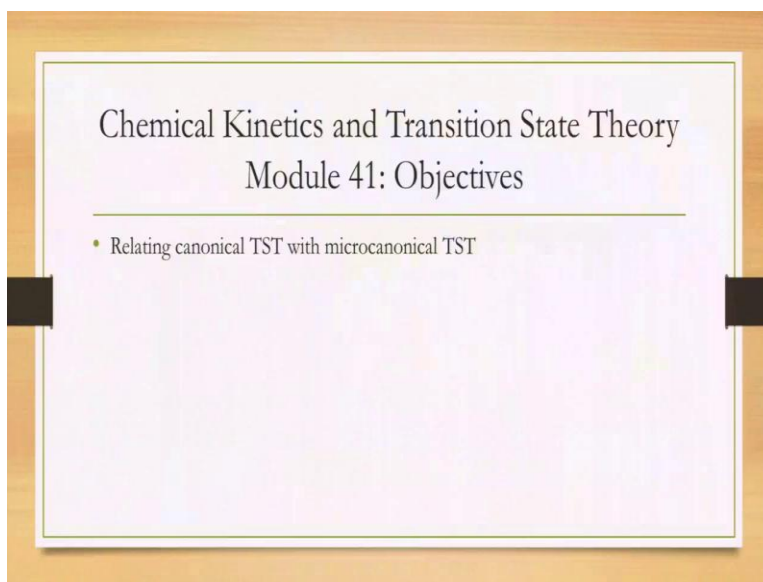


Chemical Kinetics and Transition State Theory
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Lecture 41
Canonical TST from microcanonical RRKM model

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Hello, and welcome to module 41 of Chemical Kinetics and Transition State Theory. In the last module, we derived the transition state theory estimate of rate constant at constant energy. For the rest of the course, we were deriving transition state theory at constant temperature. So, in this module I want to connect these two.

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TST rate constants

$$k_{TST}(E) = \frac{W^\ddagger(E - E_a)}{h g_R(E)}$$

$$k_{TST}(T) = \frac{k_B T}{h} \frac{Q_{T.S.}^\ddagger}{Q_R} e^{-E_a/k_B T}$$



So, these are the two expressions we have derived. At constant temperature, this is the expression that we have played around with over several modules and this is the expression we derived in the last module of the rate constant at constant energy.

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From microcanonical to canonical ensemble

$$k(T) = \int_0^\infty dE \cdot P_T(E) \cdot k(E)$$

$$k(E) = \frac{W^\ddagger(E - E_a)}{h g_R(E)}$$

$$P_T(E) = \frac{g(E) e^{-\beta E}}{\int_0^\infty dE g(E) e^{-\beta E}}$$

$$P(\vec{r}, \vec{p}) = \frac{e^{-\beta H(\vec{r}, \vec{p})}}{N}$$



So, today let us look if we can derive one from the other, particularly I will go from microcanonical to canonical. If I have to calculate k of temperature, one way of writing this is actually I can integrate over all energies, find the density of energies and k of E . So I find the rate

constant at given energy, find what is the density at that energy and just integrate the product over all energies that will give me the correct constant at a given temperature.

So, k of E we will use the transition state expression, E minus E_a . What is ρ ? That is the question. So we have been writing ρ of x comma p as e to the power of minus beta H of x comma p divided by the normalization constant. If I want to write it as a function of one number, energy, well, you noticed that this H is nothing but energy. However, there can be degeneracy of energy, there can be intensity of energy, and the density is given by g . So think about it.

At a given energy, what is my ρ , what is the density? Well, the density of x comma p is this. This is my true Boltzmann distribution. And H is nothing but energy. But we note that ρ of E is nothing but e to the power of minus beta E , but I have several possible x comma p where the energy is equal. So I must multiply e to the power of minus beta E by the density at that given energy or the number of states I have at that energy and g essentially represents the number of states at that energy.

So, at some energies, I might have many, many more states. So my ρ is higher. My overall density is higher then. So it is a product. But I must also integrate over all because I must normalize it properly. So I get this.

