

Fundamentals of Statistical Thermodynamics

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Lecture: 50

Contributions to equilibrium constant (continued)

Let us continue our discussion on contributions to equilibrium constant. In the previous lecture, we discussed how to get an expression for the number of molecules in the products or in the reactants. Reaction that we are talking about is R reactants in equilibrium with products and we have come up with an expression something like this. So, our main aim is to get N_P divided by N_R . Now number of products and number of reactant molecules. Our system was like this, this was for reactants and this was for products and this difference is ΔE_0 . This is what we are talking about and then we have various energy levels all this and that these also has various energy levels and we are talking about their distribution. So, let us talk about $\sum_i n_i$ for reactants. This I am talking about for reactants. This is equal to number of moles of reactants. Remember, I am talking about reactants and this is equal to N by Q into summation. Let me put R because I am talking about reactants. I will just put R for reactants exponential minus βE . I am just putting R. You can put small r capital R whatever.

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$$\text{Reactants } \sum_i n_i = N_R = \frac{N}{q} \left(\sum_r e^{-\beta \epsilon_r} \right) \quad \underline{\epsilon_r}$$

$$N_R = \frac{N}{q} \cdot q(R) \quad \dots (i)$$

$$\text{Products } \sum_i n_i = N_P = \frac{N}{q} \cdot \sum_p e^{-\beta \epsilon'_p}$$

$$N_P = \frac{N}{q} \cdot \sum_p e^{-\beta(\epsilon_p + \Delta \epsilon_0)} = \frac{N}{q} \left(\sum_r e^{-\beta \epsilon_r} \right) e^{-\beta \Delta \epsilon_0} = \frac{N}{q} \cdot q(P) \cdot e^{-\beta \Delta \epsilon_0}$$

$$K = \frac{N_P}{N_R} = \frac{q_P}{q_R} \times e^{-\Delta_r E^0/RT}$$

What are these ϵ_r ? This energy ϵ_r or you can read this as ϵ_r whatever way you say or I am reserving for reactants. So, that means when I talk about this and I measure the energy of any of the level of reactants that is with reference to the zero-point energy of the reactants. This one gives me N_R is equal to N by q into this one is nothing, but the partition function when you only consider the reactant molecules. What we have here? We have this N is the total number of molecules which are combined in the combined reactants and product sector. This is the combined for the combined system the molecular partition function. This is the molecular partition function which is only applicable to the molecules which are in the reactant side. Let us mark this as our equation number 1. Now, let us come towards the product side. Now let us talk about products. That means here I will use the same expression n_i . Now I will change to product is equal to N product and this is equal to N upon q into I am writing for product exponential minus $\beta \epsilon'_p$. Notice that I have put prime over here. I did not put prime over here. There is a reason why I did not put prime over there and I am putting prime over here. The reason for that is when you look at the products the zero-point energy level of product is above the zero-point energy of the reactants by ΔE° and these energy levels are with reference to this zero-point energy level.

Once again these energy levels of the products are with reference to the zero-point energy of the product which is shown over here. So that means when I consider the combined

system this E'_p is equal to E_p plus $\Delta E(0)$ because for the combined system the zero-point energy level is at this R level. Let us relook at what we should write now N_p is equal to N upon q into summation for products exponential minus β that is what I am saying E_p plus $\Delta E(0)$ which is equal to N by q into exponential of course, summation p minus βE_p into exponential minus $\beta \Delta E(0)$ and this is equal to N upon q and if you recognize this, this is Q of the products into exponential minus $\beta \Delta E^\circ$. We have this expression for N_p and we have this expression for N_R . Now you can take the ratio k is equal to N_p by N_R .

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$$N_R = \frac{N}{q} \sum_i e^{-\beta E_{R,i}} = \frac{N}{q} q(R)$$

$$N_P = \frac{N}{q} \sum_i e^{-\beta E_{P,i}} = \frac{N}{q} \sum_i e^{-\beta(E_{R,i} + \Delta E_0)} = \frac{N}{q} e^{-\beta \Delta E_0} \sum_i e^{-\beta E_{R,i}} = \frac{N}{q} q(R) e^{-\beta \Delta E_0}$$

$$K = \frac{N_P}{N_R} = \frac{q_P}{q_R} \times e^{-\Delta_r E^\circ / RT}$$

Diagram: Energy levels for reactants (R) and products (P). The zero-point energy level for products is higher than for reactants by ΔE_0 .

