Chemical and Biological Thermodynamics: Principles to Applications

Prof. Nand Kishore
Department of Chemistry and Biochemistry
Indian Institute of Technology, Bombay

Lecture - 32
Tutorial - 2
Equilibrium constant

Keeping in mind the significance of the equilibrium and equilibrium constant; we will discuss few more numerical problems so that this concept becomes very very clear.

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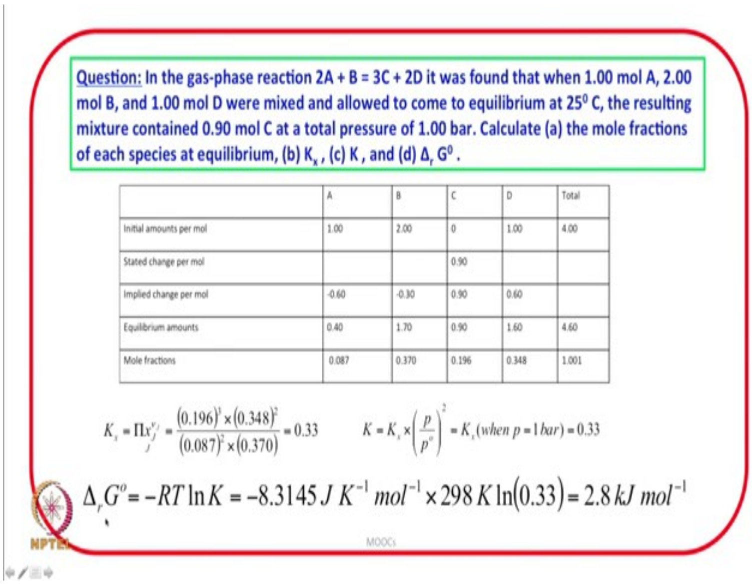

Question: In the gas-phase reaction 2A + B = 3C + 2D it was found that when 1.00 mol A, 2.00 mol B, and 1.00 mol D were mixed and allowed to come to equilibrium at 25^0 C, the resulting mixture contained 0.90 mol C at a total pressure of 1.00 bar. Calculate (a) the mole fractions of each species at equilibrium, (b) K_x, (c) K, and (d) $\Delta_r G^0$.

	A	B	C	D	Total
Initial amounts per mol	1.00	2.00	0	1.00	4.00
Stated change per mol			0.90		
Implied change per mol	-0.60	-0.30	0.90	0.60	
Equilibrium amounts	0.40	1.70	0.90	1.60	4.60
Mole fractions	0.087	0.370	0.196	0.348	1.001

$$K_x = \prod_j x_j^{\nu_j} = \frac{(0.196)^3 \times (0.348)^2}{(0.087)^2 \times (0.370)} = 0.33 \qquad K = K_x \times \left(\frac{p}{p^o}\right)^2 = K_x (when\ p = 1\ bar) = 0.33$$

$$\Delta_r G^o = -RT \ln K = -8.3145\ J\ K^{-1}\ mol^{-1} \times 298\ K \ln(0.33) = 2.8\ kJ\ mol^{-1}$$

Now, let us take another question the question is in the gas phase reaction 2 A plus B going to 3 C plus 2 D; it was found that when 1 mole of A; 2 mole of B and 1 mole of D were mixed and allowed to come to equilibrium at 25 degree Celsius, the resulting mixture contained 0.9 mole of C, at a total pressure of 1 bar. Calculate the mole fractions of each species at equilibrium; the value of K X the value of K and delta R G naught.

