Chapter 3. Kinetic Calculations

3.1. Introduction

This chapter provides general background information to complement the kinetic calculations reported in Chapters 4 to 6. The following sections will provide an overview of the concepts and approximations behind transition state theory (TST), covering essential statistical thermodynamic topics such as the molecular partition function and its components, and the calculation of equilibrium constants. Tunneling calculations will also be covered, as a complementary part of quantum kinetic calculations on systems where light particles are transferred.

The rate constants for chemical reactions can show different temperature dependencies. Some reactions are reported to have negative activation energies. Several explanations for this phenomenon will be discussed. The consideration of the reactant complex formation has been one of the ideas proposed to explain this situation.

3.2. Essential statistical thermodynamics

Statistical mechanics bridges the gap between the microscopic world of molecules, atoms, electrons and photons, and the macroscopic world of thermodynamics and the properties of materials. The goal of this branch of physics, in which mechanics and probability theory are mixed, is the understanding and prediction of macroscopic phenomena and the calculation of macroscopic properties from the properties of the individual components of the system.

Statistical mechanics is based on either classical or quantum mechanics, with equilibrium and non-equilibrium versions. The branch dealing with thermodynamic properties is known as statistical thermodynamics, or more fully as equilibrium quantum statistical mechanics.[1]

The partition function is without any doubt the most important quantity in statistical thermodynamics. Once known as a function of the temperature, volume and number of particles in a system, all thermodynamic quantities, including heat capacities, entropies and equilibrium constants, can be calculated.[2]

The molecular partition function (Q) can be expressed as a sum over states (3.1), or a sum over energy levels, in which the degeneracy factor g_i has to be considered (3.2):

$$Q_{Total} = \sum_i \exp(-\frac{E_{T_i}}{k_B T}) \tag{3.1}$$

$$Q_{Total} = \sum_i g_i \exp(-\frac{E_{T_i}}{k_B T}) \tag{3.2}$$

In these expressions k_B is Boltzmann's constant, T is temperature and i is the index that numbers the states (3.1) or energy levels (3.2).

The partition function indicates the average number of energy levels (or states) that are thermally accessible to a molecule at the temperature of the system. At T = 0 K only the ground state is accessible and Q equals g_0, the degeneracy of the ground state, but at very high T, virtually all states are accessible, and Q is very large.

Since in statistical thermodynamics different ensembles (*i.e.*, collections of imaginary replications of the system) such as the canonical, microcanonical and grand canonical ensembles are defined for practical use, different kinds of partition functions refer to each of them.

As mentioned in the previous chapter, the total energy of a molecule can be expressed as a sum of contributions from the kinetic energy (E_K) of the nuclei and electrons, and the potential energy (E_P) of nuclear, electronic and electron-nuclear interactions:

$$E_T = E_K(\text{nuclei}) + E_K(\text{electrons}) + E_P(\text{nuclei}) + E_P(\text{electrons}) + E_P(\text{electrons} - \text{nuclei}) \tag{3.3}$$

This total energy can also be expressed by the sum of contributions from the different molecular modes of motion: translational (trans), rotational (rot), internal-rotational (int-rot), vibrational (vib) and electronic (elect):

$$E_T = E_{trans} + E_{rot} + E_{int-rot} + E_{vib} + E_{elect} \tag{3.4}$$

Strictly speaking the ground state energy of the molecule should be added to the above expression but it is usually excluded in standard textbooks.[3] The above expression is an approximation since, apart from translational motion, these modes are not completely independent. However, in most cases this approximation is satisfactory. Approximations that assume that two modes of motion are not coupled, *i.e.*, that do not interchange energy, are called adiabatic approximations. One such approximation, already mentioned in Chapter 2 (the Born-Oppenheimer approximation), allows the separation of electronic and vibrational motions. Another approximation of this kind is one in which the molecule is treated as a rigid body, permitting the separation of rotations and vibrations.

By combining expressions (3.2) and (3.4), the molecular partition function can be rewritten as:

$$Q_{Total} = \left(\sum_i g_i \exp(-\frac{E^i_{trans}}{k_B T})\right)\left(\sum_i g_i \exp(-\frac{E^i_{rot}}{k_B T})\right)\left(\sum_i g_i \exp(-\frac{E^i_{int-rot}}{k_B T})\right)\left(\sum_i g_i \exp(-\frac{E^i_{vib}}{k_B T})\right)\left(\sum_i g_i \exp(-\frac{E^i_{elect}}{k_B T})\right)$$

$$Q_{Total} = Q_{trans}\ Q_{rot}\ Q_{int-rot}\ Q_{vib}\ Q_{elec} \tag{3.5}$$

The different contributions to the total molecular partition function (that is dimensionless) have magnitudes that decrease in the following order: $Q_{trans} > Q_{rot} > Q_{int\text{-}rot} > Q_{vib} > Q_{elect}$. Each contribution can be investigated separately and can be calculated, in principle, from spectroscopic data.

3.2.1. ***Translational partition function***

The translational component of the total partition function must be calculated from a sum over all the translational energy levels available to a molecule confined to a cubic box of

volume V = RT/p (the molar volume of an ideal gas at temperature T and pressure p; R is the ideal gas constant):

$$Q_{trans} = \sum_i \exp(-\frac{E^i_{trans}}{k_B T}) \tag{3.6}$$

If the translational energy levels are considered to be very close to each other, this sum may be approximated by an integral to obtain expression (3.7):

$$Q_{trans} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V \tag{3.7}$$

where m is the mass of the molecule and h is Planck's constant. For the calculation of V the standard pressure, p^0 = 1 atm, will be used in the calculations presented in the next chapters.

Expression (3.7) is sometimes rewritten in a different form:

$$Q_{trans} = \frac{V}{\Lambda^3} \qquad \Lambda = \frac{h}{(2\pi m k_B T)^{1/2}} \tag{3.8}$$

The parameter Λ is called the thermal wavelength and is used to judge whether the approximation that led to the expression of Q_{trans} is valid. This is the case if many states are occupied, which requires Q_{trans} to be large. Λ must be small compared with the linear dimensions of the container. For example, for H_2 at 298 K, Λ = 71 pm and for a heavier molecule, O_2, Λ = 18 pm. The heavier the molecule the more satisfactory the approximation.

3.2.2. ***Rotational partition function***

A model system that approximately represents the rotation of a diatomic molecule is the rigid rotor. In this model the molecule is considered a central-force system consisting of two masses with a fixed interparticle distance. In such a model it is assumed that when the molecule rotates no vibration occurs, and *vice versa*. This model, when extended to a polyatomic system, is referred to as the rigid molecule (body) system. The free rotation of

a rigid molecule is described classically in terms of the principal moments of inertia, magnitudes that are calculated relative to three mutually perpendicular axes (principal axes) that intercept in the molecular centre of mass. In order to calculate the moments of inertia the mass and Cartesian coordinates of the atoms that form the molecule are needed. If the molecule is not considered a rigid rotor, the value of these parameters would be constantly changing.

The free rotation of a rigid molecule is also quantized and the development of expression (3.9) leads to expressions (3.10), for a diatomic molecule, and (3.11), for a polyatomic system.

$$Q_{rot} = \sum_i g_i \exp(-\frac{E^i_{rot}}{k_B T}) \tag{3.9}$$

$$Q_{rot} = \frac{1}{\sigma} \cdot \frac{8\pi^2 I k_B T}{h^2} \tag{3.10}$$

$$Q_{rot} = \frac{1}{\sigma} \cdot \frac{8\pi^2 (8\pi^3 I_A I_B I_C)^{1/2} (k_B T)^{3/2}}{h^3} \tag{3.11}$$

In these expressions, I is the moment of inertia of a diatomic molecule, and I_A, I_B and I_C are the principal moments of inertia of a polyatomic molecule with respect to its principal axes. The constant σ is called the symmetry number, rotational symmetry number or external symmetry number. The inclusion of σ in the above expressions accounts for the fact that for symmetrical molecules less thermally accessible rotational states are available because of the indistinguishability of states.