So, N by Q N by q will cancel out you have q_p by q_R into exponential minus $\beta \Delta E^\circ$. I will elaborate on this $\beta \Delta E^\circ$ is equal to ΔE° by $k T$ and if I want to express per mole then I will multiply by N_A . So, k times N_A will become R if I am expressing per molecule ΔE° by $k T$ is enough and if I am expressing per mole then I will multiply a numerator and denominator by N_A . So, then this per molecule energy will become per mole and k will become R . So, what we have done is by the arguments of the number of molecules which are occupying the energy levels corresponding to reactants and the number of molecules which are occupying the energy level corresponding to product we have come up with an

expression which is same as that we get from the derived expression.

But what is the key result of this and what are the key points that we should remember? One is that the value of k is dependent upon N_p and N_R and we have discussed that N_p or N_R is going to depend upon the population of each state. When I talk about population of each state that means we are talking about entropy and when I am talking about what is lying about what? Where product is lying about reactants 0 their 0-point energies are separated with a positive number that means we are talking about an endothermic reaction. So, basically k which decides ΔG° ΔG° is minus $RT \log k$ it incorporates what we derived what we discussed in chemical thermodynamics that ΔG° is a combination of ΔH° and ΔS° . Let us now take a very specialized specific example in that example let us consider that the reactant has only one ground state available the other upper excited states are so far apart and the product has a uniform ladder of energy levels. The system that we are discussing here is R in equilibrium with B we have reactants which has only one ground state available that means can I write q^R which is equal to summation generally we write like this $\sum_j g_j \exp(-\beta E_j)$ only ground state is there degeneracy is 1 that means the value is equal to 1 because $E(0) = E$ for J is equal to 0 the energy level is 0 therefore, $\exp(0)$ is equal to 1 for q reactant we know, but for product what is given to us that it has a large number of evenly closed spaced levels.

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$R \rightleftharpoons P$

Consider that R has only a single accessible level, which implies that $q_R = 1$

Also consider that P has a large number of evenly, closely spaced levels

$$q^R = \sum_j g_j e^{-\beta E_j} = 1$$

$$q^P = \sum_j e^{-\beta E_j} \quad E_j = jE$$

$$q^P = 1 + e^{-\beta E} + (e^{-\beta E})^2 + \dots$$

$$q^P = \frac{1}{1 - e^{-\beta E}}$$

Careful examination says that this is a uniform ladder of energy levels that means when I talk about Q_p is equal to summation J exponential minus βE_j there here E_j is equal to J times E because this each energy level is separated by E and J can start from 1 to 0 1 2 etcetera because the 0 of this is lying above that of reactant by ΔE (0). We have already derived this expression we are not going to get into the details of that q_p this is a uniform ladder of energy levels which is 1 plus exponential minus βE plus exponential minus βE exponential minus βE square plus so on sum of a G_p that means my q product is equal to 1 over 1 minus exponential minus βE we have derived this kind of expression earlier. I have an expression for q products and I have an expression for q reaction do not worry get confused by this rotation this actually means q reactant and this actually means q of product and we know their difference in 0 point energy levels is ΔE° and since I have both these q 's and I know ΔE° now I can write an expression for the equilibrium constant what is that equilibrium constant it is equilibrium constant will be equilibrium constant will be equal to q_p over q_r into exponential minus ΔE° by $R T$. We have just discussed that q reactant is equal to 1 we have also discussed that q product is equal to 1 over 1 minus exponential minus βE . Now suppose if the temperature is high or if energy levels are very very very close compared to this temperature this spacing is very small or the temperature is

high then I can write q_p is equal to 1 over 1 minus I can since this is going to be small if temperature is high then 1 minus βE plus so on.

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Consider that R has only a single accessible level, which implies that $q_R = 1$

Also consider that P has a large number of evenly, closely spaced levels

$$K = \frac{q(P)}{q(R)} e^{-\Delta E_0 / RT} ; \quad q(R) = 1$$

High temp $q(P) = \frac{1}{1 - (1 - \beta E + \dots)} = \frac{1}{\beta E} = \frac{kT}{E}$

$$K = \frac{kT}{E} \times e^{-\Delta E_0 / RT}$$

This we have discussed earlier this is equal to 1 upon βE or is equal to kT upon E this is a high temperature result we have q_p we have q_R substitute in this q_p is kT upon E so here we have kT upon E q_R is 1 so do not need to worry into exponential minus ΔE° by RT . For this specific example the expression for equilibrium constant is kT by E into exponential minus ΔE° by RT . Ok we have derived some expression is this expression telling us anything qualitatively or quantitatively well this particular expression only applies to the given condition. If the system given to you if the system changes remember that the corresponding expressions final expressions are also going to change. This particular expression which applies to this system now let us see what qualitative information we can derive from it.

