This course material is supported by the **Higher Education Restructuring Fund**
allocated to **ELTE** by the **Hungarian Government**

Reaction Rate Theories

auxiliary material for the M. Sc. course

Reaction Kinetics

Ernő Keszei

Eötvös Loránd University, Institute of Chemistry

Budapest, 2016

Foreword

Learning (and teaching) the theoretical basis of chemical kinetics is not an easy task. Since the diversification of master programmes, shorter undergraduate programmes – typically three years in most European countries – do not offer sufficient courses in physical chemistry to gain a deeper insight into chemical kinetics. A textbook for beginners that would contain sufficient details but avoid outdated theories and methods is not really available. Though there are several excellent textbooks on more advanced topics in reaction kinetics, they typically presuppose quite a good knowledge of theoretical basics, thus their understanding poses problems for the average graduate student.

A modern textbook should take into account the needs of such students. In addition, at the end of the 20th and beginning of the 21st century, chemical kinetics has been developed concerning both experimental and theoretical tools in such a manner, that there is no need to overemphasize the brute approach based on the "order" of reaction, neither to oversimplify emerging systems of ordinary differential equations. Traditional, not fully justifiable simplification of the kinetic equations and "linearization" of functions are not at all needed, as there are plenty of easily available integrators and nonlinear numerical methods. Such traditional approaches are helpful for the students at most to understand old research papers and results described in them.

Similarly, "formal kinetics" does not need to be introduced either in its long used old-fashioned version; since chemistry nowadays is a truly molecular science having solid quantum mechanical and statistical thermodynamic foundation, chemical kinetics should also be based on this foundation. Thus the introduction to the subject should be based on the transition state theory, which is the most widely used and still powerful picture concerning the kinetic aspect of chemical reactions.

According to these considerations, the goal of this text is to introduce the student into the science of temporal evolution of chemical reactions by a molecular-statistical interpretation, and to refer to this picture whenever possible. The author hopes that students reading this text will find it easy to understand and – at the same time – will acquire a genuine knowledge on reaction kinetics that is readily applicable in practice.

Budapest, January 2016 Ernő Keszei

Contents

1. Introduction

Reaction kinetics is the branch of physical chemistry which deals with the temporal evolution of chemical reactions. It provides explanation as to why some reactions do not take place, although their products would be much more stable thermodynamically than the reactants are; it accounts for the fact that some reactions go very fast while some other rather slowly. Furthermore, it also provides several useful tools to calculate the actual rate of reactions within a wide variety of circumstances, including *e. g.* the dependence of the rate on temperature, pressure, the solvent applied, *etc*.

The most important goal of kinetic research is the identification and characterisation of elementary molecular events which make possible the transformation of reactants into products. At the time of the beginning of reaction kinetic studies – in the second half of the 18th century when mechanical models dominated natural sciences – the scheme of these simple molecular events that constitute the overall reaction has been called as the *mechanism* of the reaction, which term survived and is still widely used. This means that the *elementary* steps of the reaction – the most simple events when typically two molecules directly encounter – are identified, and the complex reaction mechanism is constructed from these elementary steps. Most real-life chemical reactions comprise quite a number of such elementary steps; the number of them *e. g.* in gas reactions can be as much as a few hundreds. The overall rate of these reactions can successfully be calculated over a wide range of circumstances if we can calculate the rate of all the constituent elementary reactions within the given conditions, and also know the way of their connection within the reaction mechanism. This is the reason why the theory of elementary reactions has a paramount importance in chemical kinetics.

However, to explore the precise mechanism of composite reactions is not an easy task. To be able to construct a reliable mechanism, we have to identify all the components which take part in the process of the reaction, even if they are short-lived and have rather low concentration. We also have to keep track of the temporal evolution of possibly all these components, although this is not always possible. In many reactions, there are so called *intermediates* (substances formed from the *reactants* and readily removed in consecutive reactions leading to the *products*) that are rather short-lived and present only in very low concentrations, thus they easily remain unnoticed for the experimentalist. After having traced the temporal evolution of as many components of the reacting mixture as possible, the task of the kineticist is to construct a suitable mechanism that can explain all the concentration changes as a function of time. Consequently, theories of composite reactions also constitute an important topic of reaction kinetics.

To successfully model reactions the way explained above, we need an unambiguous definition of the rate of change of the amount of components taking part in the reaction. There exists an IUPAC recommendation for the definition of the *rate of reaction*. For the sake of this definition, we shall write stoichiometric equations in a special form, so that the equation is set equal to zero. The advantage of this form is that reactants and products (species on the left-hand side and on the right-hand side in the more common equation) can be treated the same way, thus simplifying the mathematical treatment. The general stoichiometric equation of this form can be written as:

$$\sum_{i=1}^{R} \nu_i A_i = 0 \tag{1.1}$$

The symbol A_i in this equation denotes the stoichiometric formula of the species i and ν_i (lower case Greek “nu”) is the *stoichiometric number* of this species. The index i runs over all the *reacting species* whose number is R. (Components that do not react – *e. g.* an inert solvent – should have a zero stoichiometric number, thus it is superfluous to include them in the sum.) As an example, let us write one of the possible equations of the formation of water:

$$-1\ H_2 - ½\ O_2 + 1\ H_2O = 0 \tag{1.2}$$

In this equation, $A_1 = H_2$, $A_2 = O_2$, $A_3 = H_2O$, $\nu_1 = -1$, $\nu_2 = -½$ and $\nu_3 = 1$. However, we are too much used to write stoichiometric equations in the usual left side – right side form. Thus we usually write the equation itself in the traditional form

$$H_2 + ½\ O_2 = H_2O\ , \tag{1.3}$$

but we consider the stoichiometric number ν_i of the reactants (left side) to be *negative*, while those of the products (right side) to be *positive*. In the rest of this text, we always interpret stoichiometric equations this way.

The rate of a particular reaction should be defined naturally in such a way that it should be independent from the choice of the component taking part in the reaction whose amount would be used for the temporal evolution. To formulate such definition, let us introduce the *extent of reaction* ξ also used in thermodynamics, but for use in the definition of the rate of reaction, it is sufficient to specify its change as

$$d\xi = \frac{dn_i}{\nu_i}\ . \tag{1.4}$$

The definition of the *rate of the reaction* which is written in the above explained general form (1.1) can then be written as:

$$r = \frac{d\xi}{dt} = \frac{1}{\nu_i}\frac{dn_i}{dt} \tag{1.5}$$

According to this, the SI unit of the rate of reaction is mol (stoichiometric equation) / s. In the chemical praxis, concentrations are much more convenient to measure than amounts of substances. Taking this into account, let us calculate from the above definition the rate of change of molar concentration of a species. Using the definition of the molar concentration as $c_i = n_i / V$, we get

$$\frac{1}{\nu_i}\frac{d(c_i V)}{dt} = \frac{1}{\nu_i}\left(V\frac{dc_i}{dt} + c_i\frac{dV}{dt}\right) \tag{1.6}$$

This equation reveals that the rate of change of the molar concentration dc_i/dt also depends on the rate of change of volume. If the volume does not change during the reaction, the rate of reaction can be obtained by multiplying dc_i/dt by the volume of the reacting system, and dividing it by the stoichiometric number. Accordingly, we can state that *in case of reactions at constant volume*, the change of molar concentration is identical to the stoichiometric number times the *rate of reaction divided by the volume*:

$$\frac{dc_i}{dt} = \frac{1}{V}\frac{dn_i}{dt} = \frac{\nu_i}{V}\frac{d\xi}{dt} \tag{1.7}$$

Within chemical kinetic context, the quantity dc_i/dt is usually called simply as the rate of reaction. However, we should be aware that this quantity is proportional only to the rate of reaction in case of constant volume reactions, when the proportionality constant is the volume V divided by the stoichiometric number ν_i. In condensed phase reactions (*e. g.* in solutions) this is typically true to a good approximation, thus the proportionality can be assumed. Further on in this text, we also consider dc_i/dt as the rate of the reaction. However, in gas phase reactions, if there is a change in number of moles during the reaction, this proportionality does not hold and the change of volume should also be taken into account. It is worth mentioning also that the latest recommendations of IUPAC suggest to use the term "*rate of conversion*" for $d\xi/dt$ and the „rate of reaction" for $\frac{1}{\nu_i}\frac{dc_i}{dt}$. Anyway, naming of the terms does not change their relation as explained above.

As we have seen, the definition of the reaction rate (in both versions) refers to a particular stoichiometric equation as it contains the corresponding stoichiometric numbers. It is worth mentioning that even this definition is only valid if during the (composite) reaction, there won't be any accumulation of an intermediate, and no other "by-products" are formed beside those included in the stoichiometric equation. (This is the case for elementary reactions where this definition can always be used.) Thus, in case of composite reactions it is more convenient to refer to the change of the amount (or concentration) of a *component*, or equivalently to the *rate of consumption* for reactants and the *rate of appearance* for products.

2. Theories of elementary reactions

Thermodynamics tells us that a chemical reaction taking place in a closed, rigid and thermostated system sooner or later reaches equilibrium where the free energy F of the reacting mixture is minimal, as a function of the concentrations. However, we also know that, quite often, this does not happen. Let us imagine such a container filled with hydrogen and oxygen at room temperature and atmospheric pressure; there won't be any reaction between the two components and the system would stay in this metastable state for any length of time provided that circumstances would not change. Thinking in terms of thermodynamics, metastable equilibria in (composite) systems can usually be maintained easily by separating the subsystems with a suitable wall. The constraint exerted by this wall can maintain the metastable equilibrium that would be transformed into a stable equilibrium without the presence of the wall.