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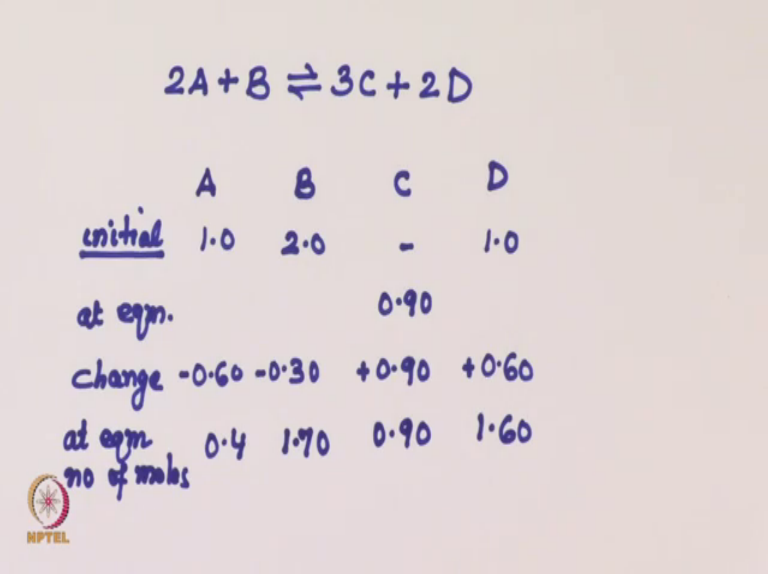

$2A + B \rightleftharpoons 3C + 2D$

	A	B	C	D
initial	1.0	2.0	-	1.0
at eqm.			0.90	
change	-0.60	-0.30	+0.90	+0.60
at eqm no of moles	0.4	1.70	0.90	1.60

Let us see how to approach this question; 2 A this is the chemical reaction; 2 A plus B in equilibrium with 3 C plus 2 D and the given information to us is that you are mixing 1 mole of A, 2 mole of B and 1 mole of D. You mix A, B and D and then you allow the reaction to come to an equilibrium and eventually when you are mixing A, B and D; C will be formed and the equilibrium at some point will be attained.

So, what we will do is; we will list A, B, C and D initial amounts; what are the initial amounts of A; 1.0, 2.0; initially C was nothing and D was 1.0 and then it is given that at equilibrium C was formed 0.9 mole of C were formed. So, if I write at equilibrium 0.9 moles of C were formed. So, what is the change if I calculate the change; how much will be the change for A?

If you look at here; 2 A forms 3 C; therefore, the amount of change in A will be equal to two third of the amount of change in C. Because 2 A is forming 3 C; therefore, the amount of change in A will be equal to two third of the amount changed in C. Since the amount changed in C is 0.9; two third of 0.9 is 0.6; that is two third of 0.9 and for B it is one third; one third is 0.30 and for C anyway the change is same because there was nothing in the beginning and for B also; two third of C is the change. Let me put negative and negative here; positive and positive here because these are reactants, this reactance are consumed and product is formed.

Therefore at equilibrium number of moles this will be 0.4, this will be 1.70, this will be 0.90, this will be 1.60. So, I hope this calculations are very clear; it is very important to understand how we arrived at this numbers. Now, let us go back to the slide and look at the table; we have calculated the equilibrium amounts in terms of number of moles A is 0.4, B is 1.7, C is 0.9 and D is 1.6; the total addition of all this is 4.6.

And once I know the equilibrium amount and total number of moles, I can calculate mole fraction because mole fraction will be the number of moles divided by the total number of moles; that is 0.4 divided by 4.6 will come out to be 0.087 in this case; 1.7 divided by 4.6 will be 0.37 in this case, 0.9 divided by 4.6 is going to be 0.196 and 160 divided by 4.6 is going to be 0.348 and of course, when you are add all the mole fractions this has to come to 1.

So, we have calculated the mole fractions at equilibrium and immediately we can calculate K X; K X will be equal to mole fraction of C raised to the power 3 into mole fraction of D raised to the power 2 divided by mole fraction of A square into mole fraction of B and once you substitute these numbers, we get a value of 0.33; K X we have been able to get 0.33.