A formal way of obtaining the value of σ is by determining the order (number of elements) of the rotational subgroup of the molecule, the point group of the molecule with all but the identity and the rotations removed. For example, the rotational subgroup of HCHO, a C_{2v} molecule, is $\{E, C_2\}$, so $\sigma = 2$; the rotational subgroup of NO_3 in the D_{3h} point group is $\{E, 2C_3, 3C_2\}$, so $\sigma = 6$.

To obtain expressions (3.10) and (3.11), the sum derived from expression (3.9) is replaced by an integral (as for translations) after assuming that at high temperatures many rotational levels are occupied and the separation between neighbouring states is much smaller than k_BT, the characteristic thermal energy.

A useful way of expressing the temperature above which the previous approximation is valid, is by means of the rotational temperature, θ_{rot}, that can be calculated using expression (3.12). For $T >> \theta_{rot}$, the approximation is valid; some typical values are listed in Table 3.1. Heavy and big molecules have large moments of inertia and thus very large Q_{rot}. This situation reflects the closeness in energy (compared with k_BT) of the rotational levels and that a large number of them are accessible at room temperature.

$$\theta_{rot} = \frac{h^2 c}{8\pi^2 k_B I} \tag{3.12}$$

Table 3.1. Rotational and vibrational temperatures.[(a)]

Molecule	θ_{rot}/K	θ_{vib}/K
H_2	88	6330
HCl	9.4	4300
I_2	0.053	309

[(a)] Taken from reference 2

*3.2.3. **Vibrational partition function***

The simplest description of a vibration is given by the harmonic oscillator. Such an oscillation occurs when a particle experiences a restoring force (k) that is proportional to its displacement (x), according to Hooke's law. The harmonic oscillator has a parabolic potential energy V ($V \propto x^2$) and the greater the curvature of the potential at the equilibrium position, the greater the force constant k (see Fig. 3.1):[4]

$$k = \left(\frac{\partial^2 V}{\partial x^2}\right)_0 \tag{3.13}$$

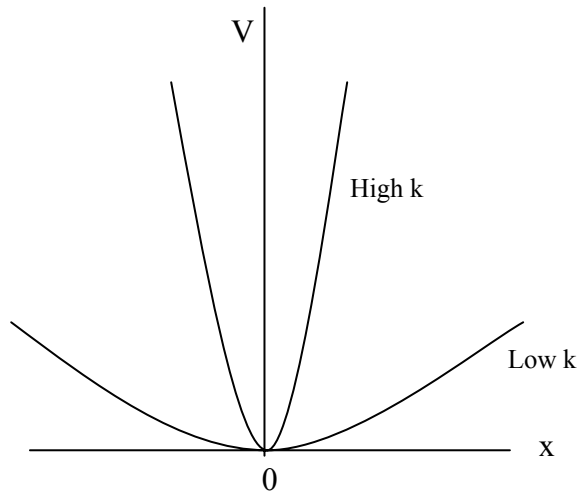

Figure 3.1. Potential energy curve for a harmonic oscillator.

The total energy computed by a geometry optimization (see Section 2.8) is the minimum on the potential energy curve. However, as an indirect consequence of the Heisenberg uncertainty principle, the molecule always has some vibrational motion, even at 0 K. This vibrational energy at 0 K is called the zero-point energy (ZPE) which is used to correct the calculated total energy of a molecule when energy differences or thermochemical data are to be calculated at 0 K. If calculations at higher temperatures are to be performed, another correction, the *thermal correction to the energy* (TCE), must be considered. The TCE contains the ZPE plus the contributions to the total energy from vibrations at temperatures higher that 0 K.

Following the harmonic approximation, the ZPE is calculated as:

$$\mathrm{ZPE} = \frac{1}{2} hc\bar{\nu} \tag{3.14}$$

where c is the speed of light, and $\bar{\nu}$ is the wavenumber associated with the oscillation, calculated according to the following expression (μ is the reduced mass of the 'diatomic' molecule):

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \tag{3.15}$$

The quantized energy levels of the harmonic oscillator model are equally separated by an energy equal to $hc\bar{\nu}$. As the bond energy increases, the force constant also increases together with the separation between neighbouring vibrational energy levels.

The quantum mechanical description of a harmonic oscillator[5] does not exactly describe molecular vibrations that behave somewhat anharmonically, but does provide a useful approximate treatment for low vibrational quantum numbers.

An oscillator is mechanically anharmonic if the restoring force (k) is not strictly proportional to its displacement (x). It has a non-parabolic potential energy curve: the potential becomes less confining as x increases and the energy levels become closer together than in a harmonic oscillator; Fig. 3.2 shows the potential energy curves for the two models. Vibrations become strongly anharmonic at high excitations.

The harmonic values of $\bar{\nu}$ are obtained directly from the Hessian matrix (Section 2.8). One of the most direct ways to calculate anharmonic corrections to the vibrational frequencies is to compute higher-order derivatives (3rd, 4th, and so forth) of the energy with respect to the coordinates of the system; this requires considerably more computer resources.[6]

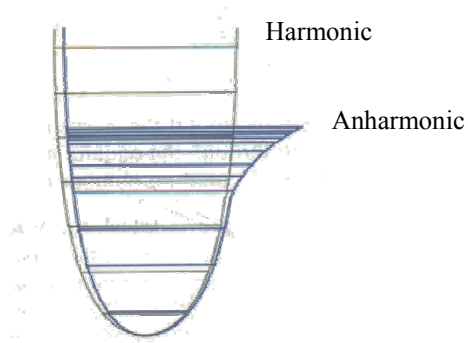

Figure 3.2. Harmonic and anharmonic potential energy curves.
Reproduced from reference 4.

In a polyatomic molecule with N atoms there are 3N-6 vibrational normal modes (3N-5, if the molecule is linear). If anharmonicities are small, these vibrational modes (each of which has its vibrational partition function) can be considered independent, and the total vibrational partition function may be expressed as:

$$Q_{vib} = \prod_{j}^{3N-6 \atop 3N-5} Q_{vib}(j) \tag{3.16}$$

where $Q_{vib}(j)$ is the partition function of the jth normal mode. Normal modes of vibration may not be independent when the potential is strongly non-parabolic; the motion of one mode may stimulate another mode into vibration.

If the harmonic oscillator energy levels are incorporated into equation (3.17), the vibrational partition function of the different normal modes may be calculated as indicated in equation (3.18):

$$Q_{vib}(i) = \sum_{i} \exp(-\frac{E^{i}_{vib}}{k_B T}) \tag{3.17}$$

$$Q_{vib}(j) = \frac{1}{1 - \exp\left(-\frac{hc\bar{\nu}_j}{k_B T}\right)} \tag{3.18}$$

The bigger the wavenumber of a vibrational mode, the lower its contribution to the total vibrational partition function. It is convenient to refer to the quantity $hc\bar{\nu}/k_B$ as the vibrational or characteristic temperature, θ_{vib} (some examples are listed in Table 3.1). Two extreme cases that lead to simplifications of equation (3.18) can be identified. When θ_{vib} is large compared with T, the fraction of molecules in vibrational excited states is small and $Q_{vib} \approx 1$. At temperatures higher than θ_{vib}, Q_{vib} can be calculated as:[7]

$$Q_{vib} = \frac{T}{\theta_{vib}} \tag{3.19}$$

3.2.4. ***Internal-rotational partition function***

In polyatomic molecules, some of the 3N-6 vibrational degrees of freedom can exist as mutual rotation of the different fragments of the molecule or as more complicated mutually consistent motion. These additional degrees of freedom are called internal rotations, torsions or conformational transformations.

In molecules such as ethane, the internal rotation around the single carbon-carbon bond is one of the most important internal degrees of freedom (see Fig. 3.2).

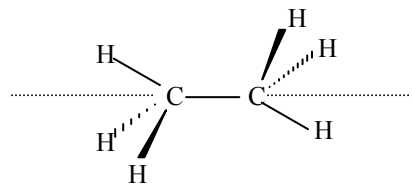

Figure 3.3. Schematic representation of the internal rotation about the C-C bond in ethane.