Returning to the example of hydrogen and oxygen, let us imagine two compartments of a closed, rigid, thermostated system with a compartment containing hydrogen twice as large as the other one containing oxygen, both having the same pressure. If the subsystems are also closed, *i. e.*, the interior wall does not allow for material transport, then the metastable state without even mixing the two components would be maintained. In this state, both hydrogen molecules and oxygen molecules move randomly within the volume occupied, frequently having collisions with each other. Let us remove the separating wall with a suitable method (*e. g.* breaking the wall with an external actuator), and wait for a while. What happens after the removal of the wall? Molecules do continue the same random movement as before, and – as a consequence of this random movement – they will mix completely to form a homogeneous mixture which is stoichiometric regarding the hydrogen:oxygen ratio.

At this point, it is worth to draw some conclusions. There are some textbooks – not really considering the nature of mixing – which state that hydrogen and oxygen *have a tendency* to mix after the removal of the separating wall. Well, a gas consists of *molecules*, thus any "tendency" can only be attributed to molecules of the gas. However, gas molecules are not bothered by this change; they have a fast random motion with frequent collisions before as well as after the removal of the separating wall. In other words, they *do not have any tendency*. *This is exactly the reason* for a homogeneous mixing. Should they have any other "tendency" in addition to their random movement, they would not mix homogeneously.

There are other (educational) resources emphasizing that a *chemical equilibrium is dynamic*. This statement is based on the fact that a chemical reaction in equilibrium proceeds with equal rate to both directions. We can easily realise that this statement is valid for *any equilibrium*. In both compartments of the container in the previous example, molecules move randomly all over the accessible volume. In equilibrium, the same number of them will walk over to one part of the container on average, as the number that walk to the opposite direction, which guarantees the maintenance of a homogeneous distribution. But this way, the (metastable) equilibrium is *dynamic*; molecules are constantly running back and forth. Exactly the same happens when the separating wall is removed. The vigorous random motion of molecules leads quite quickly to a homogeneous distribution within the enlarged volume, and thus to a homogeneous mixing. This new equilibrium is also dynamic; the same number of hydrogen molecules will walk away from the surroundings of oxygen molecules, as the number that walk towards them in the opposite direction. Thus we can conclude that *every macroscopic equilibrium is microscopically dynamic*. (As a matter of fact, we should also note that in microscopic volume elements, there are of course *fluctuations*, but they cancel within greater (macroscopic) volumes.)

Let us return to the stoichiometric hydrogen-oxygen mixture. According to thermodynamic calculations, the constant volume – constant temperature mixture is largely metastable, as the free energy of formation of water (at room temperature) is – 300,6 kJ/mol. This would make possible an important decrease in free energy on water formation with respect to hydrogen and oxygen, as their free energy of mixing is only a meagre – 1,58 kJ/mol. Despite this large driving force, the reaction does not take place. Remembering the case with mixing after the removal of the separating wall we could think that there is some constraint that prohibits the process to the chemical equilibrium, *i. e.* water formation. Obviously, there is no macroscopic "wall" that hinders the reaction in the homogeneous mixture; we should rather look for a "molecular level" hindrance. Furthermore, we also know from chemistry that placing *e. g.* porous platinum into the mixture, water formation would quickly happen. This means that the "molecular level" wall can also be removed, though – as we shall see later – catalysts typically do not "remove" the wall, rather provide a way for molecules to bypass it.

This chapter deals with the details of the "molecular wall" which prohibits chemical reactions, and with the means molecules have at their disposal to "climb" that wall.

2.1 Collision theory

There are several theoretical approaches to describe chemical reactions at a molecular level. One of the simplest is the kinetic theory of gases that provides a way to calculate the collision frequency of molecules. In addition, we can also calculate the portion of molecules that have enough energy to overcome the resistance originating in the stability of the reactants, thus promoting the formation of reaction products.

Let us consider the following general gas reaction:

$$\mathrm{A} + \mathrm{B} \rightarrow \text{products} \tag{2.1}$$

To calculate the reaction rate, we use the following model. Molecules are considered as rigid elastic spheres. The motion of a molecule A in the direction of a fixed molecule B is described in a coordinate system with its origin at the centre of mass of molecule B (see Fig. 2.1). In this coordinate system, molecule A approaches molecule B with a relative velocity $v = v_\mathrm{A} - v_\mathrm{B}$. Let us denote the radius of molecule A by r_A, that of molecule B by r_B, and the sum of the two by $d = r_\mathrm{A} + r_\mathrm{B}$. Distance b – called the *impact parameter* – is the closest perpendicular distance of the centres of mass of molecules A and B along the trajectory of molecule A. If $b > d$, A passes by B without collision, but if $b < d$, A collides with B and gets deflected. In other words, if the centre of mass of B is within a cylinder of radius d around the trajectory of the centre of mass of A, collision happens, but if it is without, no collision happens. (A usual way of expressing this in a quantitative way is that the *total collision cross section* or *effective target area* of B presented to A is $S = d^2\pi$.)

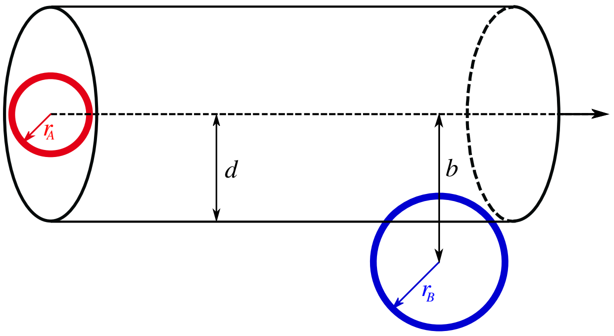

Figure 2.1 Notation for the description of collisions between molecule A (red) and molecule B (blue). The dashed line indicates the trajectory of molecule A approaching the stationary molecule B. Collision occurs if the centre of mass of B is within the collision volume indicated by the cylinder of radius d. In the figure, $b > d$, thus there is no collision. (Keszei 2015)

The traveling molecule A thus sweeps $d^2\pi v$ “collision volume”. The number of its collisions with molecules B depends on the *number density* N_B of molecules B. If there are N_B molecules B in one volume unit gas, then one molecule A collides with $N_B d^2\pi v$ molecule B within unit time.[1] This is valid for each molecule A, thus the overall number of collisions between A and B can be given as $Z' = N_\mathrm{A} N_\mathrm{B} d^2\pi v$, where N_A is the number density of molecules A.

---

[1] Evidently, the direction of the moving molecule changes with each collision, but the collision volume will be a cylinder of radius d further on as well, thus this would not change the validity of the formula.

The expectation value $M(v)$ of the velocity of molecules can be calculated using the Maxwell distribution for the absolute value of their velocity. If we perform this calculation for the relative velocity of two molecules, then we should use the *reduced mass*, which can be given with the masses of the individual molecules as

$$\mu = \frac{m_\mathrm{A} m_\mathrm{B}}{m_\mathrm{A} + m_\mathrm{B}} \ . \tag{2.2}$$

Substituting this in the expression of the expectation value we get:

$$M(v) = \sqrt{\frac{8k_\mathrm{B}T}{\pi\mu}} \ , \tag{2.3}$$

where T is temperature and k_B the Boltzmann constant. Writing this mean velocity into the expression of Z', we get the result

$$Z' = N_\mathrm{A} N_\mathrm{B} d^2 \pi \sqrt{\frac{8k_\mathrm{B}T}{\pi\mu}} \ . \tag{2.4}$$

This is the total number of collisions, irrespective if there will be a reaction, or not, between the colliding molecules. Colliding molecules whose collision energy along the direction of collision is below a threshold E_a cannot surmount the *energy barrier* necessary for the reaction, thus they undergo an *elastic collision*. Molecules whose collision energy along the direction of collision exceeds this value will undergo an inelastic collision leading to reaction. (These are called *reactive collisions*.) Accordingly, to calculate the reaction rate, we have to calculate the portion of collisions leading to reaction. For this purpose, we use the part of Maxwell-Boltzmann distribution describing the probability density of kinetic energy – which we call the Boltzmann distribution. According to this, the proportion of collisions having greater than E_a energy can be given as

$$\frac{Z'_{E_\mathrm{a}}}{Z'} = e^{-\frac{E_\mathrm{a}}{RT}} \ , \tag{2.5}$$

where Z'_{E_a} is the number of collisons with higher energy than E_a, while Z' is the total number of collisions.