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Partition function

$$\int_0^E g(E') e^{-\beta E'} dE' = \frac{1}{h^{3N}} \int_0^E dE' \int d\vec{x} \int d\vec{p} \delta[H(\vec{q}, \vec{p}) - E'] e^{-\beta E'}$$


$$= \frac{1}{h^{3N}} \int d\vec{x} \int d\vec{p} \left[\int_0^E dE' \delta[H(\vec{x}, \vec{p}) - E'] e^{-\beta E'} \right] \quad 0 < E' < E$$

$$= \frac{1}{h^{3N}} \int d\vec{x} \int d\vec{p} e^{-\beta H(\vec{x}, \vec{p})}$$

$$\int_0^E g(E') e^{-\beta E'} dE' = Q_R$$

$$g(E) = \frac{1}{h^{3N}} \int d\vec{q} \int d\vec{p} \delta[H(\vec{q}, \vec{p}) - E]$$

$$\int_a^b dx f(x) \delta(x - x_0) = \begin{cases} f(x_0) & \text{if } a < x_0 < b \\ 0 & \text{otherwise} \end{cases}$$



From microcanonical to canonical ensemble

$$k(T) = \int_0^{\infty} dE \cdot \rho(E) \cdot k(E)$$

$$k(E) = \frac{W^{\ddagger}(E - E_a)}{h g_R(E)}$$

$$\rho(E) = \frac{g_R(E) e^{-\beta E}}{\int_0^{\infty} dE' g_R(E') e^{-\beta E'}}$$

$$\rho(\vec{r}, \vec{p}) = \frac{e^{-\beta H(\vec{r}, \vec{p})}}{N}$$



Let us just look at this denominator I just wrote very quickly. So in the denominator I wrote. Now, we will replace the expression of g of E that we had written last lecture. I always forget h to the power of $3N$ so let me write that very first, 0 to E , g of E is integral over all x integral over all p delta let me write dE here of H of q comma, I am sorry, I have changed my language, so let me just write x here p here minus E , e to the power of minus beta E .

I will take the integral of e inside, e to the power of minus beta E . I look at this expression and I realize this is equal to what. I should be integrating over E prime, I am sorry, otherwise things become very confusing. I was using both E s to be the same. I should not be doing that. Well, E prime lies between 0 and E . Therefore, this H I can simply replace here. So, I am using this relation of Dirac-delta function, where E prime is the same as x . My function is e to the power of minus beta x and this is my Dirac-delta function.

Now, what is this integral equal to? Anybody remember still? What is it? Partition function. So integral from 0 to E , g E prime, e to the power of minus beta E prime dE prime is equal to Q . Now, here when you are doing this integral, this ρ was supposed to be an, only over reactant space.

So, basically what we then do is we consider this to be only reactant partition function, because again it is the same idea as always. We are only thinking that my entire population is limited to reactants. There is nothing in the population in the product side. So, I am integrating only over reactants to everything at this R sub-level.

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Canonical TST rate

$$k(T) = \frac{\int_0^\infty dE e^{-\beta E} g_R(E) k(E)}{\int_0^\infty dE e^{-\beta E} g_R(E)} = \frac{1}{g_R} \int_{E_a}^\infty dE e^{-\beta E} \frac{W^\ddagger(E-E_a)}{h g_R(E)}$$

$$= \frac{1}{h g_R} \int_{E_a}^\infty dE e^{-\beta E} \frac{W^\ddagger(E-E_a)}{h}$$

$$= \frac{1}{h g_R} \left[\int_{E_a}^\infty W^\ddagger(E-E_a) e^{-\beta E} dE - \int_{E_a}^\infty dE \frac{dW^\ddagger(E-E_a)}{dE} \frac{e^{-\beta E}}{-\beta} \right]$$

$\int_0^{E_a} W^\ddagger(E-E_a) e^{-\beta E} dE = 0$

$$= + \frac{k_B T}{h} \frac{1}{g_R} \int_{E_a}^\infty dE g^\ddagger(E-E_a) e^{-\beta E}$$

$k_{TST}(E) = \frac{W^\ddagger(E-E_a)}{h g_R(E)}$

So, k of T, I have to find this formula and I have shown that this thing is equal to nothing but QR. That is good. So, I get 1 over QR g R of E, k of E. Now k of E, I will use this formula what we had derived in the last lecture. This cancels here. So that makes me happy. Integral 0 to infinity dE. I will do an integration by parts here. I will call this as my first function, this as my second function. So I will write this as W dagger.

Let me, before I do that, let me do one more thing. I realize that this integration that I am doing should be only from Ea to infinity, because if E is less than Ea, kTST of E is actually equal to 0. So the reaction happens only if energy is greater than Ea. The entire microcanonical transition state theory rate that we are deducing is for energies above Ea. This W dagger has no sense if E is less than Ea. So our integral of energy is only from Ea to infinite. Why? Because energy less than Ea, my k of E itself is 0. So I can replace this 0 to Ea directly.

So, I am integrating by parts now. I am calling this one as first, this one as second. So I integrate second one, I get this from Ea to infinity minus integral I again write 0 I do not know why dE minus integral of differentiation of first function, integral of second function like this. Look at the first term. This is actually equal to 0. So, I, let me put infinity here. I realize e to the power of minus beta infinity is 0. I put Ea here. I realized W dagger of Ea minus Ea equal to W dagger of 0 which is equal to 0.