There are three ways to treat an internal rotation depending upon its barrier to rotation (V_0): as a free rotor, a hindered (restricted) rotor or a harmonic oscillator.[3,8,10]

If the barrier to rotation is much less than k_BT (*ca.* 2.5 kJ/mol, or about 207 cm^{-1}, at 298 K), then the internal rotation may be considered free. $Q_{int\text{-}rot}$ for such a rotor may be calculated as follows:[9,10]

$$Q_{int-rot} = \frac{\left(8\pi^3 I' k_B T\right)^{1/2}}{h\sigma_{int}} \tag{3.20}$$

where I' is the reduced or effective moment of inertia for the internal-rotation and is given by equation (3.21):

$$I' = \frac{I_1 \cdot I_2}{I_1 + I_2} \tag{3.21}$$

In the above expression, I_1 and I_2 are the moments of inertia of the rotating tops calculated with respect to the common axis for internal rotation:

$$I_n = \sum_i m_i r_i^2 \tag{3.22}$$

where m and r are the mass (in kilograms) of each atom and its distance (in meters) to the common axis of internal rotation, respectively.

If the barrier to internal rotation is much greater than k_BT, the torsion can be considered a non-rotating harmonic oscillator, and its treatment is the same as for the other vibrations. For the intermediate cases in which the torsional barrier is comparable to k_BT, the internal rotation may be treated as a hindered rotor for which the value of V_0 needs to be determined and there are no simple analytic solutions.[11] The internal rotation around the carbon-carbon single bond in ethane is a hindered internal rotation with a potential barrier of about 12 kJ/mol.[12] There are several reviews and monographs concerned with the calculation of internal rotations.[13]

The free and hindered rotor models require the consideration of an internal (also called effective) symmetry number, that is the symmetry number for the internal rotation, σ_{int} (see equation (3.20)). This parameter equals the number of minima (or maxima) in the torsional potential energy curve; for the torsion of a methyl group, $\sigma_{int} = 3$. The vibrational frequencies corresponding to torsions must be deleted (*i.e.*, ignored in the calculation of Q_{vib}) if the torsion is treated as a free or hindered rotation.

The centre of mass and thus, the principal moments of inertia for the overall (external) rotation will change as the torsional motion is executed. The approximation of considering these modes of motion as non-coupled could be very serious for torsions in big molecules such as polymers.

The treatment of internal rotations is especially important in TSs, where several motions may have to be treated as free or hindered rotors.[14] The harmonic oscillator treatment of

these modes of motion may cause significant error. The identification of such degrees of freedom by inspection of the normal modes in Cartesian coordinates is not an easy task, and the use of internal coordinates has been found more convenient.[15]

3.2.5. ***Electronic partition function***

As a general case, the electronic partition function may be calculated by:

$$Q_{elect} = g_0 + \sum_i g_i \exp(-\frac{\Delta E^i_{elect}}{k_B T}) \tag{3.23}$$

where g_0 is the degeneracy of the electronic ground state and ΔE_{elect} is the energy difference of the excited states with respect to the ground state. In the calculation of Q_{elect}, factors such as the degeneracy of the electronic states and the existence of low lying excited states, have to be considered.[1b,2,7]

The electronic levels of atoms and molecules are usually much further apart than the vibrational level in molecules. For the H atom for example, the first electronic excited state is about $1.6 \cdot 10^{-18}$ J above the ground state, and at ordinary temperatures this state makes a negligible contribution to the partition function. As a useful rule it has been said that if the difference in energy between an excited and the ground electronic state divided by k_B is greater than 5 K, the excited state can be ignored in the calculation of Q_{elect} at usual temperatures.

Another factor to consider is the degeneracy of an electronic state. If excited electronic states are ignored, $Q_{elect} = g_0$. Nearly all stable molecules are closed-shell systems and their excited states are high enough to be neglected except at very high temperatures, so for these cases the electronic partition function is unity. Important exceptions are O_2, NO, and most free radicals.

For atoms, the degeneracy of the electronic ground state is determined by the total electronic angular momentum, represented by the quantum number j. This magnitude is a combination of the spin (s) and orbital (*l*) angular momenta, which has positive values

between l + s and l – s. For every j there are (2j + 1) possible orientations in a magnetic field, corresponding to identical energies, so $g_0 = 2j + 1$.

For molecules, in addition to spin degeneracies, some states have spatial degeneracies. This situation is more common for diatomics. Linear molecules with spatial symmetry other than Σ (which has zero total angular momentum), *e.g.*, Π or Δ, have spatial degeneracy of 2. If there are both spin and spatial degeneracies, spin-orbit coupling lifts the degeneracy, often significantly.

As shown in the sections above, exact analytical expressions for the calculation of the different contributions to the molecular partition function cannot be obtained. All modes of motion are considered as not being coupled and in the calculation of each contribution assumptions have to be made. These approximations are avoided by using the energy levels identified spectroscopically and by evaluating the sums explicitly, but for species that have not yet been detected or isolated, such as TS's and reactant and product complexes, among others, there is no other alternative.

The evaluation of the total molecular partition function requires only a knowledge of the mass of the system (Q_{trans}), its geometry (Q_{rot}, $Q_{int\text{-}rot}$), vibrational frequencies ($Q_{int\text{-}rot}$, Q_{vib}) and the energies of low-lying electronic excited states with respect to the ground state (Q_{elect}).

3.2.5. ***The calculation of equilibrium constants***

One of the most important thermodynamic functions is the Gibbs free energy (G). For a system of N indistinguishable independent particles (*i.e.*, an ideal gas), G may be expressed in terms of the total molecular partition function, as follows:

$$G - G(0) = -nRT \ln\left(\frac{Q}{N}\right) \tag{3.24}$$

Since $N = n \cdot N_A$ (where n is the number of moles and N_A Avogadro's number), the above expression can be conveniently rewritten in terms of the molar partition function, $Q_m = Q/n$:

$$G - G(0) = -nRT \ln\left(\frac{Q_m}{N_A}\right) \tag{3.25}$$

For a species X, under standard conditions, *i.e.*, when $p = p^0 = 1$ atm, equation (3.25) can be written in as:

$$G_X^0 - G_X^0(0) = -nRT \ln\left(\frac{Q_{X,m}^0}{N_A}\right) \tag{3.26}$$

where $Q_{X,m}^0$ is the standard molar partition function of X.

The equilibrium constant K_{eq} for a reaction is related to the standard Gibbs energy of reaction:

$$\Delta_r G^0 = -RT \ln K_{eq} \tag{3.27}$$

By combining expressions (3.26) and (3.27) the equilibrium constant for a general reaction:

$$aA + bB \rightarrow cC + dD \tag{3.28}$$

is given by the expression:

$$K_{eq} = \frac{\left(Q_{C,m}^0/N_A\right)^c \cdot \left(Q_{D,m}^0/N_A\right)^d}{\left(Q_{A,m}^0/N_A\right)^a \cdot \left(Q_{B,m}^0/N_A\right)^b} \exp\left(-\frac{\Delta_r E_0}{RT}\right) \tag{3.29}$$

For simplicity, equation (3.29) will be written as:

$$K_{eq} = \frac{\left(Q^C\right)^c \cdot \left(Q^D\right)^d}{\left(Q^A\right)^a \cdot \left(Q^B\right)^b} \exp\left(-\frac{\Delta_r E_0}{RT}\right) \tag{3.30}$$

where Q^X is the standard molar partition function of X divided by N_A, and $\Delta_r E_0$ is the difference in molar energies of the ground states (including ZPEs) of the products and reactants. In other words, $\Delta_r E_0$ is the molar reaction internal energy at T = 0 K.

3.3. Transition State Theory

Collision theory and transition state theory (TST) are fundamental theories of bimolecular elementary reactions.[16] The following chapters of this part of the thesis are applications of TST to rate constant calculations.