Multiplying the total number of collisions Z' by this ratio, we get R, the number of reactive collisions per unit time, *i. e.* the rate of reaction. After some rearrangement, this rate can be written in the following form:

$$R = d^2 \pi \sqrt{\frac{8k_\mathrm{B}T}{\pi\mu}} e^{-\frac{E_\mathrm{a}}{RT}} N_\mathrm{A} N_\mathrm{B} \tag{2.6}$$

We can see that the first four factors do not depend on the concentration (*i. e.* on the number densities of A and B), thus, the product of these factors can be considered as a coefficient independent of concentration what we call *rate coefficient*:

$$k = d^2\pi\sqrt{\frac{8k_\mathrm{B}T}{\pi\mu}}\,e^{-\frac{E_\mathrm{a}}{RT}} \tag{2.7}$$

Using this notation, the rate of the reaction can be written as $R = k\,N_\mathrm{A}N_\mathrm{B}$. We can sum up this result the following way. The rate of reaction (2.1) is proportional to the product of the concentration of the reactants, containing the concentration-independent proportionality factor k. This latter can be given by Eq. (2.7), which is the expression of the rate coefficient according to collision theory. It is worth noting that the literature on gas reactions typically uses the unit molecules/(cm^3 s) for the reaction rate – as a consequence of the above treated calculations. The coefficient $d^2\pi\sqrt{\frac{8k_\mathrm{B}T}{\pi\mu}}$ of the exponential function – originating from the collision number – is usually denoted by Z and called the *collision frequency factor*. Comparing its expression to Eq. (2.6), we can alternatively express it as $Z = Z'/(N_\mathrm{A}N_\mathrm{B})$. Using this, the rate coefficient can be written as the product of the collision frequency factor and the Boltzmann factor:

$$k = Z\,e^{-\frac{E_\mathrm{a}}{RT}} \tag{2.8}$$

Rate coefficients and related reaction rates calculated from the collision theory expression naturally inherit all approximations used in the above derivation. The most simplifying approximation is to treat molecules as small elastic spheres and using classical mechanical laws of elastic collisions. Molecules are of course more complicated entities. Another rather simplifying approximation is to simply take into account collisions above a threshold energy to lead to reaction, which does not take into account the structure of the molecules. According to this, we expect that the rate coefficients and reaction rates calculated this way are best valid for reactions between monatomic reactants – which is in fact supported by experimental evidence.

2.2. Transition state theory

Unlike collision theory, transition state theory (TST) takes into account the internal structure of molecules, in non-reactive and reactive collisions as well. Its basic idea is that the fate of colliding molecules is determined by the actual location of all atoms within, along with their interactions. Whether the outcome is a reaction, and the rate of the reaction itself, depends on these interactions. There are several versions of the transition state theory; the first and most simple being the so called *quasi-equilibrium* description which we shall explore next. Before going into details of the theory, we shall refresh relevant statistical thermodynamical relations which make it possible to describe constant temperature and constant volume, and also constant temperature and constant pressure systems. However, as TST is also based on potential energy surfaces, let us discuss them first.

2.2.1. Potential energy surfaces in reactive systems

Transition state theory (TST) is based on the hypothesis that interactions of colliding molecules can be described in terms of the interactions of all the atoms contained in the reactant molecules. However, this interaction is not described in terms of time but the spatial arrangement of the interacting atoms that we call *configuration*. The relevant quantity that would govern the fate of the interacting atoms is the *potential energy* as a function of this configuration. A convenient visualisation method is to plot the potential energy as a function of the spatial coordinates of the atoms. This (multidimensional) surface is called the *potential energy surface*, which we shall denote by the acronym *PES*.

The simplest PES is a plain two-dimensional curve, the *potential energy curve of a diatomic molecule*. This curve can be seen on Fig. 2.1 for the case of a ground state hydrogen molecule. Negative potential energy values indicate attractive force, positive values repulsive force between the atoms. It can be seen from the figure that the minimum of the potential energy curve is at the equilibrium distance of 76.2 pm. Placing the hydrogen atoms closer to each other, attraction is decreasing radically with decreasing distance and it changes into repulsion within small distances. The curve then rises very steeply, indicating strong repulsion. Placing the two atoms further from each other than the equilibrium distance, their attractive interaction diminishes with increasing distance. At large enough distances, their interaction becomes zero and the molecule can be considered as dissociated.

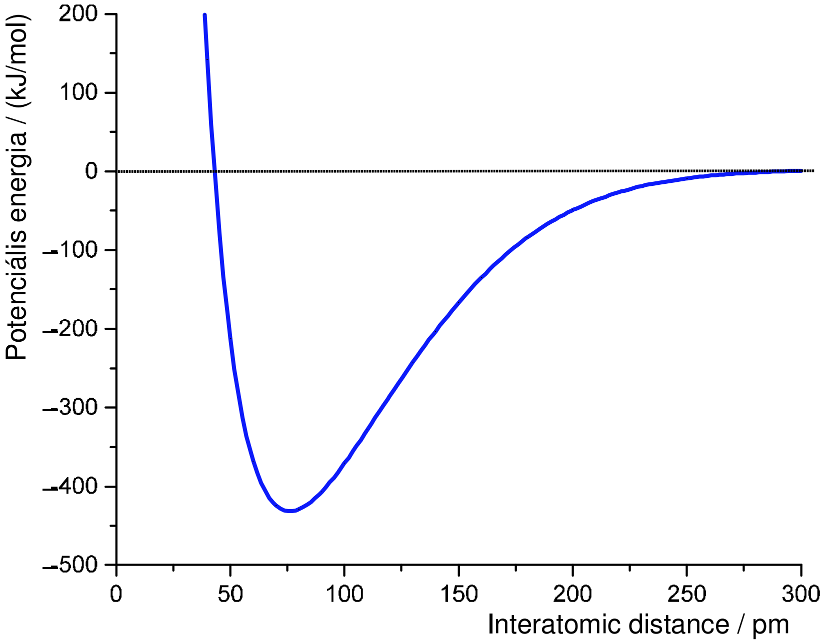

Figure 2.1 Potential energy of a hydrogen molecule as a function of interatomic distance. (Czakó 2015; plotted by Keszei 2015)

Chemical reactions can be interpreted in the PES diagrams as changes in the spatial arrangement (*configuration*) of the atoms; *i. e.* a movement of the configuration point on the surface from the arrangement of *reactants* until that of the *products*. Stable molecules can always be found at the bottom of "valleys" characterized by a minimum in potential energy; thus the reaction path is a trajectory from the reactant valley to the product valley. Accordingly, the rate of reaction can be determined by calculating the speed at which the atoms taking part in the reaction arrive from the reactant valley (across the PES) to the product valley. To calculate this rate, we can use several methods. We shall deal first with the simplest one which is based on the presupposition that the thermodynamic equilibrium is always maintained between the reactants and a specific configuration we call *transition state*. This method is called the *quasi-equilibrium* description.

Coming back to the PES; in general, it is a multidimensional surface which shows the potential resulting from the interaction of all the atoms in the reacting molecules as a function of the configuration of the atomic nuclei, for all the relevant configurations that could occur during the reaction. To illustrate this surface, for practical reasons, we should choose a simple case. One of the first surfaces calculated has been the hydrogen exchange reaction H_2 + H, with some further simplification, namely in its *collinear* form. This means that the reaction

$$H_2 + H \rightarrow H + H_2 \tag{2.9}$$

is restricted to take place in a way when the three hydrogen atoms involved in the reaction are located always along a line; *i. e.* the reaction proceeds via a "head-on" collision only. This restriction enables us to uniquely specify the configuration by two interatomic distances only, and, as a result, we can visualise the emerging PES in a tridimensional diagram. (Without the collinear restriction, we would have to use a third coordinate, *e. g.* an angle characterizing the orientation of the H_2 molecule with respect to the H atom.)

Let us choose the distances of the two terminal hydrogen atoms from the medial one as the two coordinates to describe the configuration. Identifying the hydrogen atoms by the letters A, B and C, one distance is between the nuclei A–B, the other one between those of B–C. (Let us call them simply as distance A–B and distance B–C.) The PES diagram constructed this way shows the potential energy as a function of these two distances. The reaction itself can be represented by the simple scheme seen on Figure 2.2.

Prior to the reaction, the (non-rotating) molecule AB and the lone hydrogen atom C approach each other along the direction of the bond between the atoms A and B. When the actual collision occurs, the newly formed (non-rotating) molecule BC and the atom A recoil, according to the laws of the conservation of energy and momentum.

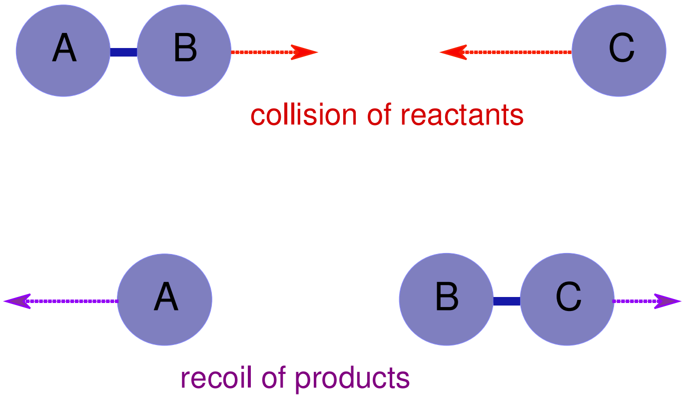

Figure 2.2 Schematic diagram of the collinear reaction $H_2 + H \rightarrow H + H_2$. Top: colliding reactants before reaching the transition state. Bottom: recoiling products after having passed across the transition state. (Keszei 2015)

