressure, we need to substitute, we need to put here the pressure dependence of volume and that we can conveniently discuss for an ideal gas because we know the ideal gas equation.

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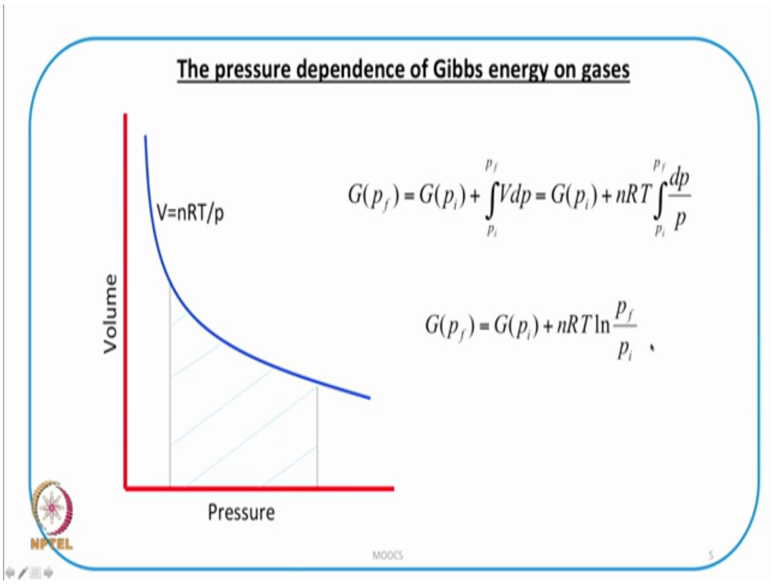

The pressure dependence of Gibbs energy on gases

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp = G(p_i) + nRT\int_{p_i}^{p_f} \frac{dp}{p}$$

$$G(p_f) = G(p_i) + nRT\ln\frac{p_f}{p_i}$$

We can go back to the slide for the volume. If i put V is equal to n R T by p, then I end up this equation and if you go a step further, then Gibbs free energy at a final pressure is equal to Gibbs free energy at initial pressure plus n R T log p final over the p initial. This is one way. Other is we just plot V against p and for an ideal gas you know V against p will it turn out to be something like that and then, within the limits P i to p f, the area under the curve should give us the value of the integral and hence, should give us a the pressure dependence of Gibbs free energy.

So, thus the pressure dependence of Gibbs free energy can be easily understood from this type of relation that is G at p f is equal to G at P i plus n R T log p f by P i. However, this equation is strictly applicable to ideal gases to perfect gases. So, what we have discussed so far on the properties of Gibbs function is that the temperature dependence and pressure dependence of Gibbs energies give a lot of information and I have mentioned this again and again that knowledge about the changes in Gibbs free energy or Gibbs function is extremely important because routinely we connect the criteria of spontaneity, feasibility of the process whether the reaction will take place or not directly with the values of delta G at constant temperature and pressure. So, not only qualitatively, but quantitatively the temperature dependence of Gibbs energy or pressure dependence of Gibbs energy gives a lot of information.

Now, I will switch over to another extremely important concept which is again based on the Gibbs free energy and that is the chemical potential. As we will see later on that chemical potential is central when we come to discussion on equilibrium. One can talk about the changes in Gibbs free energy, but we will see that it makes much more sense and it is very useful when we talk about the changes in chemical potential especially when we discussed equilibrium or equilibrium constants. What is chemical potentia? How it is connected to Gibbs free energy?