In 1935, Eyring[17] and, independently, Evans and Polanyi,[18] developed a simple and general formulation for the calculation of reaction rates that has been called *transition state theory* (TST) and is still being used in many studies.[19] Other names have been given to this theory, such as *activated complex theory*, *absolute rate theory*, *classical TST* and *conventional TST*.[16a,20]

The simplest reaction profile for an elementary reaction is represented in Fig. 3.4. As the reaction takes place, the reactants (React) make contact with the right energy and geometry, and the potential energy of the system rises to a maximum. The molecular arrangements of the reacting species in the area around the maximum (represented by a circle in Fig. 3.4) is called the *activated complex*. The climax of the reaction is at the maximum of the potential energy, the point at which the reactants have come to such a degree of closeness and distortion (called the *transition state*, TS) that a small further distortion converts them into the products of the reaction (Prod). The TS is the molecular system whose configuration corresponds to the first-order saddle point on the potential energy surface. Sometimes, the terms *activated complex* and TS are used as synonyms.[2,21]

TST focuses its attention on the TS of a bimolecular elementary reaction and calculates its concentration by making use of statistical thermodynamic concepts. As in all scientific theories, various assumptions and approximations are involved in its implementation.[16a]

It is based on the *equilibrium hypothesis* which states that even when the reactants and products are not at equilibrium with each other, the TS is always at equilibrium with the reactants, whose energy distribution is in accordance with the Maxwell-Boltzmann distribution law. Furthermore, it is assumed that once the maximum of the potential energy curve has been surmounted, such molecular systems cannot turn back and form reactant molecules again. Another approximation is the separation of the motions of the system over the maximum from the motions associated with the TS. In this theory the chemical reaction is treated in terms of classical motion over the barrier, ignoring quantum effects; although as will be discussed below this is not completely true.

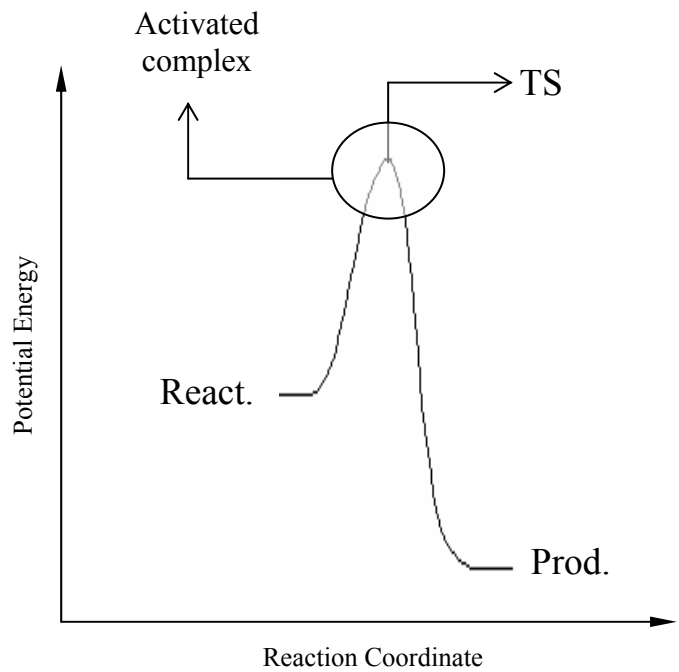

Figure 3.4. Energy profile of an elementary reaction.

For a general reaction: React $\leftrightarrows$ $[TS]^{\neq}$ $\leftrightarrows$ Prod

by applying basic concepts of statistical thermodynamics, the constant for the equilibrium between reactants and the TS can be written as:

$$K_{eq}^{\neq} = \frac{[TS]}{[Reac]} = \frac{Q^{TS}}{Q^{React}} \exp\left(-\frac{\Delta E_0}{RT}\right) \tag{3.31}$$

where ΔE_0 is the hypothetical energy of activation at 0 K, calculated by:

$$\Delta E_0 = \left(E^{TS} + ZPE^{TS}\right) - \left(E^{React} + ZPE^{React}\right) \tag{3.32}$$

The partition functions and the energy difference must be calculated with respect to the same reference state, in this case the zero-point vibrational energy level.

Since the imaginary frequency of the TS ($\nu^{\neq}$) corresponds to a loose vibration without restoring force, it is supposed to be much smaller than the frequency of an arbitrary vibration, *i.e.*, $hc\nu^{\neq}/k_BT << 1$, and the expression in the exponential of equation (3.18) can be expanded in a Taylor series, so that the partition function of the vibrational component of the imaginary frequency can be calculated by:

$$Q_{vib}(\overline{\nu}^{\neq}) = \frac{1}{1 - \exp\left(-\frac{hc\overline{\nu}^{\neq}}{k_BT}\right)} = \frac{1}{1 - \left(1 - \frac{hc\overline{\nu}^{\neq}}{k_BT} + \cdots\right)} \approx \frac{k_BT}{hc\overline{\nu}^{\neq}} \tag{3.33}$$

Further application of the assumptions discussed above leads to the following expression for the rate constant (k has also been referred to as *specific reaction rate*[22] or *rate coefficient*):[2,16a]

$$k = \kappa \frac{k_BT}{h} \cdot \frac{Q^{TS}}{Q^{React}} \exp\left(-\frac{\Delta E_0}{RT}\right) \tag{3.34}$$

In the previous expression, κ is the *tunneling factor* or *tunneling correction*, that will be discussed in Section 3.4; Q^{TS} is the standard molar partition function of the TS divided by N_A, ignoring the contribution of the imaginary frequency to the vibrational partition function.

TST, like every theory, has limitations.[16,25b] That is why there have been so many improvements and extensions to it, such as variational TST (VTST),[23] quantum TST,[24]

among others. But all the modified theories are considerably more complicated than TST and cannot be expressed in as compact a form.[16a,25,26]

3.3.1. ***Unimolecular reactions***

Unimolecular reactions in the gas phase have been known for nearly a century.[27] Examples of such reactions are dissociations and isomerizations. In addition, unimolecular fragmentation of gas phase ions forms the basis for mass spectrometry analysis.[28]

Following the Lindemann theory, the rate constant for a unimolecular reaction k_{uni} is a function of pressure. Collisions can either energize or de-activate a gas molecule, and maintain a Boltzmann distribution of the reactant molecules throughout its energy levels. At low pressures k_{uni} is directly proportional to the total pressure, however, at high pressure k_{uni} is independent of pressure. Under high-pressure conditions collisional de-activation is much faster than the unimolecular reaction, an equilibrium distribution of the reactants is maintained, and the classical TST formula can be applied to calculate the rate constant.[16b]

Considerable experimental work concerning gas phase unimolecular reactions has been devoted to energy-selected systems.[29] All detailed statistical theories of unimolecular reactions begin with the calculation of the rate constant as a function of the internal energy, k(E), also known as the microcanonical rate constant.

The Rice-Ramsperger-Kassel-Marcus/quasi-equilibrium theory (RRKM/QET) assumes the existence of a TS. According to this theory, the expression for k(E) is given by:

$$k(E) = \frac{\sigma\ N(E - E_0)}{h\rho(E)} \tag{3.35}$$

where E_0 is the critical energy of activation (not necessarily equal to the Arrhenius activation energy, see below), $\rho(E)$ is the density of vibrational states of the reactant molecule at energy E, $N(E - E_0)$ is the sum of the vibrational states from 0 to $E - E_0$ in the

TS, and σ is the reaction path degeneracy (equivalent to the rotational symmetry number, see Section 3.2.2). The application of equation (3.35) requires the knowledge of the energy barrier and the vibrational frequencies of the reactant and of the TS. Although this theory has been (and still is) widely used for the quantitative description of unimolecular reaction kinetics,[30] it is not a simple theory to be implemented; it will not be applied in the following chapters.

3.3.2. ***Femtochemistry***

The development femtosecond pulsed lasers and their applications to chemistry in the form of femtochemistry has made possible the study of molecular motions in the ephemeral TSs of physical, chemical and biological changes.[31] The significance of these studies was manifested in the 1999 Nobel Prize, awarded to Ahmed Zewail for his groundbreaking work in femtochemistry.