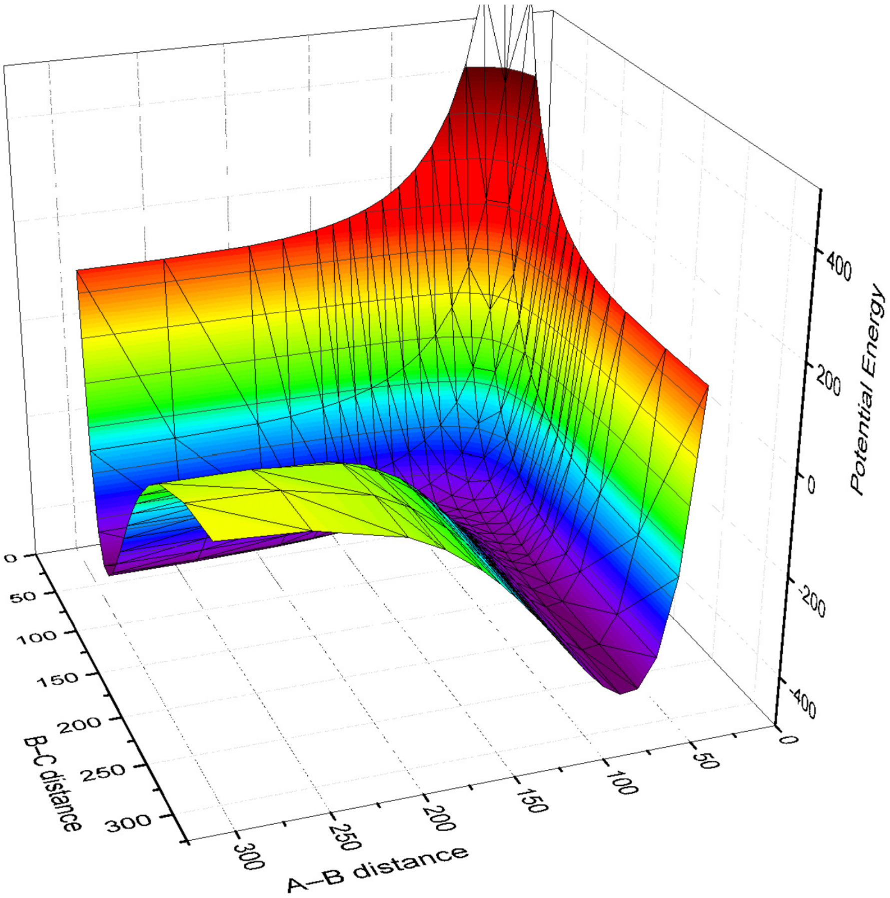

Figure 2.3 Potential energy surface of the collinear reaction $H_2 + H \rightarrow H + H_2$: potential energy of three collinearly arranged hydrogen atoms (A, B and C) as a function of interatomic distances. Sections at 300 pm A–B or B–C distance are practically identical with the diatomic potential energy curve of a hydrogen molecule. (Czakó 2015; plotted by Keszei 2015)

We can track this reaction on the PES diagram in terms of the two distances chosen. In the region of configurations characteristic of the reactant molecule AB, the section of the PES along the direction A–B at constant (large) distances B–C is expected to show the same shape as that of an equilibrium ground state potential energy curve of a hydrogen molecule, as seen on Fig. 2.1. We also expect a similar shape of the section along the direction B–C at large distances A–B. The PES shown as a perspective on Fig. 2.3 has been constructed based on an efficient quantum mechanical calculation.[2] At small internuclear distances, a low valley is clearly seen which extends from the reactant valley at small A–B and large B–C distances (representing the reactant AB molecule and a distant C atom) to the product valley at large A–B and small B–C distances (representing the product BC molecule and a distant A atom).

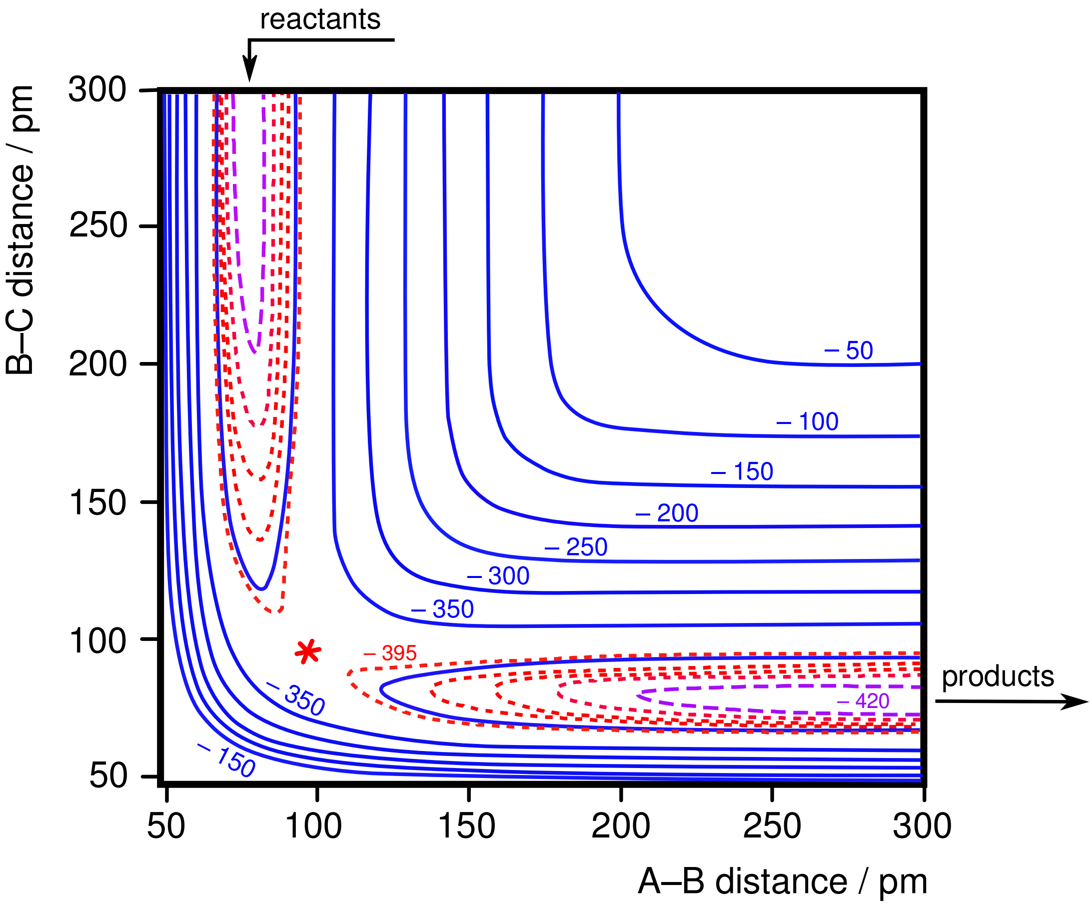

Figure 2.4 Contour map of the potential energy surface of the collinear reaction $H_2 + H \rightarrow H + H_2$. The distance in level of the blue continuous lines is 50 kJ/mol. Red dashed lines show elevations ten times closer, at 5 kJ/mol distances. (Czakó 2015; plotted by Keszei 2015)

On the perspective seen in the figure, we cannot have a proper look inside the bent valley. However, – similarly to topological maps – we can project the tridimensional PES into a contour

---

[2] The method of calculations has been the full configuration interaction using augmented correlation-consistent polarised basis; abbreviated as full-CI / aug-cc-pVDZ. (Calculations have been performed by Gábor Czakó. All further data concerning this reaction are from these calculations.)

map which can be completely shown on the printed page or a flat screen. This can be done by projecting lines connecting equipotential loci onto a plain which is horizontally oriented in the tridimensional diagram. This contour diagram contains all information about the fully tridimensional surface. As the bottom of the bent valley in this case is quite shallow, the diagram shown in Fig. 2.4 is constructed in a way that contour lines at the bottom of the valley are closer to each other (red dashed lines; at 5 kJ/mol level differences) than those further from the bottom of the valley (blue continuous lines; at 50 kJ/mol level differences).

2.2.2. Statistical formulation of the equilibrium constant

Within the context of the quasi-equilibrium transition state theory, it is presupposed that the reaction leading to the transition state is in thermodynamic equilibrium. We shall describe this equilibrium using molecular properties of the reacting species, based on the results of statistical thermodynamics. Before actually applying these results for the case of transition state formation, let us recall briefly relevant formulae to use for the calculation of the equilibrium constant of chemical reactions at constant temperature and pressure. For these circumstances we shall need partition functions in canonical ensembles.

A canonical ensemble can be characterised by its temperature, volume and composition. (This latter will be given as the *number* of molecules, instead of the amount of substances.) Accordingly, a canonical ensemble is such a collection of virtual states of a large number of particles, whose volume, temperature and number of particles is fixed. (It represents a thermodynamic system of fixed volume and fixed composition which is in thermal equilibrium with a thermostat at fixed temperature.) Alternatively, the canonical ensemble can also be called an N, V, T ensemble. On this ensemble, the *free energy function*

$$F(T,V,N) = -k_{\mathrm{B}}T \ln Q(T,V,N) \tag{2.10}$$

can easily be calculated. The function $Q(T, V, N)$ is called the *canonical partition function*, and k_{B} is the *Boltzmann constant*. This macroscopic partition function can be calculated from the *molecular partition functions* of the constituting molecules as

$$Q = \prod_{k=1}^{N} q_k \quad , \tag{2.11}$$

where N is the total number of molecules and q_k is the (full) molecular partition function.

Assuming that the occupancy of any molecular mode is independent of the occupancy of other molecular modes, the molecular partition function can be factorised into the product of the translational, rotational, vibrational and electronic contributions:

$$q_k = q^{\mathrm{trans}} \cdot q^{\mathrm{rot}} \cdot q^{\mathrm{vib}} \cdot q^{\mathrm{el}} \tag{2.12}$$

In such cases, a suitable method to calculate the full molecular partition function is to calculate the translational, rotational, vibrational and electronic contributions separately.

