Fundamentals of Statistical Thermodynamics

Prof. Nand Kishore

Department of Chemistry

Indian Institute of Technology, Bombay

Lecture: 47

Relation between equilibrium constant K and partition function q (Applications-1)

Welcome back. We have been discussing equilibrium constant. Equilibrium constant which is a very important thermodynamic quantity because not only from an academic point of view, but from an industrial point of view, this thermodynamic quantity derives a lot of meaning. As discussed in the previous lecture, in industry it is important to have as much yield as possible and equilibrium constant is nothing, but the ratio of the activities of products divided by that of the reactants. And if activities are equal to concentrations, we generally write this as ratios of the concentrations weighted by their stoichiometric numbers. And then in industry we are also interested in knowing how to optimize various parameters, so that you can improve upon the value of equilibrium constant.

In statistical thermodynamics, we are interested in connecting equilibrium constant with the partition function, and that is what we have done in the previous lecture, where we connected equilibrium constant with molecular partition function by the expression which is given on this slide. Equilibrium constant is equal to the product of $q_{j,m}^0$ by N_A raised to the power stoichiometric number into exponential minus $\Delta R E^\circ$ by $R T$. We also discussed that suppose if we apply this to this kind of reaction A moles of A plus B moles of B in equilibrium with C moles of C, then how to write this K is the product of $q_{j,m}^0$ by N_A raised to the power ν raised to the power g into exponential minus $\Delta_r E^\circ$ by $R T$, which is the same expression that is written above. But what I will do is now I will put a positive number for the products and a negative stoichiometric number for the reactants.

See Slide time: 5:17

$$aA + bB \rightleftharpoons cC$$

$$K = \left\{ \prod_{J} \left(\frac{q^o_{j,m}}{N_A} \right)^{\nu_J} \right\} \times e^{-\Delta_r E_0/RT}$$

$$K = \prod_{J} \left(\frac{q^\theta_{J,m}}{N_A} \right)^{\nu_J} \times e^{-\Delta_r E_0/RT} = \left(\frac{q^\theta_{c,m}}{N_A} \right)^{c} \left(\frac{q^\theta_{A,m}}{N_A} \right)^{-a} \left(\frac{q^\theta_{B,m}}{N_A} \right)^{-b} \times e^{-\Delta E_0/RT}$$

$$K = \frac{\{q^\theta_{c,m}/N_A\}^c}{[q^\theta_{A,m}/N_A]^a \cdot [q^\theta_{B,m}/N_A]^b} \cdot e^{-\Delta E_0/RT}$$

So, how we expand it? Positive for the products, product is C that means $q^\circ_{j,m}$ by N_A, this will be raised to the power c into $q^\circ_{a,m}$ by N_A raised to the power minus a pay attention to this I am putting a negative sign because a is a reactant into $q^\circ_{b,m}$ by N_A raised to the power minus b again because b is a reactant then into exponential minus ΔE° by R T. This can further be written as K equal to now I will write this as q m by N_A raised to the power c divided by $q^\circ_{a,m}$ by N_A raised to the power a continuation into $q^\circ_{b,m}$ by N_A raised to the power b into exponential minus ΔE° by RT.

See Slide time: 10:57

Evaluate the equilibrium constant for the dissociation $Na_2(g) = 2Na(g)$ at 1000 K from the following data: Rotational constant = 0.1547 cm^{-1}; vibrational wavenumber = 159.2 cm^{-1}, zero point dissociation energy = 70.4 kJ mol^{-1}. The Na atoms have doublet ground terms.

Planck's constant $h = 6.626 \times 10^{-34} J s$
Boltzmann constant $k = 1.381 \times 10^{-23} J K^{-1}$

$$K = \left\{ \frac{\frac{q^2(Na)}{N_A^2}}{\frac{q(Na_2)}{N_A}} \right\} \times e^{-\Delta E_0/RT} = \frac{q^2(Na)}{q(Na_2)} \cdot \frac{1}{N_A} \cdot e^{-D_0/RT} = \frac{q^T(Na) \cdot g(Na)}{q^T(Na_2) \cdot q^R(Na_2) \cdot q^V(Na_2) \cdot g(Na_2)} \cdot \frac{1}{N_A}$$

$$K = \frac{kT q_X^2 \Lambda_{X_2}^3}{p^o g_{X_2} q_{X_2}^R q_{X_2}^V \Lambda_X^6} \times e^{-D_0/RT}$$

10:57 / 31:43

This is how we expand this product, that means it is a similar way of writing equilibrium constant as you have done in discussing chemical thermodynamics that is for the products you write in the numerator and for the reactants you write in the denominator and then there is an additional term which is an exponential term taking into account the difference in zero-point energy that has to come in this expression.