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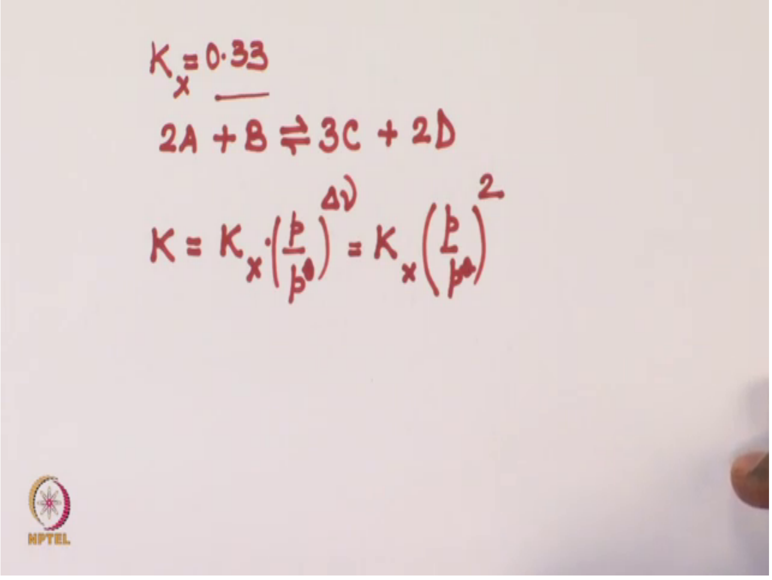

If we have K X is equal to 0.33 and the reaction is 2 A plus B in equilibrium with 3 C plus 2 D and we just in the previous lecture, we derived this equation K is equal to K X into p by p naught raised to the power delta nu. And can I write this as K X into p by p naught raised to the power delta nu will be 3 plus 2 is 5; 5 minus 3 is equal to 2.

Now, if I know the total pressure at equilibrium and I know the value of K X; I can get the value of K; K X is known and if p is 1 bar then K is equal to K X and this is the condition which is given to us. Let us go back to the slide, we derive this in the previous lecture and we just discuss that when p total pressure is 1 bar; p naught is anyway 1 bar; K will be equal to K X therefore, the value of K comes out to be 0.33.

If we know K now immediately we will be able to calculate the standard reaction Gibbs energy; delta R G naught delta R G naught is minus RT log K. You substitute the value of R in appropriate units the value of T and log K; we get overall value 2.8 kilojoules per mole; delta R g naught at this composition that is delta R G naught; actually this is the standard reaction Gibbs energy turns out to be positive in this case. Because the K value is less than 1; that is why delta R G naught turns out to be positive.

So, this question describes that how you can make use of the information on just the amount of one of the reactants or one of the products to calculate the amount of the other species present at equilibrium. And once you know the amount of each species present at equilibrium, then you also know the total amount you can calculate the mole fractions and from the mole fractions one can calculate K X and once you have K X and the total pressure information; you can calculate the value of K.

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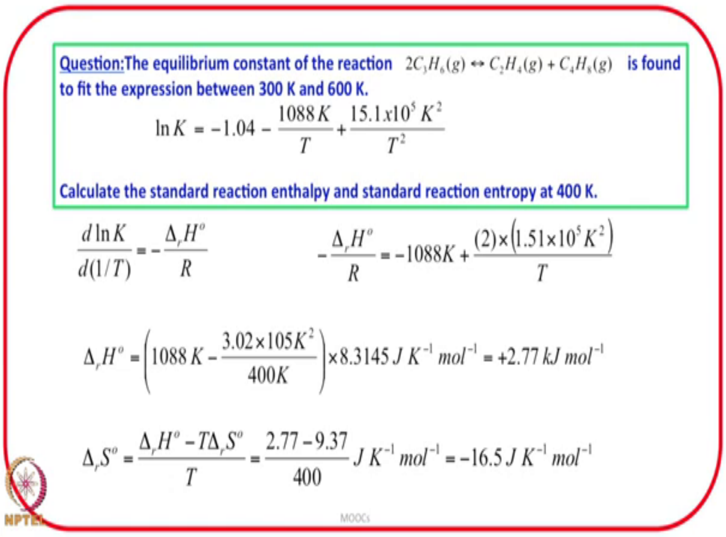

Question: The equilibrium constant of the reaction $2C_3H_6(g) \leftrightarrow C_2H_4(g) + C_4H_8(g)$ is found to fit the expression between 300 K and 600 K.