In a typical experiment, a femtosecond pulse is used to excite a molecule to a dissociative state; a second pulse is fired at an interval after the first one and it is set at an absorption frequency of one of the free fragmentation products. The intensity of such absorption is a measure of the abundance of the dissociation product. In a similar study on the ICN molecule, it was possible to detect that the CN absorption signal remains zero until the fragments are separated by about 6 Å, which takes about 205 fs (1 fs = 10^{-15} s).

Femtosecond spectroscopy has also been used to examine analogues of the activated complex involved in bimolecular reactions; a molecular beam can be used to produce a van der Waals molecule, such as IH···OCO. The H-I bond can be dissociated by a femtosecond pulse, in which case the H atom is ejected towards the O atom of the neighbouring CO_2 molecule to form HOCO. Hence, the van der Waals molecule acts as a source of a species that resembles the activated complex of the reaction:[2]

$$H + CO_2 \rightarrow [HOCO]^{\neq} \rightarrow HO + CO \qquad (3.36)$$

3.4. Tunneling calculations

It is sometimes necessary to correct the rate constant calculation by a factor that takes account of the possibility that some reactant molecules can be transformed into the products of the reaction without having surpassed the activation barrier and that not every activated complex becomes transformed into the products. Such a quantum-mechanical correction is achieved by what has been named the *tunneling correction* and will be discussed in the present section. The book by Bell[32] has been a very important material source for this topic.

The suggestion that quantum-mechanical tunneling might be a significant factor in some chemical reactions was first made more than seventy years ago by Hund.[33,34] Fig. 3.5 illustrates the meaning of the term *tunnel effect*:

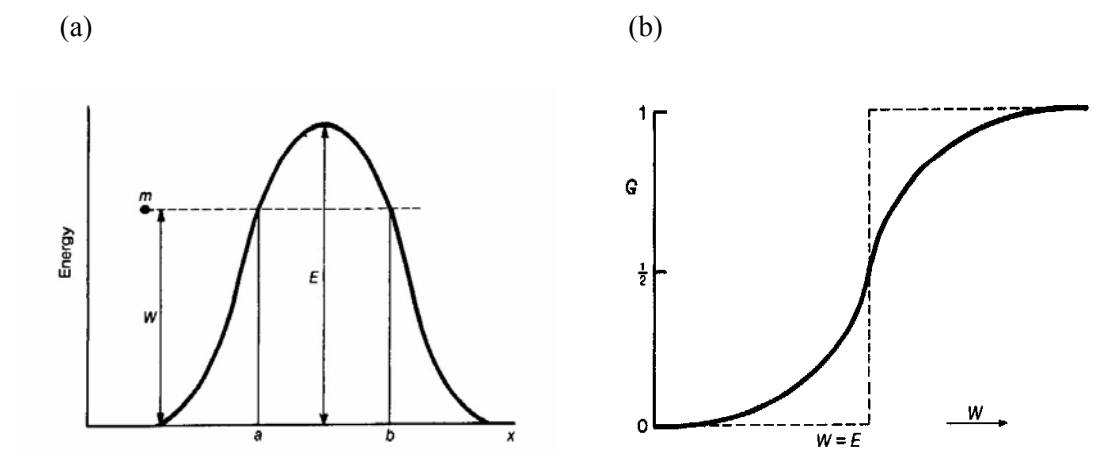

Figure 3.5. Passage of a particle across classical and quantum potential energy barriers.
(a) Particle approaching a potential energy barrier;
(b) Plot of the permeability (G) as a function of the energy of the particle (W).
Reproduced from reference 32.

Fig. 3.5(a) shows a particle of mass m and energy W approaching a potential energy barrier of height E. The magnitude G, called the *permeability* or *transmission coefficient*,

represents the probability that the particle will appear on the right-hand side of the barrier. G varies with W in a way that depends on the type of barrier considered. Fig. 3.5(b) is a plot of G as a function of W. The broken line represents the predictions of classical mechanics and the everyday experience with macroscopic objects: the probability is zero as long as W < E, and rises abruptly to unity when W = E, staying at this value for all higher values of G. When going from classical to quantum mechanics, the broken line is replaced by a continuous curve, whose exact form depends not only on the height of the barrier, but also on its width and shape and on the mass of the particle.

The quantum-mechanical curve of G *vs.* W has the following limiting behaviour:

$$\lim_{W \to 0} G(W) = 0 \qquad \lim_{W \to \infty} G(W) = 1 \tag{3.37}$$

The most impressive feature of the continuous curve is that it predicts non-zero permeabilities even when W < E (*i.e.*, the particle penetrates the barrier, it tunnels through the barrier). In addition, for some values of W > E, there is some probability that the particle be reflected by the barrier.

The tunnel effect is a consequence of the wave-particle duality of matter postulated by de Broglie in 1925,[35] and represented mathematically by the expression:

$$\lambda = \frac{h}{mv} \tag{3.38}$$

For macroscopic systems λ is very small compared with the dimensions of the particles and classical mechanics can be applied with sufficient accuracy. For molecular systems deviations from classical behaviour take the form of quantization (*e.g.*, the existence of discrete energy levels). For a free particle (*e.g.*, e^-, H, H^+, H^-) approaching an energy barrier such deviations are manifested as the tunnel effect. However, most reacting systems may involve both quantization and the tunnel effect, but it is often convenient to treat these phenomena separately.

So far reference to the tunneling effect has been made in a qualitative manner. However, there are ways to obtain quantitative estimates of its magnitude, named the *tunneling correction* or *tunneling factor*, κ.

The tunneling correction is defined as the ratio of the quantum-mechanical (k_Q) to the classical (k_C) barrier-crossing rate, and can be calculated in terms of the previously mentioned parameters as follows:

$$\kappa = \frac{k_Q}{k_C} = \frac{\exp(\frac{E}{k_B T})}{k_B T} \int_0^\infty G(W) \exp(-\frac{W}{k_B T}) dW \tag{3.39}$$

To obtain κ, the permeability G needs to be evaluated. To do so, the Schrödinger equation for a given potential energy barrier must be obtained, and its solutions interpreted. Usually several simplifications of the tunneling process are made: the barrier is considered unidimensional and the mass of the particle is assumed to remain constant during the process.

Several types of one-dimensional barriers have been used to model tunneling, such as rectangular, triangular and parabolic, among others. The parabolic barrier (Fig. 3.6) is of particular importance in chemical problems since it represents a more realistic representation of a real barrier (at least when tunneling involves only the upper part of the barrier). Furthermore, for the parabolic barrier an exact expression for the permeability can be obtained, that can be explicitly integrated.[36] Most types of barriers lead to expressions for G that require numerical integration, thus κ cannot be explicitly evaluated.

The Wigner correction,[37] is a very simplistic way of estimating small tunneling factors by assuming a parabolic potential for the nuclear motion near the TS:

$$\kappa = 1 + \frac{1}{24} \cdot \frac{hc\bar{\nu}^{\neq}}{k_B T} \tag{3.40}$$

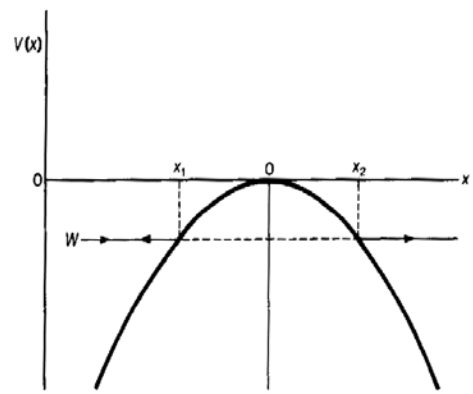

Figure 3.6. An infinite parabolic barrier.
Reproduced from reference 32.