The translational partition function in three dimensions is given by

$$q^{\mathrm{trans}} = \left(\frac{2\pi m k_{\mathrm{B}} T}{h^2} \right)^{3/2} \cdot V \ , \tag{2.13}$$

where V is the volume of the container, m the mass of the molecules and h the Planck constant. It is convenient to introduce the *thermal wavelength* Λ:

$$\Lambda = \frac{h}{\sqrt{2\pi m k T}} \tag{2.14}$$

Applying this shorthand notation, the translational partition function can be written in a compact way as:

$$q^{\mathrm{trans}} = \frac{V}{\Lambda^3} \tag{2.15}$$

Typical values of the translational partition function are rather large; in 100 cm^3 oxygen gas at 25 °C, $\Lambda = 17.8$ pm and the value of q_{trans} is $1.773 \cdot 10^{30}$.

The rotational partition function of a molecule of general shape is the product of the partition functions related to the three independent rotational modes:

$$q^{\mathrm{rot}} = \frac{1}{\sigma} \left(\frac{k_{\mathrm{B}} T}{h c} \right)^{3/2} \sqrt{\frac{\pi}{ABC}} \tag{2.16}$$

Here, A, B and C are the rotational constants associated to the three rotational axes, and c is the velocity of light in vacuum. The Greek letter σ denotes the *rotational symmetry factor*. Its significance is that, when the molecule rotates through 360°/σ degrees, it results in a configuration that is indistinguishable from the one from which it started, and the same configuration occurs σ times during a complete rotation. This symmetry – unlike energy degeneration – decreases the number of states, thus also reduces the partition function. In case of the ammonia molecule, $\sigma = 3$, while for a methane molecule, it is 12, as this molecule has four threefold rotational axes. It is also worth noting that the indistinguishable rotational state also occurs at a rotation of 180 degrees for *homonuclear* diatomic molecules, thus the value of σ is 2 for them. A general (heteronuclear) diatomic molecule has only two (equivalent) rotational axes, thus its rotational partition function is simpler:

$$q_{\mathrm{lin}}^{\mathrm{rot}} = \frac{k_{\mathrm{B}} T}{h c B} \tag{2.17}$$

In case of a homonuclear rotor, this should be divided by two. At ambient temperatures, there are quite a lot of rotational states occupied. Thus, the value of the rotational partition function is also relatively high, at the order of magnitude of a few thousands.

The vibrational molecular partition function of a harmonic oscillator of frequency v can be given as:

$$q^{\text{vib}} = \frac{1}{1 - e^{-\frac{h\nu}{kT}}} \tag{2.18}$$

The vibrational partition function has the same expression for all (harmonic) normal modes. Thus, the full vibrational partition function can be written in the form

$$q^{\text{vib}} = q^{\text{vib}}(1) \cdot q^{\text{vib}}(2) \cdot \ldots \cdot q^{\text{vib}}(n) \ , \tag{2.19}$$

where the n different factors comprise all normal modes. A molecule constituted of K atoms can be considered as a mechanical object of K point masses, thus it has $3K$ mechanical degrees of freedom. Three of those degrees describe translation, two (if the molecule is linear) or three (if the molecule is nonlinear) describe rotation. Thus a linear molecule has $3K - 5$, a nonlinear multiatomic molecule has $3K - 6$ vibrational degrees of freedom, and the same number of (independent) normal vibrational modes. As vibrational excitation needs considerable energy compared to the available thermal energies at ambient temperatures, the typical value of $q^{\text{vib}}(i)$ for normal modes at ambient temperature is between 1 and 3.

When calculating the electronic partition function, we should take into account the following. For most molecules, the energy of the lowest electronically excited state is high enough that at ambient and not too much higher temperatures, excited states contribute to a negligible amount to the electronic partition function. As a consequence, its value can be considered as 1. However, there are some important exceptions. There exist molecules whose electronic ground state is degenerated. The electronic partition function for them is identical to their *electronic degeneracy* g^{E} instead of the usual 1:

$$q^{\text{el}} = g^{E} \tag{2.20}$$

Molecules whose first electronic excited state is such that its energy is very close to that of the ground state are also an interesting exception. An example which exhibits both properties is the molecule NO, having two degenerate ground states and two low-lying excited states. Setting its ground state energy at zero, its partition function is

$$q^{\text{el}}_{\text{NO}} = 2 + 2e^{-\frac{\varepsilon^*}{kT}} \ , \tag{2.21}$$

Where ε^* is the energy of the excited state with respect to that of the ground state.

Having calculated the contributions to the molecular partition function as described above, for a one-component gas – if the independent occupancy applies – the macroscopic partition function of a system of N (identical) molecules can be written in the following form:

$$Q = \frac{1}{N!}\left(q^{\text{trans}} \cdot q^{\text{rot}} \cdot q^{\text{vib}} \cdot q^{\text{el}}\right)^{N} \tag{2.22}$$

The division by N! is necessary for the reason that gas molecules are indistinguishable from one another. As a consequence, there are as much indistinguishable states in a gas as the possible arrangement of gas molecules exchanging them with each other. The number of these permutations is exactly N! If the gas has more than one component, containing N_j molecules of the j-th kind, the partition function naturally becomes

$$Q = \prod_{j=1}^{K} \frac{1}{N_j!}\left(q_j^{\text{trans}} \cdot q_j^{\text{rot}} \cdot q_j^{\text{vib}} \cdot q_j^{\text{el}}\right)^{N_j}, \tag{2.23}$$

where K is the number of components. It is worth noting that the factorisability of the molecular partition functions is strictly valid only for an ideal gas. In case this approximation cannot be done within a reasonable error, the macroscopic partition function Q is usually computed using numerical simulations on canonical ensembles containing a great number of molecules. For the sake of simplicity, in the remaining part of this text we shall use the ideal gas approximation.

We can calculate the chemical equilibrium constant K at constant temperature and pressure for a general reaction $\sum_{i=1}^{R} \nu_i A_i = 0$ using the molecular canonical partition functions the following way:

$$K = \prod_{i=1}^{R}\left(\frac{q_i^{\ominus}}{N_{\text{A}}}\right)^{\nu_i} \cdot e^{-\frac{E_0}{RT}} \tag{2.24}$$

In this equation, $q_i^{\ominus}$ stands for the *standard molecular partition function* of component i in the *molar volume* at the standard pressure. Accordingly, the number of particles is replaced by the Avogadro constant N_{A}. E_0 in the exponent is the *zero point energy of the reaction*. We should emphasize again that Eq. (2.24) is strictly valid only if the reaction mixture behaves as an ideal gas. However, the equation is generally also valid if the fraction $q_i^{\ominus}/N_{\text{A}}$ is replaced by the correct molar partition function $Q_i^{\ominus}$:

$$K = \prod_{i=1}^{R}\left(Q_i^{\ominus}\right)^{\nu_i} \cdot e^{-\frac{E_0}{RT}} \tag{2.25}$$

E_0 in the exponent remains the zero point energy of the reaction. In case of non-independent molecular modes, the standard molar partition function $Q_i^{\ominus}$ can be calculated the above mentioned way, by numerical simulations.

From a chemical point of view, the previous two equations have paramount importance. If the reacting molecules are not too large, quantum chemical methods can provide the energy of all molecular modes to a good precision, thus we can calculate relevant partition functions. For large molecules, we can use spectroscopic data to calculate energies of molecular modes, thus we can also calculate equilibrium constants. If an equilibrium constant is known from experiments for a certain reaction, the equilibrium constant for a related reaction can also be calculated using the statistical expression. In this case, we should factorise the partition function as the product of the same contributions and the modified contributions due to changes in some reactants or products. To calculate the unknown equilibrium constant, it is sufficient to know the ratio of the modified contributions to the original ones. Eq. (2.24) has also a great importance in chemical kinetics; the quasi-equilibrium transition state theory is based on this expression.

Due to the great importance of this expression, let us show the actual form of the general equation for two commonly occurring reactions. For a *bimolecular reaction* (leading to a single product) according to the stoichiometric equation

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} \ , \tag{2.26}$$

the equilibrium constant reads as follows:

$$K = \frac{N_\mathrm{A} q_\mathrm{C}^{\ominus}}{q_\mathrm{A}^{\ominus} q_\mathrm{B}^{\ominus}} e^{-\frac{E_0}{RT}} \tag{2.27}$$

For a *unimolecular reaction* (leading to a single product) according to the stoichiometric equation

$$\mathrm{A} \rightleftharpoons \mathrm{B} \ , \tag{2.28}$$

we can write the equilibrium constant as

$$K = \frac{q_\mathrm{B}^{\ominus}}{q_\mathrm{A}^{\ominus}} e^{-\frac{E_0}{RT}} \ . \tag{2.29}$$

As we can see, the Avogadro constant does not figure in the formula if the sum of the factors in the numerator and the denominator are the same.