$$\ln K = -1.04 - \frac{1088\,K}{T} + \frac{15.1x10^5\,K^2}{T^2}$$

Calculate the standard reaction enthalpy and standard reaction entropy at 400 K.

$$\frac{d\ln K}{d(1/T)} = -\frac{\Delta_r H^o}{R}$$

$$-\frac{\Delta_r H^o}{R} = -1088K + \frac{(2)\times\left(1.51\times10^5 K^2\right)}{T}$$

$$\Delta_r H^o = \left(1088\,K - \frac{3.02\times105K^2}{400K}\right)\times 8.3145\,J\,K^{-1}\,mol^{-1} = +2.77\,kJ\,mol^{-1}$$

$$\Delta_r S^o = \frac{\Delta_r H^o - T\Delta_r S^o}{T} = \frac{2.77-9.37}{400}\,J\,K^{-1}\,mol^{-1} = -16.5\,J\,K^{-1}\,mol^{-1}$$

Let us take another question now; the question is the equilibrium constant of the reaction to C 3; H 6 gas forming C 2; H 4 gas plus C 4; H 8 gas is found to fit the expression between 300 K and 600 K; log K is equal to minus 1.04 minus 1088 by T in Kelvin plus 15.1 into 10 is to the power 5 by T square in Kelvin square. Calculate the standard reaction enthalpy and standard reaction entropy.

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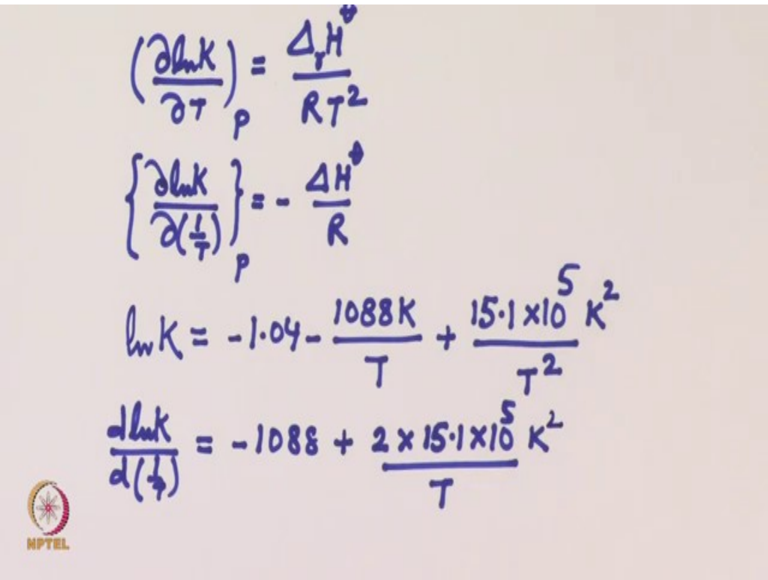

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta_r H^\ominus}{RT^2}$$

$$\left\{\frac{\partial \ln K}{\partial (\frac{1}{T})}\right\}_p = -\frac{\Delta H^\ominus}{R}$$

$$\ln K = -1.04 - \frac{1088K}{T} + \frac{15.1 \times 10^5 K^2}{T^2}$$

$$\frac{d \ln K}{d(\frac{1}{T})} = -1088 + \frac{2 \times 15.1 \times 10^5 K^2}{T}$$

This question again describes the effect of temperature on equilibrium constant and Van T Hoff equation is a very useful equation in dealing with such questions; Van T Hoff equation is D log K by D T; at constant pressure is equal to delta R H naught by R T square. Another form of this equation I can write 2 log K; 1 by T instead of T; let me write 1 by T at constant pressure, it will be minus delta H naught by R.

Because D 1 by T is minus 1 T square and eventually that will then convert into this form of the equation. Why I have done why I have transformed into derivative with respect to 1 by T is because the given information to me is log K is equal to minus 1.04, minus 1088 Kelvin divided by temperature plus 15.1 into 10 raised to the power 5; K square these are K Kelvin is introduced to get rid of the unit is T square what I have is team the denominator that is why if I differentiate with respect to 1by T; it will be easy.