In industry how to optimize a process so that you get a higher value of equilibrium constant or a higher value of yield is very very important. Now how to improve the value of equilibrium constant how to increase the value of equilibrium constant or how to decrease the value of equilibrium an equally valid question will depend upon various factors.

Number one is the reaction exothermic or endothermic number two what is the stoichiometry of the reaction that is the value of Δn_g we are talking about gas phase reaction. The exothermicity of the reaction endothermicity of the reaction is going to guide us whether the temperature should be increased or temperature should be lowered. Similarly, the reaction is going to be increased the number of moles participating in the reactants and the product will also tell us whether the pressure should be increased or pressure should be decreased.

And accordingly suppose if the reaction is endothermic, you remember Le Chatelier principle. What is Le Chatelier principle Le Chatelier principle is that if a reaction at equilibrium is disturbed by an external factor then the reaction will shift in such a direction so as to undo the effect of the externally applied disturbance. For an endothermic reaction according to Le Chatelier principle if you increase the temperature the value of equilibrium constant also increases. For an exothermic reaction on the other hand earlier I talked about endothermic reaction that is increase in temperature will increase the value of equilibrium constant. For an exothermic reaction an increase in temperature leads to reduction in the value of equilibrium constant.

Similarly, you can talk about the effect of pressure total pressure is increased at equilibrium then also the reaction composition at equilibrium will shift according to Le Chatelier principle. That means, it will move towards the direction where the pressure is lower. The Le Chatelier principle should also be applicable over here that means, the discussion that we had should also be extendable to alteration in temperature and alteration in pressure. The treatment that we are covering over here here in the expressions for example, if you look at the expression for the equilibrium constant it has Boltzmann constant, it has absolute temperature, it has energy that energy is the spacing between the adjacent energy levels of the product, it has gas constant it has temperature and it has the difference in the zero-point energy levels. So, we should be able to address the effect of temperature over here. Obviously, when you are going to alter the temperature the population of the states here corresponding to p is going to change. What is the prediction here? This one where the zero-point energy level of the product is higher than the zero-point energy level of the reactant that means, we are talking about an endothermic process. If I increase suppose the reactant has some population and if I increase the temperature then the population of upper

states is going to increase. If the population of upper states that is the products is going to increase that is going to raise the value of equilibrium constant, but is the same answer we can get from this expression that we can try to obtain by comparing this factor versus this factor. The increase in temperature or the decrease in temperature is going to lead to what? Before I start discussing that I want to reiterate that in statistical thermodynamics what we have discussed is discussed equilibrium constant in terms of population of lower states.

Different energy levels when I talk about population of different energy levels that means, I am also simultaneously addressing the entropy and if at the same time I am talking about the $\Delta E(0)$ this $\Delta E(0)$ which is the difference in the zero-point energy levels that means, here I am talking about exothermicity or endothermicity ok. So, if $\Delta E(0)$ is positive the situation looks like this if $\Delta E(0)$ is negative you should be able to redraw the similar figure if $\Delta E(0)$ is negative. We can address the exothermic reactions we can address the endothermic reactions. So, in the next lecture what we are going to discuss is that when we increase the temperature or when we decrease the temperature then which factor becomes dominant and in which direction the equilibrium constant will move. Once again obtaining an optimum value of equilibrium constant is very very important in this study and that is why the reaction conditions need to be modified so that you can achieve the desired results. Here by using the concept of statistical thermodynamics we are trying to explain that what is the effect of disturbance of external factors on the equilibrium constant. One such external factor that we are discussing at present is temperature. Therefore, the effect of temperature on any equilibrium becomes very important because depending upon exothermicity or endothermicity the value of equilibrium constant will become higher or lower. More qualitative and quantitative insights into equilibrium constants are still possible from the derived expressions, but those we will discuss in the next lecture.

Thank you very much. Thank you.