2.2.3. The quasi-equilibrium transition state theory

The underlying assumptions of this theory are the following. Let us suppose that the (overall) reaction is in equilibrium. This equilibrium is maintained by the colliding molecules AB and the atoms C – in case they have enough energy – reaching the saddle point in the valley (marked by a red asterisk in the contour map; this is the transition state) which is the highest potential state along the bottom of the valley. (Note that the progress of the reaction on the PES is not represented by the trajectory of the three nuclei – as seen on Fig. 2.2 – but by the trajectory of one single point representing the configuration of the three nuclei.) According to the assumption of quasi-equilibrium, this state is in a thermodynamic equilibrium with the reactants. If the overall reaction is in equilibrium, there is also a thermodynamic equilibrium between the transition state and the products. We can represent this overall equilibrium with the following stoichiometric scheme:

$$H_2 + H \rightleftharpoons H\cdots H\cdots H \rightleftharpoons H + H_2 \tag{2.30}$$

In the transition state, the terminal hydrogen atoms are at equal distances from the medial one, which is considerably large (94.5 pm) compared to the equilibrium distance in an H_2 molecule, which is 76.2 pm. Accordingly, the two bonds in this state are quite loose and they can easily break. To get to this state, the reactant molecule AB and the atom C have to expend 38.8 kJ/mol from their energy. This energy barrier between the reactant valley and the product valley will be called simply as the *energy barrier* – conform to the usual wording. The energy barrier can also be visualised in a two-dimensional plot if the projection to a horizontal plane of the line at the very bottom of the valley is “stretched” into a linear coordinate, and the potential energy is plotted as a function of the configurations represented by this coordinate.

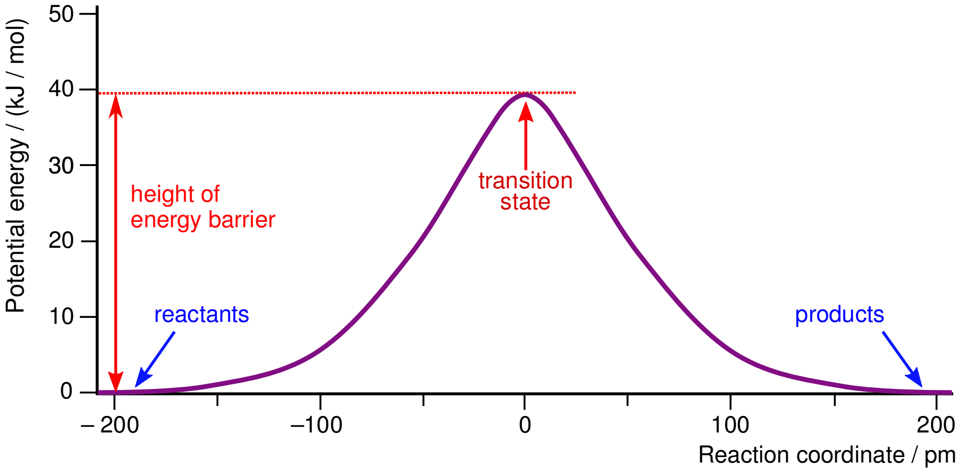

Figure 2.5 Change of potential energy during the collinear reaction $H_2 + H \rightarrow H + H_2$. The reaction coordinate is the trajectory along the bottom of the valley in the PES. The scale is chosen such that its value is zero at the transition state; it is negative in the direction of the reactants and positive in the direction of the products. (Czakó 2015; plotted by Keszei 2015)

Reaction (2.30) represents the reacting mixture when reactants and products are in thermodynamic equilibrium. The quasi-equilibrium transition state theory assumes that the first equilibrium is maintained (in a statistical thermodynamic sense) also in the case of a complete removal of the products from the reacting mixture, *i. e.* when the backward reaction cannot occur. A second assumption is that, when the reactants arrive at the transition state, they always become products. (It can be interpreted on the PES that once the reactants have "climbed" to the saddle point, their momentum towards the product direction will move them across the potential barrier. This picture is formed based on a classical mechanics description, not on a quantum mechanical one.) Consequently, the unidirectional reaction model (from left to right) can be represented with the following stoichiometric scheme:

$$\mathrm{H_2 + H \rightleftharpoons H\cdots H\cdots H \rightarrow H + H_2} \tag{2.31}$$

Applying these two assumptions, we can calculate the rate of reaction such that we first calculate the concentration of the transition state based on the first equilibrium, then we calculate the rate of dissociation of the transition-state complex into the products.

Let us begin with the description of the first equilibrium. The equilibrium constant can be written the following way:

$$K^{\ddagger} = \frac{[\mathrm{ABC}^{\ddagger}]}{[\mathrm{AB}][\mathrm{C}]}\ , \tag{2.32}$$

where the reactant H_2 molecule is denoted by AB, the reaction partner H atom by C, and the transition state by $\mathrm{ABC}^{\ddagger}$. (From here on, we shall use the usual "double dagger" sign as a superscript to denote the transition state.) From the equilibrium constant, it is easy to express the concentration of the transition state molecules:

$$[\mathrm{ABC}^{\ddagger}] = K^{\ddagger}[\mathrm{AB}][\mathrm{C}] \tag{2.33}$$

We shall express next the equilibrium constant $K^{\ddagger}$ using the statistical expression:

$$K^{\ddagger} = \frac{N_A\, q^{\ominus}_{\mathrm{ABC}^{\ddagger}}}{q^{\ominus}_{\mathrm{AB}}\, q^{\ominus}_{\mathrm{C}}}\, e^{-\frac{E_0}{RT}} \tag{2.34}$$

Upon substitution of this into the previous expression, we get the statistical expression for the concentration of the transition state:

$$[\mathrm{ABC}^{\ddagger}] = \frac{N_A\, q^{\ominus}_{\mathrm{ABC}^{\ddagger}}}{q^{\ominus}_{\mathrm{AB}}\, q^{\ominus}_{\mathrm{C}}}\, e^{-\frac{E_0}{RT}}\, [\mathrm{AB}][\mathrm{C}] \tag{2.35}$$

The decomposition of the transition state molecules into product(s) proceeds by the breaking of the bond between the atoms A and B. In the course of this bond breaking, the stretching vibrational mode of the bond A···B becomes a translational mode, as the two atoms will not approach each other anymore – as they did during the vibrational motion in the molecule AB – but separate definitely. This dissociation can be described in two ways. We could factor out the molecular partition function of the stretching vibrational mode of A···B form the standard molecular partition function $q^{\ominus}_{\mathrm{ABC}^{\ddagger}}$, and substitute the product of the translational partition functions of A and BC in place of it. (This can be done based on the factorisation rule that full partition functions can be given as the product of the partition functions of independent molecular modes.) We can derive the formula describing the dissociation in a more simple way taking into account that the dissociation proceeds with the frequency of the stretching mode of the loosened A···B bond. This loose bond further loosens during dissociation (as the atom A and the molecule BC are separating). Thus we can assume that, by factoring out the standard molecular partition function of the stretching mode of this bond, we can apply the approximation for a low value of the vibrational energy $h\nu$ with respect to the average kinetic energy $k_{\mathrm{B}}T$ equipartioned at two degrees of freedom. The vibrational molecular partition function of a harmonic oscillator of frequency ν can be given as:

$$q^{\mathrm{vib}} = \frac{1}{1 - e^{-\frac{h\nu}{kT}}} \tag{2.36}$$

Taking into account the inequality $h\nu << k_{\mathrm{B}}T$ we can use the approximation of the exponential term at exponents much smaller than 1, which gives the result of $1 - k_{\mathrm{B}}T$. Substituting this into the vibrational partition function leads to the following expression:

$$q^{V} = \frac{1}{1 - \left(1 - \frac{h\nu}{kT}\right)} = \frac{k_B T}{h\nu} \tag{2.37}$$

Let us write this results in place of the outfactored partition function:

$$q^{\ominus}_{\mathrm{ABC}^{\ddagger}} = \frac{k_B T}{h\nu}\, q^{\ominus}_{\ddagger} \tag{2.38}$$

Here and further on, $q^{\ominus}_{\ddagger}$ denotes the *truncated* standard molecular partition function which does not contain the contribution of the vibrational mode responsible for the dissociation of the transition state. Let us substitute this product in place of the full partition function $q^{\ominus}_{\mathrm{ABC}^{\ddagger}}$:

$$[\mathrm{ABC}^{\ddagger}] = \frac{k_B T}{h\nu}\, \frac{N_A\, q^{\ominus}_{\ddagger}}{q^{\ominus}_{\mathrm{AB}}\, q^{\ominus}_{\mathrm{C}}}\, e^{-\frac{E_0}{RT}}\, [\mathrm{AB}][\mathrm{C}] \tag{2.39}$$

At the left side of this equation we can see the concentration of the transition state molecules, while in the denominator of the first factor on the right side is the frequency of their dissociation. This frequency can be interpreted as the number of molecules that dissociate within a unit of time (in case of using SI units, within a second). Multiplying the number of transition state molecules

[ABC‡] in unit volume by the frequency ν, we get the number of molecules per unit time in unit volume, which is exactly the rate of the reaction:

$$R = \nu[\mathrm{ABC}^‡] = \frac{k_B T}{h} \frac{N_A q_‡^\ominus}{q_{\mathrm{AB}}^\ominus q_{\mathrm{C}}^\ominus} e^{-\frac{E_0}{RT}} [\mathrm{AB}][\mathrm{C}] \tag{2.40}$$

It is interesting to see that we have got a similar expression for the reaction rate as with the collision theory; the rate of the reaction can be written as $R = k\ N_\mathrm{A} N_\mathrm{B}$. However, the rate constant k is considerably different from what we have derived based on the collision theory:

$$k = \frac{k_B T}{h} \frac{N_A q_‡^\ominus}{q_{\mathrm{AB}}^\ominus q_{\mathrm{C}}^\ominus} e^{-\frac{E_0}{RT}} \tag{2.41}$$

We can also discover in this expression the striking presence of the account of molecular structure; information concerning details of the structure of the reactant molecule and the transition state is represented by their molecular partition functions. The content of partition functions comprises the contribution of all molecular modes. Thus, in addition to the translation which is accounted for by the collision theory, transition state theory takes into account the rotational, vibrational and electronic properties of the reacting molecules. Due to this feature, we can expect better agreement with experimental rate coefficients than in the case of collision theory.