See Slide time: 16:12

$$Na_2 \rightleftharpoons 2Na$$

$$K = \frac{\{q^T(Na)\}^2 \cdot g(Na)}{q^T(Na_2) \cdot q^R(Na_2) \cdot q^V(Na_2) \cdot g(Na_2)} \cdot \frac{1}{N_A} \cdot e^{-D_0/RT}$$

$$K = \frac{\left\{\dfrac{V_m^\theta}{\Lambda^3(Na)}\right\}^2 g(Na)}{\left\{\dfrac{V_m^\theta}{\Lambda^3(Na_2)}\right\} \cdot q^R(Na_2) \cdot q^V(Na_2) \cdot g(Na_2)} \cdot \frac{1}{N_A} \cdot e^{-D_0/RT}$$

$$K = \left(\frac{V_m^\theta}{N_A}\right) \frac{\Lambda(Na_2)^3}{\Lambda(Na)^6} \cdot \frac{g(Na)}{g(Na_2)} \cdot \frac{1}{q^R(Na_2) \cdot q^V(Na_2)} \cdot e^{-D_0/RT}$$

$$\frac{V_m^\theta}{N_A} = \frac{kT}{p^\theta} \qquad = k N_A T \qquad \frac{V_m^\theta}{N_A} = \frac{kT}{p^\theta}$$

Now, let us take an actual example. The question is to evaluate the equilibrium constant for the dissociation of Na₂ going to 2N_A. This is the reaction which is going on which is given to us, this is dissociation of di sodium at 1000 K from the following data: rotational constant is given, rotational constant means it is given for Na₂ because N_A cannot rotate, that is given as 0.1547 cm^{-1}; vibrational wave number, that means this is also given for Na₂, that is 159.2 cm^{-1}; and you have zero-point dissociation energy that is also for Na₂, that is 70.4 kilojoules per mole.

Further, it is given to us that the sodium atoms have a doublet ground term, that means the degeneracy of the electronic states for a sodium atom is 2. This is the data given to us; we are supposed to find the equilibrium constant for the dissociation of di sodium to sodium at 1000 K.

See Slide time: 17:37

Evaluate the equilibrium constant for the dissociation $Na_2(g) = 2Na(g)$ at 1000 K from the following data: Rotational constant = 0.1547 cm⁻¹; vibrational wavenumber = 159.2 cm⁻¹ , zero point dissociation energy = 70.4 kJ mol⁻¹. The Na atoms have doublet ground terms.

Planck's constant $h = 6.626 \times 10^{-34} J s$
Boltzmann constant $k = 1.381 \times 10^{-23} J K^{-1}$

$$K = \left\{\frac{q^2(Na)}{N_A^2}\right\} \times e^{-\Delta E_0/RT} = \frac{q^2(Na)}{q(Na_2)} \cdot \frac{1}{N_A} \cdot e^{-D_0/RT} = \frac{q^T{}^2(Na) \cdot g(Na)}{q^T(Na_2) \cdot q^R(Na_2) \cdot q^V(Na_2) N_A} \cdot \frac{1}{g(Na_2)^2} \cdot e^{-D_0/RT}$$

$$K = \frac{kT g_X^2 \Lambda_{X_2}^3}{p^o g_{X_2} q_{X_2}^R q_{X_2}^V \Lambda_X^6} \times e^{-D_0/RT}$$

How we will approach this problem is first we will write an expression for Na₂ by Na₂ by K as we just discussed we will write K for Na square by N_a square it by q_{Na2} divided by N_A right this is for the numerator I am already squaring it this is for the denominator and then I have exponential minus $\Delta E(0)$ by R T. This is now equal to q_{Na}^2 divided by q_{Na_2} into 1 over N_A this N_A is Avogadro constant not sodium into exponential instead of $\Delta E (0)$ let me write D (0) by R T what we have is the ratio of partition functions for sodium squared divided by the partition function for di sodium 1 by N_A which comes from this N_A square and N_A and then the exponential term is there. Now, you remember that N_A is an atom sodium atom and then you have q_{Na_2} , this is a di sodium that means it is a molecule. So, therefore, we have to carefully decide what contributions come in for the atom you have only translational contribution and you may have the electronic contribution.