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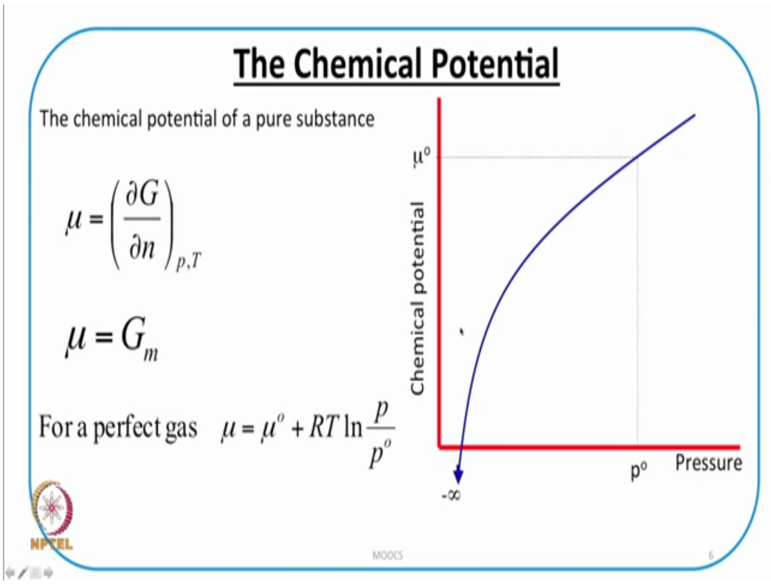

The Chemical Potential

The chemical potential of a pure substance

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{p,T}$$

$$\mu = G_m$$

For a perfect gas $\mu = \mu^o + RT\ln\frac{p}{p^o}$

Mathematically chemical potential of a pure substance is defined by dou G by dou n at constant pressure and temperature, the symbol used for chemical potential is mu and please remember that this expression is chemical potential of a pure substance which is how much is the change in Gibbs energy upon addition of 1 mol of that substance. So, it is a change in Gibbs free energy when 1 mol of a pure substance is added.

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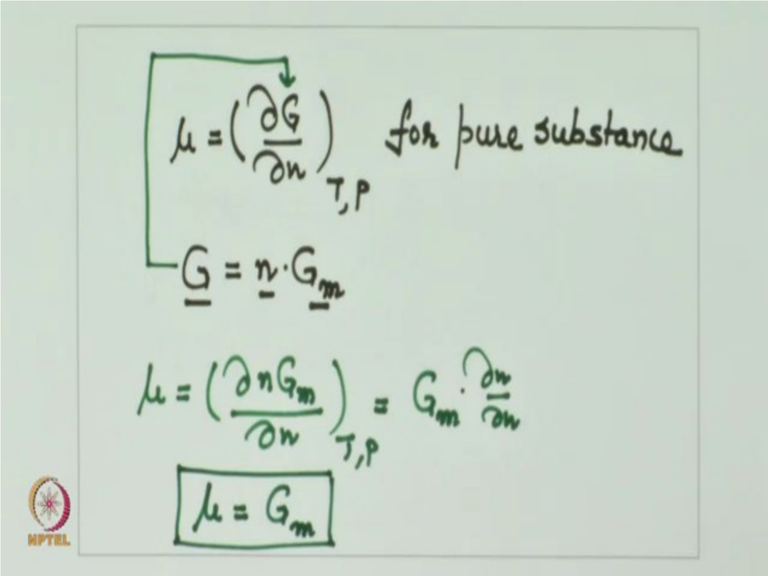

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P}$$ for pure substance

$$\underline{G} = \underline{n} \cdot \underline{G_m}$$

$$\mu = \left(\frac{\partial nG_m}{\partial n}\right)_{T,P} = G_m \cdot \frac{\partial n}{\partial n}$$

$$\boxed{\mu = G_m}$$

Let us try to get some more meaning out of it. We are talking here about mu 4 is equal to dou G by dou n at constant temperature and pressure, however this is for pure substance, Gibbs free energy. Gibbs energy I can connect with the molar Gibbs energy. By this expression, the total Gibbs energy is equal to number of moles times the molar Gibbs energy. Throughout we have resolved this symbol m subscript m to describe a property as a molar property. Now, if I substitute this G over here, what do I get is mu is equal to dou n times G m dou n at constant temperature and pressure molar Gibbs energy is a constant quantity into I have dou n by dou n. So, the answer that I get is mu is equal to G m for a pure substance. For a pure substance wherever the chemical potential appears, I can conveniently in place of chemical potential, I can also write the molar Gibbs function. Let us keep this in mind.

Now, I would like to derive this expression which is the definition of chemical potential for a perfect gas. If we are asked how do we write the chemical potential of a perfect gas, the answer will be mu is equal to mu naught plus R T log p by p naught and you remember that mu naught naught. This is standard state and standard state of a substance means the substance has to be pure. The temperature can be any, but pressure has to be 1 bar. That means, p naught here is 1 bar. How do we get this?

