Problems and solutions for Chapter 6

P.*A. (a) Detailed balance in transition state theory at a given energy. Given that the forward and reversed reaction proceed via the same transition state, show that the yield function, equation (6.4), is the same for the forward and reversed reaction. Next, based on the derivation of equation (6.5) show that the rate constant at the energy E, computed by transition state theory satisfies detailed balance. It is easier to derive the condition of detailed balance between the rates $k(E)$ of the forward and reversed reaction starting from the equality of the yield function. (b) Detailed balance in transition state theory at a given temperature. Given that the forward and reversed reaction proceed via the same transition state, show that the rates $k(T)$ of the forward and reversed reaction satisfy detailed balance meaning that their ratio is the equilibrium constant for the reaction. If you are not familiar with the statistical mechanics result for the equilibrium constant $K(T)$, reverse the question: Derive an expression for $K(T)$ starting with the transition theory expressions for the rates $k(T)$ of the forward and reversed reaction.

S.A. (a). The theoretical ability to reverse the direction of the motion along a classical trajectory means that given a transition state as a configuration of no return, the transition state for the reactants crossing over to products is the same as the transition state for the products crossing over to reactants. The number $N^{\ddagger}(E-E_0)$ of states at the transition state at the energy E is then independent of do we consider the forward or the reversed reaction. Hence the yield function, equation (6.4), $N^{\ddagger}(E-E_0)/h$, is the same. It follows from equation (6.5) that the rate constants for the forward and reversed reaction are related by

$$\vec{\rho}(E)\vec{k}(E)=\overleftarrow{\rho}(E)\overleftarrow{k}(E)$$

(b). From (a) and equation (6.7) the partition function of the transition state is the same for both directions. Therefore, from (6.11)

$$\overrightarrow{Q}(T)\exp(-\overrightarrow{E}_0 / k_\mathrm{B}T)\overrightarrow{k}(T) = \overleftarrow{Q}(T)\exp(-\overleftarrow{E}_0 / k_\mathrm{B}T)\overleftarrow{k}(T)$$

But the difference in the height of the barrier with respect to the reactants and products is the exoergicity ΔE_0 of the reaction, cf. legend of figure 6.1. Hence

$$\frac{\overleftarrow{k}(T)}{\overrightarrow{k}(T)} = \frac{\overrightarrow{Q}(T)}{\overleftarrow{Q}(T)}\exp(-\Delta E_0 / k_\mathrm{B}T)$$

P.C. The expression for the thermal rate constant. Equation (3.8) is the thermal rate constant for reactants in a particular state. Equation (A.3.3) shows how to average over the internal states of the reactants. Using the definitions of partition functions from Appendix 6.A derive equation (6.7). This involves a fair amount of changing the variable in integrations.

S.C. The starting point is the rate constant for state selected reactants, equation (3.8)

$$k_i(T) = \langle v \rangle (k_\mathrm{B}T)^{-2} \int dE_\mathrm{T} E_\mathrm{T} \sigma_\mathrm{R} \exp(-E_\mathrm{T} / k_\mathrm{B}T)$$

Taking a thermal average over the reactants, using equation (6.6) and $p_i = \exp(-E_i / k_\mathrm{B}T) / Q_\mathrm{I}$

$$\begin{aligned} k(T) &= \sum\nolimits_i p_i k_i(T) \\ &= \langle v \rangle (k_\mathrm{B}T)^{-2} Q_\mathrm{I}^{-1} \sum\nolimits_i \int_0^\infty dE_\mathrm{T} \frac{\hbar^2 k_i^2}{2\mu} \sigma_\mathrm{R}(i) \exp(-(E_\mathrm{T} + E_i) / k_\mathrm{B}T) \\ &= Q_\mathrm{T}^{-1} Q_\mathrm{I}^{-1} \int dE\, h^{-1} \sum\nolimits_i \pi^{-1} k_i^2 \sigma_\mathrm{R}(i) \exp(-E / k_\mathrm{B}T) \\ &= Q^{-1} \int dE\, Y(E) \exp(-E / k_\mathrm{B}T) \end{aligned}$$

The limit of integration over the total energy E can be taken from 0 because the cross section for state selected reactants vanishes below the energy threshold $E > E_i$ or $E_\mathrm{T} > 0$.