See Slide time: 22:47

$\Lambda(Na_2) = 8.14$ pm

$\Lambda(Na) = 11.5$ pm

$q^R(Na_2) = 2246$

$q^V(Na_2) = 4.885$

$g(Na) = 2$

$g(Na_2) = 1$

$$\Lambda = \left(\frac{\beta h^2}{2\pi m}\right)^{1/2} = \frac{h}{(2\pi m k T)^{1/2}}$$

$$q^R = \frac{1}{\sigma\, hc\, \beta B}$$

$T \gg \theta_R$ $k\theta_R = hcB$ $\underline{Na_2}$ $\left(Na - Na\right)$

$\sigma = 2$

Vibrational Contribution $3N - 5 = \boxed{1}$ Normal mode of vibration

22:47 / 31:43

So, therefore, what I will do is I will write here that q of sodium only that means q translational sodium square into if there is degeneracy of sodium divided by, I have q translational for di sodium now remember that this is a molecule. So, it will not only have translational degree of freedom, you will also have rotational di sodium, you will also have vibrational di sodium into 1 over N_A is already there into there is 1 over g_{Na_2} square into is exponential minus D (0) by R T.

See slide time: 26:32

$$\Lambda(Na_2) = 8.14 \text{ pm} \qquad \Lambda(Na) = 11.5 \text{ pm}$$
$$q^R(Na_2) = 2246 \qquad q^V(Na_2) = 4.885$$
$$g(Na) = 2 \qquad g(Na_2) = 1$$

$$\boxed{p^\theta = 1 \text{ bar}} \quad \text{Standard State}$$

$$\boxed{\Delta G^\theta} = -RT \ln K$$

$$K = \frac{kT \, q_X^2 \, \Lambda_{X_2}^3}{p^o \, g_{X_2} \, q_{X_2}^R \, q_{X_2}^V \, \Lambda_X^6} \times e^{-D_0/RT}$$

26:32 / 31:43

So, since we are talking about Na₂ in equilibrium with 2Na and we write the equilibrium constant as q translational of N_A square into the degeneracy of the ground state for N_A divided by q translational for Na₂ into q rotational Na₂ into q vibrational Na₂ into electronic contribution degeneracy of Na₂ and there was 1 over N_A term and then there was exponential minus D (0) by R T. So, we have this expression now we very much know that q translational is V_m° by $\lambda \, N_a^3$, but this is squared this is for the translational contribution then degeneracy of N_a I will write like this in the denominator I will write V_m° because everything we are treating as an ideal gas divided by λ cube of Na₂ this is translational contribution I will write rotational as such I will write Na₂ into q vibrational; I have Na₂ into the degeneracy of the ground state Na₂ into 1 over N_a into exponential minus D (0) by R T. Please note that I am writing here standard state conditions because although I am not writing $^{\circ\circ\circ}$ with all the q's it is understood that these are all standard state quantities.

Now, let us try to further solve it. So, now, I have K is equal to V_m° square by V_m° I will just write V_m° right 1 is square 1 is 1 term and here only let me include N_A I will just bring N_A along with this. Now, what I have is $\lambda_{Na_2}^3$ over λ_{Na}^6 this is the ratio of the thermal wavelengths into G of N_A over G of Na₂ this also let me combined into 1 over q R Na₂ into q V Na₂ into exponential minus D (0) by RT this is what I have. Now, we can further work upon this and see what we get P V_m° is equal to RT I am consuming N because V_m° m means