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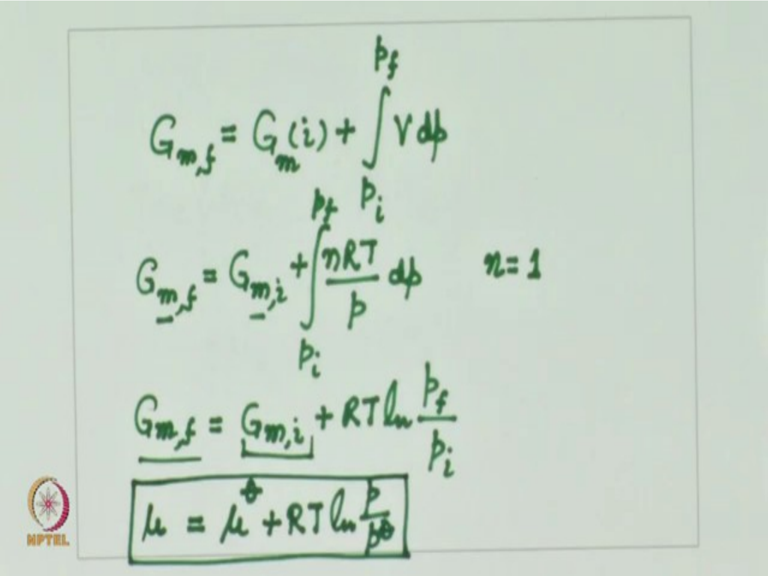

$$G_{m,f} = G_m(i) + \int_{p_i}^{p_f} V\,dp$$

$$G_{\underline{m},f} = G_{\underline{m},i} + \int_{p_i}^{p_f} \frac{nRT}{p}\,dp \qquad n = 1$$

$$\underline{G_{m,f}} = \underline{G_{m,i}} + RT\ln\frac{p_f}{p_i}$$

$$\boxed{\mu = \mu^{\ominus} + RT\ln\frac{p}{p^{\ominus}}}$$

We go back to the same equation that we derived a while ago that is G molar final is equal to G molar initial plus integration P i to p f V d p.

Let me write another line G molar final is equal to G molar initial plus instead of v, let me write n R T by p d p from P i to p f and obviously, n is equal to 1 here because we are talking about the molar properties. Let us rewrite now G m final is equal to G m initial plus R T log p final by p initial n is equal to 1 because we are talking about 1 mol. If I choose the initial state to be a standard state since we are talking about the pure substance, then we just discussed that instead of molar Gibbs function, I can write mu and if I choose the initial state to be a standard state, I will writing for G m.

I will write mu naught plus lets retain R T log p by p naught because initial pressure, the initial state is the standard state and this is the definition of chemical potential of a perfect gas and that is what is written over here. For a perfect gas, the chemical potential will be written as mu is equal to mu naught plus R T log p by p naught. Please make a note over here that this ratio is the dimensionless quantity because this p naught is equal to 1 bar and that will take care of the units of the pressure in the numerator.

When you plot chemical potential against pressure, the resulting dependence is like this. Obviously, if you look at this equation as the pressure increases, although it is a logarithmic term, the chemical potential has to go up with increase in pressure and that is what you see the dependence is like this. However, when the pressure approaches zero from this expression, log zero, the value of chemical potential will approach minus infinity. So, you must remember the pressure dependence of chemical potential looks like this and this is for ideal gas and later on when we start discussing the deviations from ideality, when we start discussing the real gases, then the chemical potential dependence on pressure will be little different from this at lower pressure region and higher pressure region and that will carry a lot of meaning, but as of now let us be very clear about the definition of chemical potential for a perfect gas and the definition of chemical potential for a pure substance. This will help us understanding when we make a switchover from the ideal system to non ideal system.

So, I hope that the pressure dependence of Gibbs free energy is very clear to you and also, that a lot of information comes out when we look at the different results will which come out while discussing the pressure dependence of Gibbs free energy and you know one of such a result is the introduction of chemical potential, and as I said chemical potential is central when it comes to the discussion of equilibrium and the whole equilibrium process when we discuss equilibrium constant will be discussed in terms of chemical potential.

Thank you very much.