E. The most direct router is to use the result from stat mech that the partition function and the entropy are related by $k_{\mathrm{B}} \ln Q = S + \langle E \rangle / T$. We prove this for the special case of internal states by starting from the general expression $S = -k_{\mathrm{B}} \sum_i p_i \ln p_i$ and using the Boltzmann expression for p_i from C above. Otherwise the result follows by starting from the stat thermo expression for $\langle E \rangle$ as given in E of chapter 3 and using (A.6.7) to relate the free energy and $\ln Q$. Once we agree that $Q = \exp(S / k_{\mathrm{B}}) \exp(-E / k_{\mathrm{B}} T)$ the expression for the entropy of activation in TST follows from the standard form of the reaction rate constant as the difference between the entropy of the internal degrees of freedom at the transition state minus the entropy of the reactants. (b). A useful image of the distribution at the transition state is to think of a harmonic potential for a coordinate perpendicular to the reaction coordinate. This is the saddle at the transition state, see figure 5.1. If this potential is shallow the rate of crossing along the reaction coordinate is high while the rate is low if the passage is tight. Computing the entropy for a thermal distribution of states of a harmonic potential of frequency ν we find that in the high temperature limit $Q = k_{\mathrm{B}} T / h\nu$ and $\langle E \rangle = k_{\mathrm{B}} T$ so the entropy increases with decreasing frequency as $\ln(k_{\mathrm{B}} T / h\nu)$. Note also how increasing the temperature makes the rate of crossing higher because more states perpendicular to the reaction coordinate can be sampled.

P. G. Transition state theory for unimolecular reactions. In the high pressure limit one can assume that the energy rich species A* has reached thermal equilibrium. (a) Verify the TST result for the rate of unimolecular dissociation $k(T) = (k_{\mathrm{B}} T / h)(Q^{\ddagger} / Q) \exp(-\beta E_0)$ where Q is the partition function for A and $Q^{\ddagger}$ is the partition function for the transition state. (b) This result looks just like the TST expression for the bimolecular thermal reaction rate constant. But this cannot be. A unimolecular reaction rate constant has different dimensions than a bimolecular one. Resolve this dilemma. (c) The thermal dissociation of ethane, $CH_3CH_3 \rightarrow 2CH_3$, has, of course, a very high value for the activation energy. But it also has an unusually high value for the measured Arrhenius A factor, roughly $A=10^{17.4}$ s^{-1}. Suggest a possible explanation. Your explanation should take into consideration that many other bond breaking unimolecular reactions have high A factors. (d) On the other hand, the thermal dissociation C_2H_5-O-CH=CH_2 $\rightarrow C_2H_4+CH_3CHO$ has a rather low A factor, roughly $A=10^{11.4}$ s^{-1}. It is suggested that the reason is that the structure of the transition state is a six member ring, which enables an H atom to move from one end of the molecule to the other with a more modest barrier. Discuss if this can explain the low A value. (e) Now generalize the TST result for the dissociation rate constant to lower pressures. You may use the steady state approximation but you must generalize the discussion in section 6.2.1 because we have shown in 6.2.2 that the rate of dissociation is a strongly increasing function of the energy of the molecule.

S.G. (a). See section 6.2.2.1 (b). The TST expression for either a unimolecular or a bimolecular rate constants is

$$k(T)=\frac{k_{\mathrm{B}}T}{h}\frac{Q^{\ddagger}}{Q}\exp(-E_0/k_{\mathrm{B}}T)$$

The first factor has the dimension of time^{-1} so the other dimensions, if any, come from the ratio of partition functions. For a unimolecular reaction this ratio is dimensionless so the dimension of the rate constant is, as expected, time^{-1}. For a bimolecular reaction the ratio of partition functions has the dimension volume. Why? Because for the A+B reactants there is a partition function per unit volume of the motion of the center of mass of A and there is also a partition function per unit volume of the motion of the center of mass of B. For the transition state there is only a partition function per unit volume of motion of its center of mass. (c) In ethane the two methyl groups are not independent of one another. For example, there is a (small but finite) barrier to rotation about the C-C bond. In the transition state for the dissociation of ethane, $CH_3CH_3 \rightarrow CH_3+CH_3$ the reaction coordinate is the C-C distance. In the transition state the two methyl groups are much more independent so entropy favors the dissociation. The same will be the case for other bond breaking processes. (d) A ring structure for the transition state means that it is more constrained than the reactants so entropy does not favor the dissociation. (e). You need to modify the discussion of section 6.2.2.1. First, as shown in section 6.2.1 the more general expression for the concentration of energy rich molecules is

$$[\mathrm{A}^*]=[\mathrm{A}]\frac{k[\mathrm{M}]}{k'[\mathrm{M}]+k_{\mathrm{d}}}$$