Now, let us differentiate this with respect to 1 by T D log K D; 1 by T what will I get? this is 0 and the next one is minus 1088 because D 1 by T of T is going to be 1 and here it is 1 by T square, it will be 2 into 15.1 into 10 raised to the power of 5 divided by T; this is what I am going to get, when I differentiate with respect to 1 by T.

Let us and of course, it will be Kelvin; let us go back to the slide; what I have discussed is that D log K by D 1 by T is minus 1088 plus 2 into 15.1 into 10 raised to the power 5 by T into K. So, once I substitute the numbers and let us see go to the slide and what do I get. I get; let me just correct over here D log K D 1 by T minus 1088 plus 2 into 15.1 into 10 raised to power 5 by T and this T is in Kelvin.

We will put the information over here look at the slide; once you substitute the number the standard reaction enthalpy comes out to be plus 2.77 kilojoules per mole. Once I have standard reaction enthalpy; I can calculate standard reaction entropy from delta G naught is equal to delta H naught minus T delta; S naught and once I use that and write look at the slide delta R; S naught is equal to delta R; H naught minus T R delta S naught divided by T.

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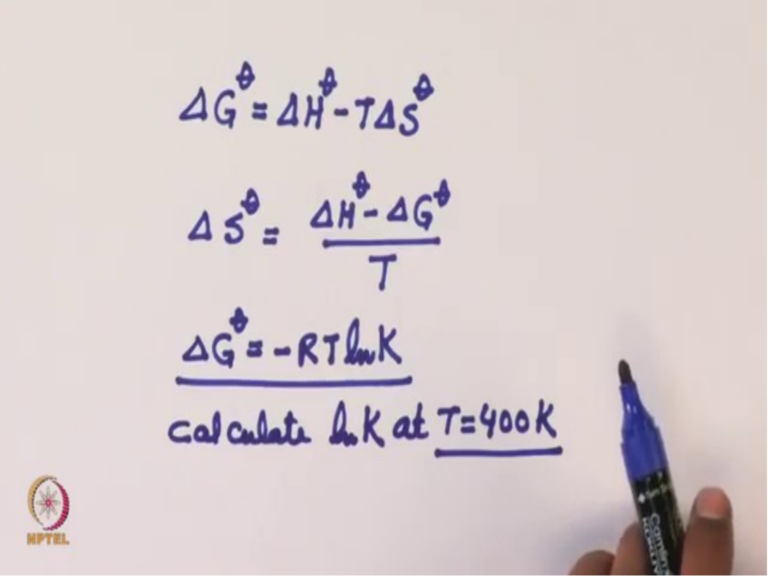

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

$$\Delta S^{\ominus} = \frac{\Delta H^{\ominus} - \Delta G^{\ominus}}{T}$$

$$\underline{\Delta G^{\ominus} = -RT \ln K}$$

calculate $\ln K$ at $\underline{T = 400\,K}$

This I am getting from delta G naught is equal to delta H naught minus T delta; S naught and you rearrange this delta S naught will be equal to delta H naught minus delta G naught divided by T.

And if we look at the slide then after you substitute the numbers; we will get a value of delta S naught is equal to; delta G naught can be calculated from minus R T log K and we have been given the expression for log K. Once you calculate the log K at a given temperature; so; what you do is calculate log K at T is equal to 400 Kelvin.

Hence that information we can substitute over here; once you substitute over there what I will have is delta R S naught is equal to; delta H naught we just calculated is 2.77.