The quasi-equilibrium description assumes that the configuration of the nuclei passes across the energy barrier exactly at the saddle point, which is equivalent to a propagation of the configuration along the very bottom of the PES valley. The saddle point has maximal potential energy along this reaction coordinate, while minimal potential energy at any other direction. Thus, if the configuration point propagates exactly along the bottom of the valley, the highest point (from the horizontal reactant valley) along this curve can be considered as the height of the barrier.

However, it is easy to show that this cannot be the case. It is well known that molecules do vibrate even at 0 K temperature – in this case, at their vibrational ground state level. In a relatively wide range of low temperatures above 0 K, only the ground state is populated, but this vibration is inevitable. Accordingly, the interatomic distance in molecules changes while oscillating around the equilibrium bond distance and moving back and forth on the potential energy curve of Fig. 2.1. This oscillation continuously changes the bond distance within the H_2 molecule also when it approaches the other reactant, the H atom. In a similar manner, the reaction product H_2 molecule also vibrates and continuously changes bond distance. Figure 2.6 illustrates the two cases. In the left panel, we can see the hypothetical non-vibrating trajectory traced by the dashed line, while the right panel shows the realistic trajectory according to oscillating H_2 molecules. We can clearly see that different trajectories with different initial vibrational phases will not cross the barrier at the saddle point but in its extended vicinity, depending on the actual phase and amplitude of the vibration. Accordingly, the "transition state" along the realistic trajectory taking into account molecular vibration is always at a different location, but we can always find the maximum potential point along any trajectory.

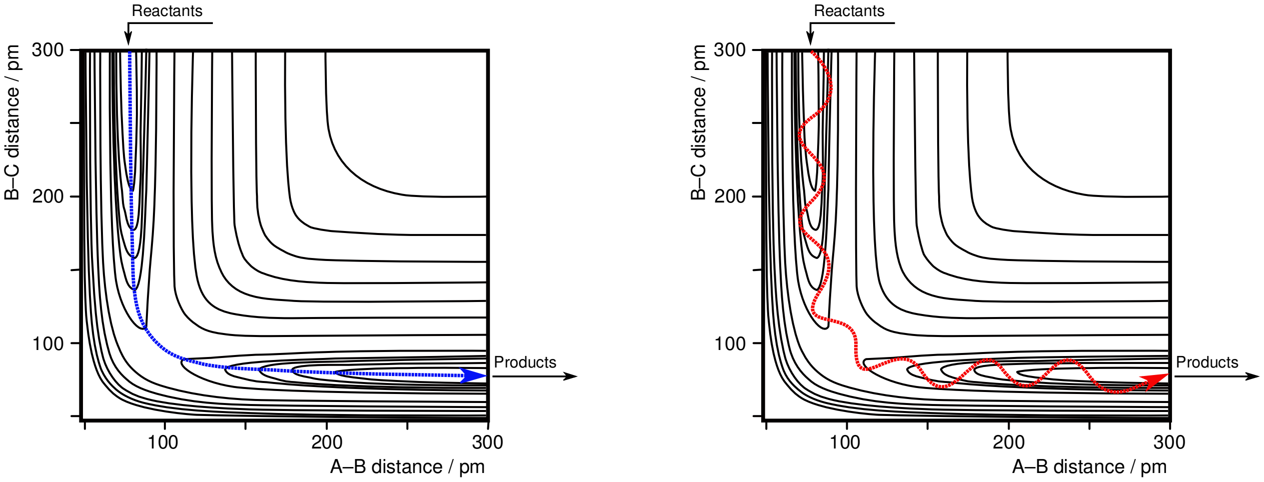

Figure 2.6 Reaction trajectories of the collinear reaction $H_2 + H \rightarrow H + H_2$ on the potential energy contour map. The left panel shows the hypothetical minimum potential trajectory that is located at the very bottom of the potential valley. The right panel shows the trajectory which is in accordance with the real-life H_2 molecule that oscillates at the actual vibrational frequency. (Keszei 2015)

To describe this more realistic procedure, we should take into account all possible trajectories with different phases and calculate the overall probability that reactants with given initial energy trespass the barrier. Performing these calculations we get the results that (at constant temperature and volume), if the probability of the configuration point at the maxima of actual trajectories corresponds to the Boltzmann distribution, we get back the quasi-equilibrium result for the reaction rate. To maintain the Boltzmann distribution throughout the reaction, it is necessary that the reaction itself be somewhat slower than the energy exchange between molecules, which proceeds via collisions. In this case, the population according to the Boltzmann distribution would not be altered.

Taking into consideration the effects due to molecular vibrations, we still did not change the description concerning its validity only for collinear reaction. In reality, reactant H_2 molecules not only oscillate but also *rotate* during the reaction, just like the newly formed H_2 molecules. Evidently, in addition to the two distances, this necessitates to take into account the angle between them, which will also continuously change during the reaction. This being an additional coordinate, the corresponding PES would be four-dimensional, thus not easy to visualise. According to detailed calculations, the smallest potential energy gap is experienced by the molecules having head-on (collinear) collisions. However, as every orientation is possible between gas molecules, we should also account for them. Another complication arises from the fact that classical mechanical calculations are not really valid for the description of molecular motion; we should use quantum mechanical description.

As we know, proper quantum mechanical calculations provide a true description of the behaviour of molecular motions. However – even if we apply the Born-Oppenheimer approximation and describe the reaction as if the nuclear configuration would have moved on the PES calculated for stationary, relaxed electrons around the nuclei – there are no sharp trajectories in quantum mechanics due to the uncertainty principle. The reality is rather a temporal series of state functions, which we could only get by resolving time-dependent Schrödinger equations. If the structure of molecules is more complex than in the simple case of the hydrogen exchange reaction, the topology of the PES also becomes more complicated. However, within the Born-Oppenheimer approximation, we can still define the transition states as a multidimensional hyperplane which divides the PES into two regions; that of the reactants and that of the products. If the wave packet representing the motion of reactants crosses this hyperplane, they will become products. If it would not pass the hyperplane (but gets “reflected”) then there will be no reaction. In quantum mechanics – and in reality of molecular motions as well – there is also a possibility for reaction via *tunnelling*. This tunnelling possibility plays an important role for small molecules (*e. g.* H_2 or D_2) especially at low temperatures. Along the intersection of the dividing hypersurface we can always find a saddle point that can be interpreted as the transition state. Once we have found this saddle point, we can substitute the truncated partition function $q_{\ddagger}^{\ominus}$ and the zero point reaction energy E_0 that correspond to this state into Eq. (2.40), and this always provides the TST reaction rate within the framework of quasi-equilibrium description. Of course, the experimental reaction rate will not necessarily agree with this calculated value, as it contains all the shortcomings of the approximations used.

Despite these shortcomings, quasi-equilibrium transition state theory is even nowadays used to describe molecular details of reactions. It reflects the qualitative properties well, and helps to understand the molecular background of reactions. As we shall discuss later in this book, it also provides a useful basis to derive temperature and pressure dependence of reaction rates. For this reason, we shall often refer to this theory when discussing molecular details of chemical reactions.

It is also worth to sum up essentials of the quasi-equilibrium TST here. This theory reflects very well molecular events happening during reactions, and can also be used for quantitative estimation of reaction rates. We can generalise its formalism in terms of the stoichiometric scheme

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB}^{\ddagger} \rightarrow \text{products} . \qquad (2.42)$$

The reaction rate coefficient related to this scheme can be calculated as follows:

$$k = \frac{k_B T}{h} \frac{N_A \, q_{\ddagger}^{\ominus}}{q_{\mathrm{A}}^{\ominus} \, q_{\mathrm{B}}^{\ominus}} e^{-\frac{E_0}{RT}} \qquad (2.43)$$

In this expression, k_B is the Boltzmann constant, T is temperature, N_A the Avogadro constant, $q_{\ddagger}^{\ominus}$ the truncated standard molecular partition function of the transition state $AB^{\ddagger}$ not including the vibration along the reaction coordinate. $q_A^{\ominus}$ and $q_B^{\ominus}$ are the standard partition functions of the reactant molecules and E_0 is the molar energy of the activation reaction (*i. e.* that of the formation of $AB^{\ddagger}$ from A and B) at 0 K temperature. Accordingly, R is the molar gas constant.

Let us also recall the assumptions underlying the derivation of this result.

1. The Born-Oppenheimer approximation is applied to construct the PES; *i. e.* every point on the PES is considered such that electrons are always relaxed to their equilibrium state. In other words, nuclear and electronic motions are separated.
2. Thermal equilibrium is supposed to apply; *i. e.* the Boltzmann distribution applies all over the PES.
3. Even if there is no equilibrium between reactants and products, an equilibrium conform to the Boltzmann distribution is maintained between the reactants and the transition states.
4. Atomic configurations that have crossed the transition state in the direction of products will become products (*i. e.* they do not turn back from the top of the energy barrier).
5. The molecular mode responsible for the dissociation of the transition state can be separated from all other molecular modes and treated as a translational mode upon dissociation.