Since the total energy is conserved we can write such an equation for each value of E

$$[\mathrm{A}^*(E)]=[\mathrm{A}]\frac{k[\mathrm{M}]}{k'[\mathrm{M}]+k_{\mathrm{d}}(E)}\frac{\rho(E)\exp(-E/k_{\mathrm{B}}T)}{Q}$$

so that, by analogy to section 6.2.2.1

$$\begin{aligned}\text{reaction rate}&=\int[\mathrm{A}^*(E)]k_{\mathrm{d}}(E)dE\\&=[\mathrm{A}]\frac{1}{Q}\int\frac{k[\mathrm{M}]}{k'[\mathrm{M}]+k_{\mathrm{d}}(E)}\rho(E)k_{\mathrm{d}}(E)\exp(-E/k_{\mathrm{B}}T)dE\\&=[\mathrm{A}]\frac{1}{hQ}\int\frac{k[\mathrm{M}]}{k'[\mathrm{M}]+k_{\mathrm{d}}(E)}N^{\ddagger}(E-E_0)\exp(-E/k_{\mathrm{B}}T)dE\end{aligned}$$

P. I. The thermal-like prior distribution. The prior distribution for energy disposal into a degree of freedom, say X, contains the factor $(1-E_X/E_{av})^m$ where E_{av} is the energy avaliable for distribution and the power m depends on how many atoms are involved. The origin of this factor is the density of translational states. What this factor does is to describe the shrinking volume in phase space as more and more of the available energy is being put into the particular degree of freedom, X. There are many situations, e.g., the distribution of rotational states of a particular vibrational manifold, where E_X/E_{av} <1. For this range show that $(1-E_X/E_{av})^m \cong \exp(-E_X/(E_{av}/m))$ is a good approximation. The distribution is then 'thermal-like' but note that the 'temperature' depends on the available energy. So the distribution of rotational states in different vibrational manifolds will have a different 'temperature'!

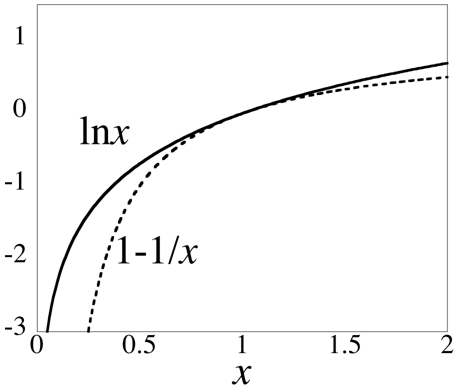
S.I. Expand in a Taylor series

$$\left(1-E_X/E_{\rm av}\right)^m = 1-m\left(E_X/E_{\rm av}\right)+(m^2/2)\left(E_X/E_{\rm av}\right)^2+..$$
$$\exp\left(-\mu E_X\right)=1-\mu E_X+\mu^2 E_X^2+..$$

To lowest order in $\left(E_X/E_{\rm av}\right)$ the two expansions agree if $\mu = m/E_{\rm av}$. As $\left(E_X/E_{\rm av}\right)$ tends to its upper limit of one, the two expressions are significantly different.

P.K. Quality of fit. Let $P^T(v)$ be a trial form for the distribution of the products vibration, say of the form (6.35). Then the quality of the fit to the measured distribution $P(v)$ is $DS^T \equiv \sum_v P(v)\ln\left(P(v)/P^T(v)\right)$. (a) Using the inequality ln(1/x)≥1-(1/x), where equality obtains if and only if x=1, show that DS^T is non negative and vanishes only for a perfect fit. (b) On the basis of (a) conclude that the best value of λ_v is when DS^T is minimal. Compute DS^T as a function of λ_v, determine the stationary point and show that it is indeed a minimum. (c) Show that this is the same value of λ_v as determined in the text, that is, by regarding equation (6.33) as an implicit equation for λ_v. *(d) Show that DS^T is the difference between the entropy of the distribution $P^T(v)$ and entropy of the experimental distribution. This is the sense in which the entropy of the distribution $P^T(v)$ is said to be maximal.

S.K. The logarithmic inequality $\ln x \geq 1 - 1/x$ with equality if and only if $x = 1$ is shown



in the figure

Then

$$DS^{\mathrm{T}} = \sum_v P(v)\ln\left(P(v)/P^{\mathrm{T}}(v)\right) \geq$$
$$\sum_v P(v)\left(1 - P^{\mathrm{T}}(v)/P(v)\right) = \sum_v P(v) - \sum_v P^{\mathrm{T}}(v) = 1 - 1 = 0$$

where the last equality means that both the actual distribution and the trial distribution are normalized.