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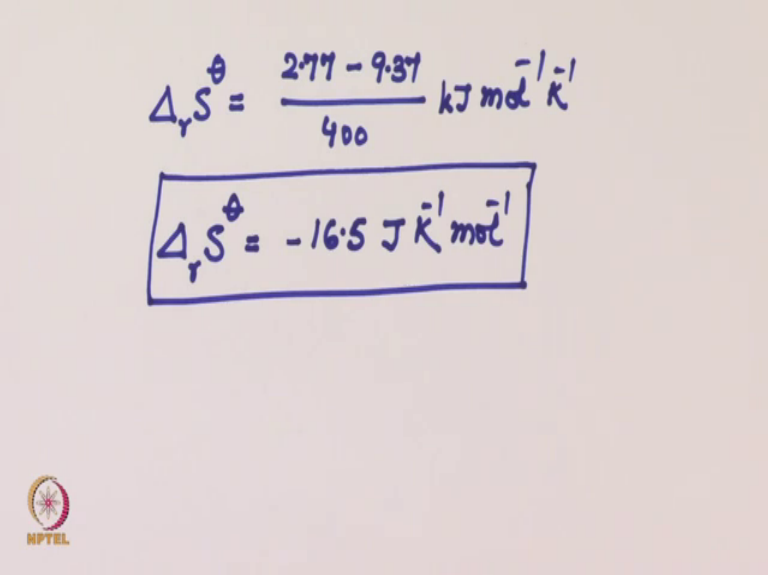

$$\Delta_r S^\ominus = \frac{2.77 - 9.37}{400} \text{ kJ mol}^{-1} \text{K}^{-1}$$

$$\boxed{\Delta_r S^\ominus = -16.5 \text{ J K}^{-1} \text{mol}^{-1}}$$

And delta G naught from minus R T log K will come out to be 9.37 these are all in kilojoules per mole; divided by 400 and this is in kilojoules per mole. Once you solve this; this number will come out to be minus 16.5 and convert into joules; of course, there will be Kelvin here, per Kelvin per mole, we get the reaction entropy also.

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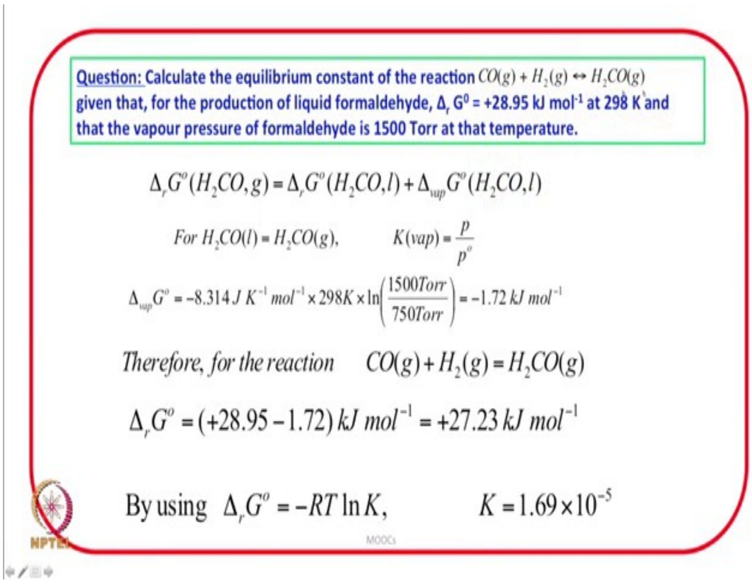

Question: Calculate the equilibrium constant of the reaction $CO(g) + H_2(g) \leftrightarrow H_2CO(g)$ given that, for the production of liquid formaldehyde, $\Delta_r G^0 = +28.95$ kJ mol^{-1} at 298 K and that the vapour pressure of formaldehyde is 1500 Torr at that temperature.

$$\Delta_r G^o(H_2CO,g) = \Delta_r G^o(H_2CO,l) + \Delta_{vap} G^o(H_2CO,l)$$

$$For\ H_2CO(l) = H_2CO(g), \qquad K(vap) = \frac{p}{p^o}$$

$$\Delta_{vap} G^o = -8.314\, J\, K^{-1}\, mol^{-1} \times 298K \times \ln\left(\frac{1500 Torr}{750 Torr}\right) = -1.72\, kJ\, mol^{-1}$$