The above expression is obtained after truncating Bell's formula for a parabolic barrier, at high temperatures or small values of $\overline{\nu}^{\neq}$. The Wigner correction has been used in several kinetic applications.[38]

*3.4.1. **The Eckart barrier***

A one-dimensional barrier shape that corresponds more closely to physical reality and for which a solution of the quantum-mechanical problem is possible, was proposed by Eckart.[39] The Eckart barrier was the first realistic type of barrier for which the tunneling problem was solved, and it has been extensively used in chemical applications.[40]

The general equation for the Eckart barrier is:

$$V(x) = \frac{Ay}{(1+y)^2} + \frac{By}{(1+y)} \qquad y = \exp\left(\frac{x - x_0}{b}\right) \tag{3.41}$$

where b is a characteristic length (thickness parameter) and x_0 indicates the origin of the barrier. The parameters A, B and b are constants related to the direct (V_1) and reverse (V_2) potential energy barriers, and to the imaginary frequency of the TS.

Fig. 3.7 shows symmetrical and unsymmetrical Eckart barriers (V^* is the potential at the maximum of the barrier, and F^* is the second derivative of the function at its maximum, calculated from $\overline{\nu}^{\neq}$). For the symmetrical function A is zero; B represents the endothermicity of the process for the unsymmetrical case.

A graphical comparison between symmetrical parabolic and Eckart barriers is shown in Fig. 3.8. The parabolic and Eckart barriers behave similarly at the top of the barrier, but the Eckart function shows a slower decrease of the potential away from the maximum.

For the Eckart barrier the Schrödinger equation can be solved exactly, thus an exact value of G can be obtained. The expression for the permeability of such a barrier and for the tunneling factor (3.42) are rather complicated in form and involve integrals which have to be evaluated numerically. Values of κ for a variety of conditions assuming an Eckart barrier have been reported.[41]

$$\kappa(W) = 1 - \frac{\cosh[2\pi(\alpha - \beta)] + \cosh 2\pi\delta}{\cosh[2\pi(\alpha + \beta)] + \cosh 2\pi\delta} \tag{3.42}$$

$$\alpha = \frac{1}{2}\sqrt{\frac{W}{C}} \qquad \beta = \frac{1}{2}\sqrt{\frac{W - A}{C}} \qquad \delta = \frac{1}{2}\sqrt{\frac{B - C}{C}} \qquad C = \frac{h^2}{8ml^2}$$

Tunneling calculations considering an Eckart-type barrier are a simple (but not as simple as Wigner or parabolic-type barrier tunneling corrections) and practical way of accounting for tunneling. The Eckart method is still widely used in the literature, although more sophisticated methods, such as the multidimensional semiclassical zero- (ZCT) and small-curvature (SCT) tunneling methods have been developed.[42] A few years ago a study on the importance of quantum mechanical tunneling effects on the kinetics of the hydrogen exchange reaction of methane in a zeolite was published.[43] In Truong's paper, the accuracy of Eckart tunneling calculations was demonstrated, in agreement with his previous work.[44] Not only were different tunneling corrections considered, but also VTST results were compared with TST calculations. The success of the TST/Eckart combination was clearly shown.

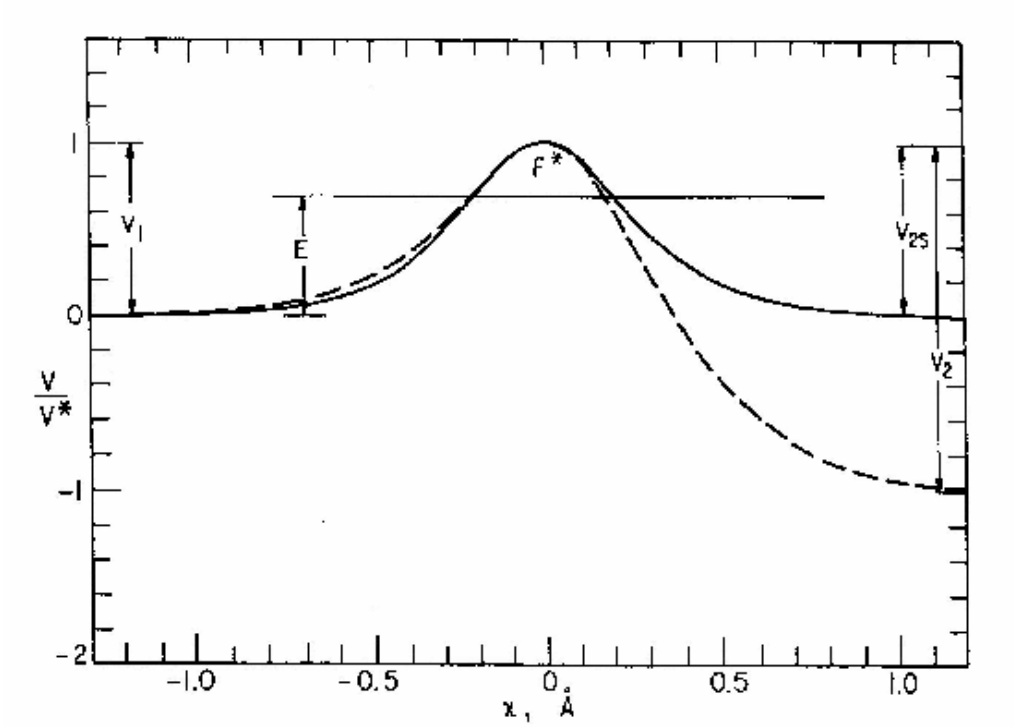

Figure 3.7. Symmetrical and unsymmetrical Eckart barriers.
Reproduced from reference 41a.

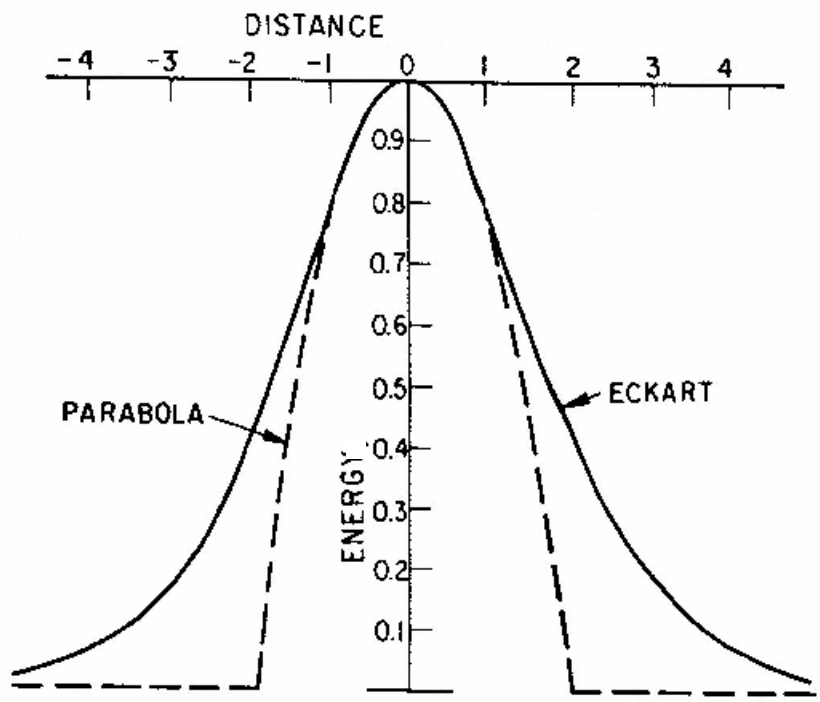

Figure 3.8. Comparison of symmetrical parabolic and Eckart barriers.
Reproduced from reference 41a.

It is well known that the Eckart method tends to overestimate the tunneling contributions especially at very low temperatures. In the papers discussed above,[43, 44] (where there is approximately the same degree of heavy-atom motion as the system moves along the reaction path, in comparison with the reactions that will be studied in Chapters 4 to 6) the Eckart corrections do not overestimate the rate constant at room temperature, as happens at much lower temperatures.