(a) $DS^{\mathrm{T}} \geq 0$ with equality if and only if $P(v) = P^{\mathrm{T}}(v)$ for all v

(b) If we take the trial functional form $P^{\mathrm{T}}(v) = \exp\left(-\lambda_0^{\mathrm{T}} - \lambda_{\mathrm{v}}^{\mathrm{T}} E_v\right)$ then we can optimize the value of λ_v^{T} by making DS^{T} as small as possible. Note that we cannot separately optimize the value of λ_0^{T} because λ_0^{T} is determined by the value of λ_v^{T} and the condition that the trial distribution is normalized

$$\exp(\lambda_0^{\mathrm{T}}) = \sum_v \exp(-\lambda_v^{\mathrm{T}} E_v)$$

For use below we note that this result implies that

$$\frac{\partial \lambda_0^{\mathrm{T}}}{\partial \lambda_{\mathrm{v}}^{\mathrm{T}}} = \exp(-\lambda_0^{\mathrm{T}})\frac{\partial \exp(\lambda_0^{\mathrm{T}})}{\partial \lambda_{\mathrm{v}}^{\mathrm{T}}} = -\exp(-\lambda_0^{\mathrm{T}})\sum_v E_v \exp(-\lambda_v^{\mathrm{T}} E_v) = -\sum_v E_v P^{\mathrm{T}}(v)$$

To minimize DS^{T} we compute it

$$
\begin{aligned}
DS^{\mathrm{T}} &= \sum\nolimits_v P(v)\ln P(v) - \sum\nolimits_v P(v)\ln P^{\mathrm{T}}(v) \\
&= \sum\nolimits_v P(v)\ln P(v) + \lambda_0^{\mathrm{T}} + \lambda_v^{\mathrm{T}} \sum\nolimits_v E_v P(v) \\
&= \sum\nolimits_v P(v)\ln P(v) + \lambda_0^{\mathrm{T}} + \lambda_v^{\mathrm{T}} \langle E_v \rangle
\end{aligned}
$$

remembering that λ_0^{T} is determined by the value of λ_v^{T}. Then

$$\frac{\partial DS^{\mathrm{T}}}{\partial \lambda_v^{\mathrm{T}}} = -\sum\nolimits_v E_v P^{\mathrm{T}}(v) + \sum\nolimits_v E_v P(v)$$

The minimal value $\left(\partial DS^{\mathrm{T}} / \partial \lambda_v^{\mathrm{T}}\right) = 0$ is when the mean value of the energy computed for the trial distribution, $\sum\nolimits_v E_v P^{\mathrm{T}}(v)$ is equal to the actual mean value, $\sum\nolimits_v E_v P(v)$

To show that the stationary point is a minimum we need to compute

$$\frac{\partial^2 DS^{\mathrm{T}}}{\partial (\lambda_v^{\mathrm{T}})^2} = -\sum\nolimits_v E_v \frac{\partial}{\partial \lambda_v^{\mathrm{T}}} P^{\mathrm{T}}(v) = \sum\nolimits_v (E_v)^2 P^{\mathrm{T}}(v) - \left(\sum\nolimits_v E_v P^{\mathrm{T}}(v)\right)^2$$
$$= \sum\nolimits_v \left(E_v - \sum\nolimits_v E_v P^{\mathrm{T}}(v)\right)^2 P^{\mathrm{T}}(v) > 0$$

(d). $DS^{\mathrm{T}} = \sum\nolimits_v P(v)\ln P(v) - \sum\nolimits_v P(v)\ln P^{\mathrm{T}}(v)$

But at the minimal value, where $\sum\nolimits_v E_v P^{\mathrm{T}}(v) = \sum\nolimits_v E_v P(v)$

$$\sum\nolimits_v P(v)\ln P^{\mathrm{T}}(v) = \sum\nolimits_v P^{\mathrm{T}}(v)\ln P^{\mathrm{T}}(v)$$

$$
\begin{aligned}
DS^{\mathrm{T}} &= \sum\nolimits_v P(v)\ln P(v) - \sum\nolimits_v P(v)\ln P^{\mathrm{T}}(v) \\
&= -\sum\nolimits_v P^{\mathrm{T}}((v)\ln P^{\mathrm{T}}(v) - \left(-\sum\nolimits_v P(v)\ln P(v)\right)
\end{aligned}
$$