$$Therefore,\ for\ the\ reaction \quad CO(g) + H_2(g) = H_2CO(g)$$

$$\Delta_r G^o = (+28.95 - 1.72)\, kJ\, mol^{-1} = +27.23\, kJ\, mol^{-1}$$

By using $\Delta_r G^o = -RT \ln K$, $\qquad K = 1.69 \times 10^{-5}$

Now, we take up another question calculate the equilibrium constant of the reaction carbon monoxide gas plus hydrogen forming H 2 CO; given that for the production of liquid formaldehyde, the standard reaction Gibbs energy is 28.95 kilojoules per mole; at 298 Kelvin and that the vapour pressure of formaldehyde 1500 torr at that temperature; How to solve this kind of question?

We have been given the information on the standard Gibbs energy of production of liquid formaldehyde and we have been actually asked to find out the equilibrium constant for the formation of gaseous formaldehyde. So, we will make use of this expression; let us take a look at the standard Gibbs energy of formation of gaseous formaldehyde will be equal to the standard Gibbs energy of formation of liquid formaldehyde; plus the standard Gibbs energy of vaporization because the liquid has to be formed convert to vapour of the formaldehyde.

Once again the standard Gibbs energy change for the formation of gaseous formaldehyde will be equal to; the standard Gibbs energy of reaction corresponding to the liquid formaldehyde plus the corresponding standard Gibbs energy change for the vaporization. And this is the vaporization process H 2 COL form in H 2 CO gaseous form and for this the equilibrium constant, we can immediately right as p by p naught. We have been discussing for a long time how to write the equilibrium constant; p is the pressure of H 2 CO and p naught is 1 bar and once we know; we can immediately substitute this information into delta G naught is equal to minus R T log K; p is 1500 torr and p naught is 750 torr; in terms of torr.

And once I calculate the number comes out to minus 1.72 kilojoules per mole. Therefore, for the reaction carbon monoxide plus hydrogen forming H 2 CO gas; we use again go back this; we use this equation and substitute the numbers the standard Gibbs energy for H two CO liquid is 28.95 given and the standard Gibbs energy change for the corresponding vaporization process is minus 1.72 kilojoules per mole; does the overall reaction Gibbs energy for the asked reaction turns out to be plus 27.23 kilojoules per mole.

And once I know the standard reaction Gibbs energy, I can immediately calculate the value of equilibrium constant by substituting the equilibrium constant into delta R G naught is equal to minus R T; log K and K turns out to be 1.69 into 10 raised to the power minus 5.

So, note the tricks used in solving this kind of question; initially we were asked to find out the equilibrium constant for this reaction formation of gaseous formaldehyde and the given information to us is the standard Gibbs energy for the production of liquid formaldehyde; that means, we must then add the thermodynamic quantity corresponding to the vaporization process; that is why we wrote this equation that the standard Gibbs energy change for the production of H 2 CO G will be equal to the corresponding standard Gibbs energy for the production of liquid formaldehyde and somehow we calculate the delta G naught for the vaporization.

Vaporization reaction all of us very clearly understand, it is liquid conversion to vapour and then we made use of the value of equilibrium constant to get the value of delta G naught and used all this kind of information to get the standard Gibbs energy change for the given reaction and once we had the information on standard Gibbs energy change, we were able to calculate the value of equilibrium constant.

So, what we notice here is that equilibrium constant depends upon the temperature and it will depend upon the temperature; only if the standard enthalpy of the reaction is a non-zero number and then if it is a non-zero; the equilibrium constant might increase or it might decrease with rise in temperature depending upon whether the process is exothermic or the process is endothermic.

And you might have noticed that while solving many of or some of these questions, we made use of state properties. The properties of state functions, so therefore when we are trying to optimise a process in industry; it is very important to understand the thermodynamics of the process. Because the thermodynamic parameters accompanying the reaction, accompanying the process; it gives us direction, it gives us guidelines to optimise the process so that the given plant gives a maximum yield of the product.

So, I hope that these questions helped in understanding further about how to improve the value of K and how the external factors affect the value of K and if the value of K is not affected; how it affects the equilibrium composition.

Thank you very much.