2.2.4. Dynamical description of the transition state theory

As we have seen, the configuration point of the reacting system typically does not pass across the saddle point but in its vicinity, at different locations depending on the vibrational phase of the reacting molecule(s). Accordingly, a correct account of the reaction rate can only be done by calculating the probability of the reactants to cross the barrier towards the products along all possible trajectories, and summing the contribution for all trajectories compatible with the state of the reactant molecules. To do this calculation, we should also interpret the notion of transition state somewhat differently than the saddle point itself.

Transition states in this new sense form a hyperplane in the PES diagram, whose dimension is less by one than that of the PES surface. This hyperplane is defined as above, by the property that, when reactant configurations cross it towards the product valley, they always become products. (On contour maps representing the collinear $H_2 + H \rightarrow H + H_2$ reaction, transition states are on a diagonal straight line connecting the lower left and upper right corners. It represents a two-dimensional straight plane on the tridimensional PES.) Transition states are thus always the highest energy points on the actual trajectory; from these points, molecules represented by the configuration point move downhills both “forward” and “backward” on the PES. Extending the quasi-equilibrium description of the TST we can say that, in order to calculate the reaction rate, we should calculate the concentration on the hyperplane of transition states and also the rate at which they cross the hyperplane to become products. However, this time we have to consider the dependence of the concentration on the actual position as well as the actual momentum of the molecules in that state.

To perform the calculations, let us introduce the following notation. The reaction coordinate (which is perpendicular to the hyperplane of the transition states) will be denoted by s, and the momentum along this coordinate by p_s. Let us denote the value of the s coordinate at the transition state (on the hyperplane) by $s^{\ddagger}$. We shall describe the motion of the configuration point not in a configuration space, but in the *phase space*, comprising also the momentum coordinates in addition to the spatial coordinates. Let us denote the probability density of the states in this phase space by $f^{\ddagger}$. This probability density function has the property that it describes the occupation by a state of a suitable quantum number n within an infinitesimal phase space element as

$$f^{\ddagger} ds dp_s = \frac{ds\, dp_s}{h} \frac{e^{-\frac{E}{k_B T}}}{q} \quad . \tag{2.44}$$

In this expression, the available number of quantum states (the *density of states*) in the phase space element $ds\ dp_s$ is $\frac{ds\, dp_s}{h}$, while the following fraction is a factor according to the Boltzmann distribution, q being the partition function of the corresponding state. The energy in the exponent at the location $s^{\ddagger}$ can be given the following way:

$$E = E_n(s) + \frac{p_s^2}{2\mu} + V_1(s) \tag{2.45}$$

In this equation, $E_n(s)$ is the energy contained in the modes associated with intermolecular degrees of freedom, $\frac{p_s^2}{2\mu}$ is the translational energy (the kinetic energy along the s coordinate) $V_1(s)$ the minimal potential energy at the intersection of the relevant s coordinate and the hypersurface. (The latter is exactly the energy of the PES at the given location.)

To calculate the reaction rate of the reactants in a state with quantum number n, we divide the elementary probability $f^{\ddagger} ds dp_s$ by ds (thus obtaining the density of states relative to unit length), then we multiply it by the velocity $\frac{ds}{dt}$ along the s coordinate. Finally, we have to integrate the expression thus obtained for all possible momenta that is directed from the reactants towards the products (*i. e.* $0 < p_s < \infty$), and sum the result for all possible quantum numbers n. The resulting expression for the rate constant is the following:

$$k = \sum_{\forall n} \int_0^{\infty} \frac{1}{hq} \frac{ds}{dt} e^{-\frac{\left(E_n(s) + \frac{p_s^2}{2\mu} + V_1^{\ddagger}\right)}{k_B T}} dp_s \tag{2.46}$$

Before actually performing the necessary operations let us make a simplification by applying the relation between the derivative (the velocity along the *s* direction) and the momentum p_s:

$$\frac{d\left(\frac{p_s^2}{2\mu}\right)}{dp_s} = \frac{p_s}{\mu} = \frac{ds}{dt} \tag{2.47}$$

We can easily see that the expression $\frac{ds}{dt}dp_s$ can be replaced by $dx = d\left(\frac{p_s^2}{2\mu}\right)$. Let us rewrite the equation (2.46) for the rate constant accordingly, and extract constant factors before the integration:

$$k = \sum_{\forall n} \frac{1}{hq} e^{-\frac{E_n^\ddagger}{k_B T}} e^{-\frac{V_1^\ddagger}{k_B T}} \int_0^\infty e^{-\frac{x}{k_B T}} dx \tag{2.48}$$

The primitive function of the integrand is $-k_B T\, e^{-\frac{x}{k_B T}}$, thus the result of the definite integration becomes $k_B T$. Let us substitute this into the expression of the rate constant and take into account that – except for the exponential function containing $E_n^\ddagger$ – all factors are constant (*i. e.* independent of the value of the quantum numbers, including also the potential energy $V_1^\ddagger$, as it is the energy of the ground state reactants), thus they can be factored out from the summation:

$$k = \frac{k_B T}{h} \frac{1}{q} e^{-\frac{V_1^\ddagger}{k_B T}} \sum_{\forall n} e^{-\frac{E_n^\ddagger}{k_B T}} \tag{2.49}$$

Note that $\sum_{\forall n} e^{-\frac{E_n^\ddagger}{k_B T}}$ is identical to the partition function of the reactants located on the hypersurface, thus that of the transition state. Let us denote this partition function by $q_\ddagger$, as it does not contain the contribution related to the translational motion across the transition state hyperplane. Summing up the previous considerations, we can write the compact form of the rate coefficient obtained from the dynamical description of the TST as follows:

$$k = \frac{k_B T}{h} \frac{q_\ddagger}{q} e^{-\frac{V_1^\ddagger}{k_B T}} \tag{2.50}$$

Considering that $q^\ddagger$ is the truncated partition function of the transition state, q is the partition function of the reactants and $V_1^\ddagger$ the ground state (zero-point) energy of the formation of the transition state, we can conclude that this result is identical to that obtained with the quasi-equilibrium description of the TST. Obviously, at some point we “smuggled” the condition of equilibrium into our dynamical derivation. Well, carefully observing the above derivation we can discover that the probability density function of the states in the phase space has been chosen according to the Boltzmann distribution. In other words, we re-introduced the assumption that there is a thermodynamic equilibrium between the reactants and the transition state molecules. Thus we can conclude that, extending the transition state from the saddle point to its wider surroundings represented by the hypersurface discussed above does not influence the results of the calculations, provided that the Boltzmann distribution is valid for the transition state.

However, there is a net gain in information if we consider that the dynamic description provides a tool to calculate the rate coefficient even if the probability density of the transition states does not follow the Boltzmann distribution. This situation can be interpreted the way that, during the reaction, higher energy states will become partially emptied with respect to their occupancy according to the Boltzmann distribution. The reason for this is that molecular collisions and related energy distribution cannot compensate for the loss of energetic reactant molecules. However, if we know the actual probability density function that describes the density of states during the reaction, we can plug it in for $f^{\ddagger}$ and readily calculate the rate coefficient.

The practical problem is that determining the relevant probability density function is not an easy task. One of the possibilities is that we perform a numerical simulation of the reacting mixture by also taking into account the reaction itself. Obviously, once we make such a simulation, there is a possibility to directly obtain the rate coefficient from the simulation. Here we do not deal with such simulations but we would like to raise the awareness of the reader that – at the beginning of the 21st century – they are typically based on moving the configurations on a previously constructed PES. As we have seen when deriving the dynamical expression of the rate coefficient, the translational movement along the reaction coordinate has been treated in a classical way by considering exact values of momenta. Thus, most of the simulations are based on classical dynamics, but they can provide quite good results for the rate coefficient. There are sophisticated methods to mimic quantum mechanical calculations on the PES, which give better results.

The full quantum dynamical calculations do not even assume the Born-Oppenheimer approximation. They describe the dynamics of the reacting molecules by a time-dependent Schrödinger equation and calculate full trajectories that either are reactive, or not. A great number of such calculations are performed for all relevant reactant states, and the number of trajectories leading to reaction is divided by the total number of trajectories, thus approximating the probability of reaction, which is equivalent to the rate coefficient. However, the solution of a time dependent Schrödinger equation still has severe limitations. At the beginning of the 21st century, reliable rate coefficients can be obtained for gas phase reactions of reactants containing only a few atoms. For reactive systems containing not more than four (not too heavy) atoms, such rate coefficients can be even more precise than experimentally determined ones. It is expected that these limitations become less severe with the advent of more powerful computers and more efficient numerical methods in the future.

Acknowledgements

Figures marked by “Czakó 2015” have been constructed based on the computation results of the potential energy for the collinear reaction $H_2 + H \rightarrow H + H_2$ by Gábor Czakó, which is gratefully acknowledged here.

All the figures have been constructed or plotted by the author.

Suggested literature

M. J. Pilling, P. W. Seakins: Reaction Kinetics, Oxford University Press, 1995

J. I. Steinfeld, J. S. Francisco, W. L. Hase: Chemical Kinetics and dynamics, 2nd edition, Prentice Hall 1998

J. de Paula, P. W. Atkins: Physical Chemistry, 10th edition, Oxford University Press, 2014

E. S. Lewis (editor): Investigation of Rates and Mechanisms of Reactions
Part I: General Considerations and Reactions at Conventional Rates, 3rd edition, Wiley 1974