P. M. The ion-molecule reaction $CH_2{=}CH_2^{+}$+ $CH_2{=}CH_2 \rightarrow C_3H_5^{+}$+$CH_3$ was studied in a crossed beam arrangement. (a) At low collision energies the product ion was observed to have an angular distribution with a forward-backward symmetry. Why does that make chemical sense? (b) As the collision energy was increased, the angular distribution became increasingly asymmetric and eventually became predominately forward. Why? And can you suggest at what energy this will happen? (c) Will you use transition state theory to compute the reaction rate at low energies? If not, what will you use? (d) If we use the $CD_2{=}CD_2^+$ instead of the $CH_2{=}CH_2^+$ ion, do we expect the ion $CD_2{=}CH_2^+$ as a possible product? Does the answer depend on the collision energy?

N. Towards biological applications mass spectrometry is increasingly concerned with ions of ever larger mass[*]. Apart from the technical problem of detection of heavy ions there is the question of a time window. An ion has to dissociate within at most a few μs's if its fragmentation is to be detected by a conventional mass spectrometer. Assume that ionization is by impact of 70 eV electrons, $e+P \rightarrow e+e+P^+$. (a) Make a reasoned guess for the excess energy of the parent ion and do not forget about the Franck Condon principle, section 7.0.1. (b) What is the range of the maximal molecular weight for the parent in order that the fragmentation of the ion can still be detected. Assume that biological molecules are made of atoms of a mean atomic weight of 7.6 and that a mean vibrational frequency is 1000 cm^{-1}. Ionization weakens bonds so take a dissociation energy of 2 eV. (c) Suggest ways for extending the range of application of analytical mass spectrometry towards higher masses. If necessary, make a literature search.

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[*] Such ions need not be formed by electron impact. There are other options. For a very successful method see Fenn and Mann (1989). See T. Nohmi, T. and J. B. Fenn, *JACS* **114**, 3241 (1992) for an example of molecular weights up to 5 million.

S.M. (a) The reaction can proceed via the cyclobutene ion. When cold this is a stable ion and corresponds to a deep well on the potential energy surface. (b). At higher collision energies the intermediate ion is energy richer and so becomes progressively shorter lived. (c). Transition state theory can be used to compute the rate of unimolecular dissociation of the cyclobutene ion. But the rate of the reaction should be computed as in section 6.2.3. (d) In the collision of $CH_2{=}CH_2 + CD_2{=}CD_2^+$ if the cyclobutene ion is long lived it can dissociate also to $CH_2{=}CD_2^+$. So this product is expected at lower collision energies where the intermediate ion lives long enough that the identity of the bonds is forgotten.

P.N. Termolecular processes and sticky collisions. Third atom-assisted processes are often assumed in chemical kinetics. A notable example is in recombination processes, e.g., $O+O_2+M \rightarrow O_3+M$, where the function of the third body, M in the example, is to take away energy and thereby stabilize the new ozone molecule. It is reasonable to conjecture that the reaction proceeds by a two step process where, in the first step $O+O_2$ (or O_2+M) undergo a collision where a long living complex is formed and it lives for long enough to collide with M (or with O). (a) Use RRK theory to estimate the lifetime of the unrelaxed O_3 complexes formed from thermal $O+O_2$. (Go for or estimate the data that you need). (b) The complex needs to collide with M before it dissociates. Is the estimated lifetime sufficient if the pressure is, say, an atmosphere?

S.N. The RRK estimate for the rate of dissociation of energy rich ozone is $\nu\left(1-E_0/E\right)^2$. ν is the frequency at the barrier E is the total energy measured from the ground state of ozone and E_0 is the minimal energy necessary to dissociate ozone. $2=3n$-6-1 where n=3 is the number of atoms, $3n$-6 is the number of vibrational modes of the nonlinear mpolecule and 2 is the number of vibrations at the transition state. 5One vibration becomes the reaction coordinate). Ozone is not a very stable molecule, $E_0 \approx 20\text{kcalmol}^{-1}$. The ozone molecule is formed from a collision of thermal reactants so these cannot bring in much more than say 1kcalmol^{-1} so $E \approx 21\text{kcalmol}^{-1}$. The lifetime of the energy rich ozone is therefore of the order of $(1/21)^{-2} \approx 0.002$ of a vibrational period. Not very long. Even at atmospheric pressure many molecules will dissociate rather be stabilized by cillisions.