molar. So, can I write this R is equal to K times Avogadro constant into T R is K times N A. So, therefore, V_m° by N_A this N_A is Avogadro constant is K T by P° right this is also not because this standard state we are talking about. So, V_m° by N_A this N_A is Avogadro constant is K T by P°. So, instead of this I can write K T by P° if I write K T by P° then I do not need the volume because we are considering the standard state conditions and applying the ideal gas equation P° V° is equal to RT I can get V_m° by N_A in terms of K T by P° K is a constant T is a given temperature P° is 1 bar that means you need not be given the volume. Once I substitute this K T by P° over here then I have this K T by P° into the ratio of the thermal wavelengths ratio of the degeneracies of the ground state electronic ground state and then I need the information about the rotational partition function I need the information about vibrational partition function and I also need the dissociation energy zero-point dissociation energy and that is what is written in this expression K T by P° you have this is g x square not q g x square λ x 2 cube g x 2 q r x 2 q vibrational x 2 λ x 6 exponential minus d 0 by RT. That means now the next problem is to evaluate the thermal wavelengths rotational partition function vibrational partition function and then proceed with the calculation.

The data given to us for λ is equal to β h square by 2 π m square root which is equal to h by 2 π m K T square root β is equal to 1 over K T h is Planck's constant we know 6.626 into 10 to the power minus 2 into 10 to the power minus 34 joules per second K is Boltzmann constant 1.381 into 10 to the power minus 23 joules per K T the temperature given to us. So, we can calculate the thermal wavelength from the knowledge of the masses of Na_2 and N_A thermal wavelength can be calculated by using these formulas the thermal wavelength of Na_2 comes out to 8.14 picometers whereas, that for N_a itself the sodium atom it comes out to 11.5 picometers this can be obtained by appropriately substituting the numbers over here. So, we know how to deal with the thermal wavelength q rotational Na_2 is a linear diatomic molecule. So, therefore, the expression that you require for the molecular partition function is that for a linear rotor and we know that q R for a linear rotor is 1 over sigma h c β B remember that this equation is a high-temperature result that means your temperature is equal if it is much higher than the characteristic rotational temperature then only you will use this equation. That means what you will do is you will use this equation K θ R is equal to h c B calculate the value of θ R because you are given Planck's

constant you know speed of light you know and the rotational constant you know the Boltzmann constant also you know substitute these numbers and get the value of rotational temperature you will see in this case where the temperature given is 1000 K is much much higher than the rotational temperature you calculate and check yourself yes it comes out to be the temperature given temperature is much much higher than the rotational temperature. So, that means, I am justified now to use this expression q^r is equal to 1 over σ h c β B we are dealing with Na_2 let us say first we will talk about Na_2.

So, if I put like this N_A Na a rotation by 180 degrees leaves the molecule in an unidentifiable state. Therefore, in complete one rotation, the same state will appear twice that means sigma in this case is equal to 2 you know the value of sigma now you know the Planck's constant speed of light β is 1 over k T and B is given to you once you substitute this you will see that you get a q R value of 2246 sodium atom is atom you cannot have rotation in that that means we do not need to worry about the rotational contribution to N_a now comes vibrational contribution again sodium atom cannot vibrate, but sodium atom cannot vibrate, but sodium molecule can vibrate. So, when we discuss vibrational contribution di sodium linear molecule. So, the number of normal number of modes of vibration is 3 N minus 5 is equal to 6 minus 5 is only 1 normal mode of vibration 1 normal mode of vibration and now if you look at the problem statement rotational constant is given, we have already used that in calculating the rotational partition function vibrational wave number is the given and we are also given the sodium atoms have doublet ground terms. So, by using q v is equal to 1 over 1 minus exponential minus β h c $\bar{\nu}$ this is the expression to be used remember this expression which I have written over here this can be used at any temperature there is no high-temperature approximation used over here an alternate way of calculation can be just like you evaluated the value of rotational temperature.