A useful measure of the barrier width is the full width of the barrier at half its height in the forward direction, $\Delta s_{½}$. It may be determined by setting: $V(x) = (A+B)^2/8A = V^*/2$ and obtaining the difference between the two roots of x. The magnitude of $\Delta s_{½}$ (usually reported in Å) depends on the direct and reverse potential energy barriers at 0 K, and on the characteristic tunneling temperature (T^*), below which tunneling is significant. This magnitude can be calculated by:

$$T^* = \frac{hc\bar{\nu}^{\neq}}{2\pi k_B} \tag{3.43}$$

An arbitrary general criterion for tunneling given by Bell could be useful for certain applications:

Negligible tunneling:	$1 < \kappa < 1.1$
Small to moderate tunneling:	$1.1 < \kappa < 4$
Large tunneling:	$\kappa > 4$

As a generalization on this topic it can be said that the smaller the mass of the particle to be transferred in a chemical reaction, the lower the temperature, and also that the narrower and larger the potential energy barrier, the greater the tunneling effect. The width of the potential energy barrier is given by the curvature at its maximum, determined by the imaginary frequency of the TS; the larger $\bar{\nu}$ the greater the curvature and κ.

3.5. Arrhenius, non-Arrhenius and anti-Arrhenius kinetic behaviours

Many rate constants show an exponential dependence on temperature that can be empirically fit by the well-known Arrhenius equation[45,46] over a relatively narrow temperature range:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \tag{3.44}$$

where T is the temperature in K and R is the ideal gas constant. E_a and A have been named the Arrhenius activation energy and pre-exponential factor, respectively.

The activation energy (when referring to an elementary process) is related to the height of the energy barrier for a reaction, the energy required to transform the reacting substance into the 'active' form. The pre-exponential factor, also known formerly as the *frequency factor*, is the rate constant of a reaction without activation energy (a barrierless reaction), or at infinite temperature where all the collisions are 'effective'.

The problem of temperature dependence of reaction rates had a great deal of controversy and uncertainty for over 60 years (from 1850 to 1910)[47] and many empirical equations to describe it were developed.[48] Even though the Arrhenius equation was not empirically the best, by about 1910 it was the only one-parameter temperature-dependence equation (since one parameter, E_a, expresses the temperature dependence) accepted because of the insight it provides on how chemical reactions proceed.

To a first approximation, the Arrhenius factor A is found to be independent of temperature for many reactions over a certain temperature range. Hence, a straight line is obtained when plotting ln k *versus* 1/T; this situation has been referred to as an Arrhenius behaviour. As the temperature range over which experiments are carried out is extended, non-linear Arrhenius plots (non-Arrhenius behaviours) are observed for some reactions.[49] The failure of the Arrhenius equation in special circumstances is well known.[50] Ironically, one of the first detected reactions to fail equation (3.43) was the inversion of sucrose,[51] a reaction whose kinetic data was used by Arrhenius in his study.[45] The

Arrhenius equation can fail, for example, in a reaction with concurrent mechanisms with quite different dependencies on temperature, or in catalytic reactions where irreversible changes take place on the catalyst at high temperatures or while approaching an explosion limit. Two additional groups of reactions not obeying equation (3.44) are the diffusion-controlled reactions in aqueous glasses,[52] and reactions where a low-mass particle (*e.g.*, H, H^+ or H^-) is transferred, in solution or in the gas phase, and tunneling is significant (*vide infra*).

For reactions in which the activation energy is small or zero, the temperature dependence of A can be significant. As a result, the empirical Arrhenius equation (3.44) is not appropriate to describe the temperature dependence, and a modified equation of the form:

$$k = BT^n \exp\left(-\frac{E_0}{RT}\right) \tag{3.45}$$

is frequently used, where B, E_0 and n are temperature independent constants characteristic of the reaction. This is the most satisfactory two-parameter equation that can be used to describe the temperature dependence of rate constants when non-linear plots of ln k *versus* 1/T are obtained. There is a good theoretical basis for this equation arising from the temperature dependence of partition functions.

It is often convenient to define the experimental Arrhenius activation energy E_a by the equation:

$$E_a \equiv RT^2 \frac{d\ln k}{dT} \equiv -R\frac{d\ln k}{d(1/T)} \tag{3.46}$$

Hence, the slope of the ln k *versus* 1/T plot at any point is equal to $-E_a/R$ and the above definition applies whether or not the Arrhenius plot is linear; if it is not, E_a (and thus A) will vary with temperature.

If a reaction obeys equation (3.45), then:

$$E_a = E_0 + nRT \tag{3.47}$$

where E_0 is the hypothetical activation energy at absolute zero.

Hence, a non-Arrhenius behaviour (curved Arrhenius plot) implies the parameters E_a and A to be temperature-dependent. This is illustrated in Fig. 3.9.

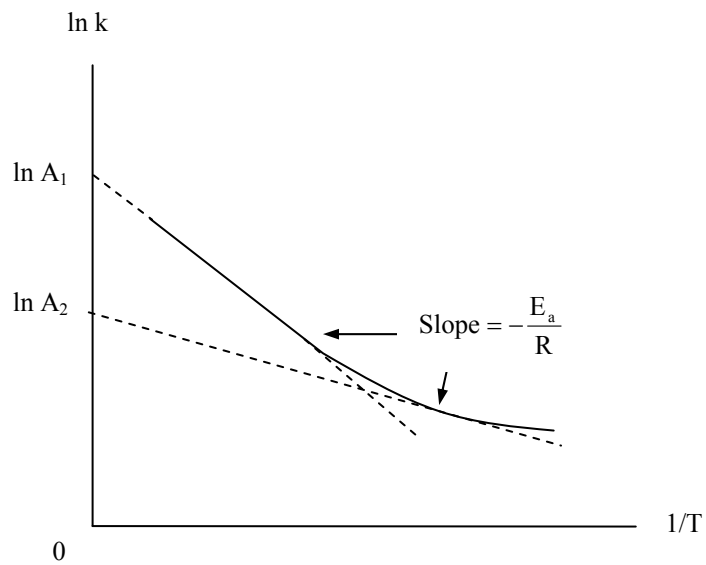

Figure 3.9. Schematic curved-Arrhenius plot showing the temperature dependence of E_a and A.

When tunneling plays an important role in the kinetics of some reactions, curved Arrhenius plots are also obtained. This, of course, will be the case for temperatures below T^*.

Since $k_Q = \kappa \cdot k_C$ (see equation (3.39)), the temperature dependence of E_a and A will be established by the following expressions:

$$(E_a)_Q - (E_a)_C = RT^2 \frac{d \ln \kappa}{dT} \tag{3.48}$$

$$\ln \frac{(A)_Q}{(A)_C} = \ln \kappa + T \frac{d \ln \kappa}{dT} = \frac{d(T \ln \kappa)}{dT} \tag{3.49}$$

where $(E_a)_Q$ and $(A)_Q$ are the Arrhenius parameters considering tunneling, and $(E_a)_C$ and $(A)_C$ are the same parameters when this quantum effect is ignored.

Since tunneling decreases as temperature increases, $d\ln\kappa/dT$ is always negative. Hence, equation (3.48) predicts that tunneling will reduce the Arrhenius activation energy. The direction in which tunneling affects the pre-exponential factor is not immediately obvious, but for small tunneling corrections a reduction of the A factor is expected.

For a chemical reaction where tunneling is significant, the appropriate way to theoretically or experimentally determine the Arrhenius parameters at a temperature below T^* requires the construction of a $\ln k$ *versus* $1/T$ plot, or the determination of the corresponding analytical expression. From the slope and the intercept of the tangent to this curve at the desired temperature, the Arrhenius parameters may be determined.

Equation (3.44) is not in general obeyed in the sense that unique constants A and E_a do not exist for each reaction.

While most reactions increase in rate as the temperature increases, there are several notable exceptions for which the Arrhenius activation energy is negative. The temperature dependence of such reactions is referred to as anti-Arrhenius. This topic will be discussed further in the following section.