W again is the total number of states for energies less than that energy, but if my energy is 0, then there are no states. So my W dagger is 0. So this term happily vanishes. So this is equal to then, I see I have a negative sign here and a negative sign here, I make that a positive, I take beta as 1 over kT. You start seeing hints of transition state theory, do not you? kT over h, 1 over kR, similar, similar. Now, what is dW dagger over dE g. So you can look that in the last module as well, dW over dE is the density.

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Canonical TST rate

$$k(T) = \frac{k_B T}{h Q_R} \int_{E_a}^{\infty} dE e^{-\beta E} g^\ddagger(E - E_a)$$

$E' = E - E_a$; $dE' = dE$; when $E = E_a$, $E' = 0$
 $E = \infty$, $E' = \infty$

$$= \frac{k_B T}{h Q_R} \int_0^{\infty} dE' e^{-\beta [E' + E_a]} g^\ddagger(E')$$

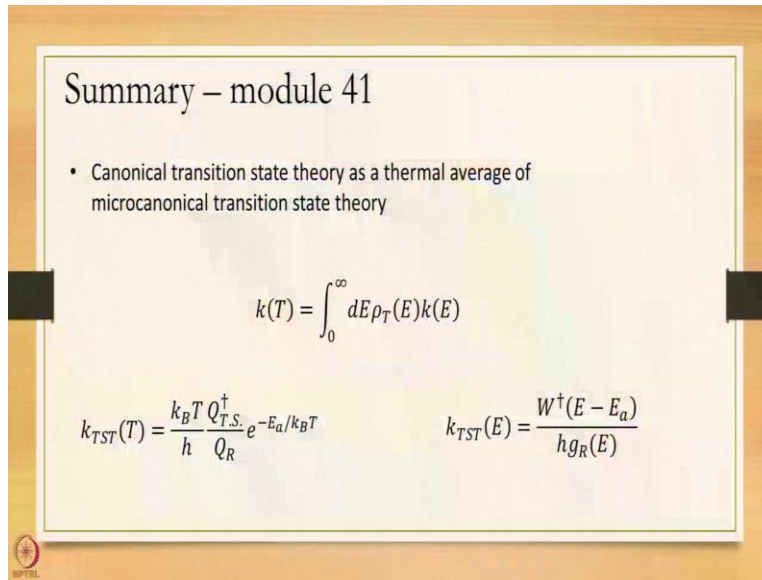
$$= \frac{k_B T}{h} \frac{\int_0^{\infty} dE' e^{-\beta E'} g^\ddagger(E')}{Q_R} e^{-\beta E_a}$$

$$R(T) = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_R} e^{-\beta E_a}$$


So, I get this expression. What do I do now? I do replacement of variables. I define E prime as E minus Ea over hQR, dE prime is dE. Let me find the limits. When E is equal to Ea, E prime equal to 0. When E equal to infinite, E prime also is equal to infinite. So my limits here are 0 to infinite now. dE is the same as the dE prime, e to the power of minus beta, E is nothing but E prime plus Ea, g of E prime.

Let me just, a few more steps, almost there, over. I will write this as QR here and I will take e to the power of minus beta Ea outside the integral. Now you realize this integral just a few slides ago we showed is equal to partition function and this partition function will be the transition state partition function because this g is the transition state. I had forgotten to write this. I remember I am following this g here. So, q dagger over QR.

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Summary – module 41

- Canonical transition state theory as a thermal average of microcanonical transition state theory

$$k(T) = \int_0^{\infty} dE \rho_T(E) k(E)$$
$$k_{TST}(T) = \frac{k_B T}{h} \frac{Q_{TS}^{\ddagger}}{Q_R} e^{-E_a/k_B T} \quad k_{TST}(E) = \frac{W^{\ddagger}(E - E_a)}{h g_R(E)}$$

So, we have derived the transition state theory at canonical ensemble that we had derived much earlier before but from a new perspective this time. We had first derived the transition state theory at constant energy in the last module. And if we just integrate over all energies with the correct thermal density multiplied by this k of E , we see that we get the same expression back.

So, this is good. This is more or less of really a consistency check what we are doing today. This, in deriving both these expressions, we have made the same set of approximations, the same model, except that the ensemble is different. Here I have canonical, here I have microcanonical, but the physics is the same. So I should be able to go from one to another and to, going from one to another is this formula. So, if I do that, I should be able to get from one expression to another and that is what we have done today. Thank you very much.