Similarly, you evaluate the value of vibrational temperature from k θ_v is equal to h c $\bar{\nu}$ calculate θ_v compare with temperature and then use the high-temperature result not required because this is a straightforward expression you know β is 1 over K T you know Planck's constant you know speed of light and we know the vibrational wave number. Once you substitute these numbers what we have is 4.885 this is the number that we are going to get third one the degeneracy of the electronic ground state for sodium atom is 2 the

degeneracy for the ground state electronic state for disodium molecule is 1. So, by now we have everything q t can be calculated from $\Phi_m°$ by λ cube, but in fact you do not need to calculate because the expression that we are going to use k is equal to k times T this is $g_x^2\lambda_x^3$ $2p°/g_x$ $2q_r^x$ 2 q_v^x $2\lambda^6$ we know we know this we know this we know this this this and dissociation energy is given to us let us look at whether it is given or not the zero-point dissociation energy is 70.4 kilojoules per mole.

Therefore, since we are given the value per mole, you will use d 0 by R T if it were given per molecule then you would have used d 0 by k T the value of p° is equal to 1 bar this is because we are invoking standard states why standard state because in all our calculations which are the expressions are based upon $\Delta G°$ is minus R T log k and we have connected everything with the standard state, and we have calculated the value of p° by Δ or the change in Gibbs free energy under standard state conditions. When we say standard state, then we are saying it is 1 bar pressure. So, now we have all the information. The given reaction was di-sodium going to 2Na, and from the knowledge of

$$K = \frac{q_{j,m}^°}{N_a^{v_g}} exp(-\Delta_r E°/RT)$$

we used this expression and then converted it into this particular expression. By substituting the various numbers at 1000 K, you see here when you solve the numerical problems, make sure that you are using the appropriate units. If you do not put the appropriate units, your final answer is going to be wrong. The given pressure P° is equal to 1 bar, and then you have converted this bar (1 bar) into Pascals (10^5 Pascals). Why introduce Pascals? Because it will take care of the units.

So, you have the Boltzmann constant, you have temperature, you have this degeneracy factor, you have this vector, you have this ratio of the thermal wavelengths, and then you have this rotational and vibrational contribution. Everything put together, you see at 1000 K, the value is 2.42.
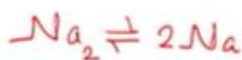
See slide time: 29:02

$$\Lambda(Na_2) = 8.14 \text{ pm} \qquad \Lambda(Na) = 11.5 \text{ pm}$$
$$q^R(Na_2) = 2246 \qquad q^V(Na_2) = 4.885$$
$$g(Na) = 2 \qquad g(Na_2) = 1$$

$$Na_2 \rightleftharpoons 2Na$$

$$K = \prod_J \left\{ \frac{q^\circ_{J,m}}{N_A} \right\}^{\nu_J} e^{-\Delta_r \mathcal{E}_0/RT}$$

$$K = \frac{1.38 \times 10^{-23}\, J\, K^{-1} \times 1000\, K \times 4 \times (8.14 \times 10^{-12}\, m)^3}{10^5\, Pa \times 2246 \times 4.885 \times (1.15 \times 10^{-11})^6} \times e^{-8.47} = 2.42$$

What we have done is that we have calculated the values of various molecular partition functions, substituted those values, used the value of dissociation energy, and we can easily get the value of the equilibrium constant. The value of the equilibrium constant obtained here is not very high, only 2.42. That means this reaction does not have a very high yield; the Δ G° of this reaction is not very highly negative. Now, it is a different matter how to improve this value. Improving the value of the equilibrium constant depends on various factors. For that, you need Le Chatelier's principle, but in this case, what we have done is we have restricted our discussion only to the equilibrium constant. So, therefore, just to recap what we have done is that by starting with this equation, we have identified that what different contributions go into the molecular partition function and from those contributions, we have evaluated this equilibrium constant. The calculations may appear a little lengthy, but the procedure is straightforward. You need information on translational contribution, which depends upon the thermal wavelength, rotational contribution, vibrational contribution, electronic contribution, and the difference in zero-point energies. Once you have this information, the calculations of the equilibrium constant are very easy.

We will take some more examples to further clarify about what factors go into the evaluation of the equilibrium constant. Remember that this equation is very simple where you have only diatomic sodium and you have sodium atom. If you have a reaction in which there are triatomic molecules and multi-atomic polyatomic molecules, the situation can be

complex. One such example we will take and further discuss, but that we will do in the next lecture. Thank you very much. Thank you.