3.6.1. ***Negative Arrhenius activation energies***

The above definition or interpretation of the activation energy is only valid when referring to elementary reactions; even for such systems some authors have indicated that a complete identification of the Arrhenius activation energy with the barrier height is not justified.[53] As more sophisticated experimental methods are developed, the number of accepted elementary reactions is reduced. In fact, one of the main conclusions of the following chapters related to computational kinetics refers to this topic.

Since most chemical reactions are complex, the meaning of the term *activation energy* needs to be modified. For non-elementary reactions, the Arrhenius activation energy is not in general simply related to the height of any single energy barrier, it is instead theoretically calculated by a linear combination of the activation energies of the single elementary steps of the proposed kinetic mechanism. The term Arrhenius activation energy will always refer to the experimentally determined kinetic parameter according to the operational definition (3.44). The validity of the proposed mechanism depends on how well it explains and reproduces the experimental data.

The reaction: $$2NO + Cl_2 \rightarrow 2ONCl \qquad (3.50)$$
is a third-order process that exhibits anti-Arrhenius behaviour, i.e., the Arrhenius activation energy is negative.[54]

For an elementary process, a negative Arrhenius activation energy is inconceivable on the basis of TST or of collision theory. The above reaction is thought to occur not by a single termolecular step but instead by a complex mechanism in which an NO molecule first forms a loose reactant complex with Cl_2 in a reversible process (steps 1 and –1), followed by the reaction between such a complex and a second NO molecule (step 2). The Arrhenius activation energy is thus given by:

$$E_a = E_{a\,(1)} + E_{a\,(2)} - E_{a\,(-1)} \qquad (3.51)$$

The negative activation energy arises because $E_{a\,(-1)}$ is greater that the sum of $E_{a\,(1)}$ and $E_{a\,(2)}$. Negative E_a are normally encountered for termolecular reactions.

A similar situation is found in the recombination reaction of I atoms, conventionally written as:

$$I + I + M \rightarrow I_2 + M \qquad (3.52)$$

where M symbolizes any molecule. This reaction can also have a negative E_a.[55]

Benson and coworkers have examined some 'elementary' gas phase reactions in which negative activation energies and/or curved Arrhenius plots have been observed experimentally.[56] They have shown that activation energies as negative as –5.0 to –7.5 kJ/mol near 300 K as well as curved Arrhenius plots can be explained by the formation of an intermediate complex. These results were obtained for the reactions of OH with CO, HNO_3 and HNO_4.

Another type of reaction important in atmospheric chemistry that shows this somewhat unusual inverse temperature dependence of the rate constants is that between alkenes and OH and, in some cases, $O(^3P)$.

The reactions of alkenes with OH radicals are very fast. The rate constants for the larger alkenes are approximately equal to the diffusion-controlled limit (*i.e.*, the reaction occurs on every collision).[57] Several explanations have been proposed to explain the anti-Arrhenius behaviour of these reactions, one of them being the formation of a weakly bound complex (also called *reactant complex* or *pre-reactive complex*) as previously explained; Singleton and Cvetanović proposed this idea in 1976.[58] In fact the role of such complexes has received increased attention in the recent literature. Some of these studies will be discussed in the following chapter.[59] In recent studies the abundance of hydrated complexes in the atmosphere is estimated and physicochemical properties are evaluated; experimental evidence of their existence is also given.[60]

Another possible explanation for negative activation energies lies in the use of the Arrhenius equation. The data for lnk *vs.* 1/T can be fit to an expression similar to (3.44) with negative values of n that for the specific case of the alkenes + OH reaction is approximately –1.5.[49,57]

A third explanation, based on collision theory, has been given by Zellner and Lorenz.[61] A $T^{-1.5}$ temperature dependence (for the alkenes + OH reactions) is predicted if the reaction cross section is assumed to increase rapidly at the threshold energy, reach a sharp maximum, and then decrease as the energy increases.

For the reaction of olefins with $O(^3P)$, Cvetanović and Singleton identified four possible explanations, some of which have aspects in common with the ones already mentioned.[62] One idea is that it is simply an elementary bimolecular reaction with an approximately zero activation energy so that the temperature dependence of the A factor becomes important. Another idea is based on the formation of a transient $O(^3P)$-alkene complex that can decompose back to the reactants or form products; in this case the complex is an electron-donor acceptor complex with the electron donor being the alkene π bond and the product is not a stable radical adduct as in the OH-alkene reactions. A third explanation refers to the existence of two or more reaction channels whose activation energies are significantly different; the addition to the double bond and atom or free radical displacement are two such reaction channels. The other explanation given by Cvetanović and Singleton refers to the crossing of potential energy surfaces: if the $O(^3P)$-olefin initial interaction has a shallow minimum and the rate determining step involves crossing in a repulsive region to an attractive potential energy surface, then intersection of the surfaces at energies lower than that of the separated reactants would result in negative activation energies.

Benson explained this paradoxical result of elementary reactions having negative activation energies in terms of the different internal energies (vibrational excitation) of the reacting molecule and its dissociating fragments, which can become very pronounced at high temperatures. Recently, a study by Benson and Dobis on the existence of negative activation energies in simple bimolecular metathesis reactions of the type: $R^\bullet + HX$ and $R^\bullet + X_2$ (X = I, Br, Cl),[63] blamed the artifacts of the experimental methods for this situation.

The anti-Arrhenius behaviour of some reactions is without doubt a very interesting and somewhat frequent phenomenon that can be found in the recent literature.[64]

3.6. General aspects regarding Chapters 4 to 6

In computational chemistry the activation energy of an elementary reaction is calculated in terms of the total energies of the TS and the reactants including their respective vibrational thermal corrections to the energy (TCE) that depends on temperature:

$$E_a = (E^{TS} + TCE^{TS}) - \Sigma(E^{React} + TCE^{React}) \quad (3.53)$$

In the following chapters Arrhenius activation energies measured in a temperature range that includes 298 K are compared with calculated activation energies using thermal corrections at 298.15 K. Calculations at 0 K are also reported.

For the mechanisms considered in Chapters 4 to 6, these activation energies are calculated by expression (3.53). Reaction enthalpies (ΔH) are also calculated at 0 and 298.15 K, and reported in kJ/mol as well. The optimum situation for a theoretical calculation of E_a and ΔH is to be within chemical accuracy, *i.e.*, within *ca.* 4 kJ/mol (that is equivalent to about 1 kcal/mol), with respect to experiment. For rate constant calculations the optimum could be expected within one order of the experimental values, although this non-established criterion is subject to change as better theoretical determinations are achieved.

In Chapters 4 and 5, the calculated activation energies correspond to different mechanisms, as will be explained. When referring to the activation energy of a complex mechanism, this quantity will be named *effective activation energy* and will be denoted E_a^{eff}. Similarly, rate constants for complex mechanisms will be referred to as *effective rate constants*, k_{eff}, and for an elementary or direct mechanism this magnitude will be named *direct rate constant*, k_D. Rate constants in units of L/mol·s will be calculated at 298.15 K.

The Gaussian98[65] set of programs was used to perform the electronic calculations reported in Chapters 4 to 6. In this commercial program all the calculated harmonic frequencies are directly included in the calculation of the vibrational partition function,

hence corrections have been made to the total partition function of the TSs to account for internal rotations that were considered to be free. The character of all stationary points (minima and TSs) considered in the reactions studied was confirmed by a frequency calculation performed at the same level as for the geometry optimizations.

The tunneling factors, κ and $\Delta s_{1/2}$, were calculated by assuming an unsymmetrical Eckart barrier (see Section 3.4.1). A modified version of the numerical integration program of Brown[66] was used for the calculation of the tunneling factor; the Gaussian quadrature was performed at 40 points for increased accuracy. The output of the program with different input parameters was compared with the results reported by Johnston[41a] for this kind of barrier, with excellent agreement. The FORTRAN programs used to calculate κ and $\Delta s_{1/2}$ were kindly provided by Dr. P. D. Pacey, at Dalhousie University.

The constants and conversion factors used in the calculations reported were obtained from reference 67.

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