Chapter 18
Theory of Rate of Reaction

Everyday experience demonstrates that, most of the time, the rate of a chemical reaction will increase with a rise in temperature. Food, for example, will spoil outside on a hot summer day much faster than it would in a refrigerator. A simple but remarkably accurate relationship for the temperature dependence of reaction rates was empirically found by the Swedish chemist Svante Arrhenius in 1889. The interpretation of the parameters in the Arrhenius equation leads to the development of the idea that when reactants convert into products, they must go through an activated state that requires a characteristic energy. This was the basis of two of the most important theories of reaction rates, collision theory and transition state theory. Collision theory, which only suffices for simple gas phase reactions, essentially views reactants as if they were particles with a certain kinetic energy. Reactions can only occur if two molecules collide with a minimum energy necessary for rearranging the bonds. Matter dynamic considerations play no role here. In transition state theory, a more comprehensive theory that can, in principle, be applied to every possible type of reaction, the rate coefficient is expressed in terms of a difference in chemical potentials between the reactants and a kind of "transition substance" ("ensemble" of all activated complexes), a so-called "potential barrier." For a deeper understanding, the transition state can be interpreted on a molecular level with the help of potential energy surfaces and the "motion" of molecules through these surfaces.

18.1 Temperature Dependence of Reaction Rate

Everyday experience demonstrates that, most of the time, the rate of a chemical reaction will increase with a rise in temperature. Food will spoil outside on a hot summer day much faster than it would in a refrigerator. The decolorization of potassium permanganate by oxalic acid in a sulfuric acid solution (a reaction we already discussed in Chap. 16) is also strongly accelerated by heating (Experiment 18.1).

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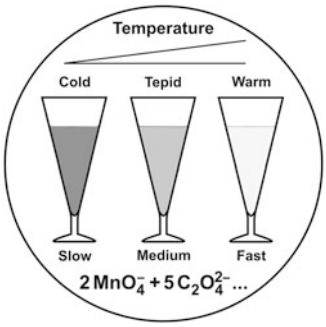


Experiment 18.1 *Temperature dependency of rate of reaction*: Potassium permanganate and acidulated oxalic acid solutions are brought to three different temperatures (in an ice bath at about 0 °C, at room temperature, and in a water bath of about 50 °C). Starting with the coldest oxalic acid solution, the potassium permanganate solution of the same temperature is added to each one. The hottest solution loses color by far the fastest.

An old rule of thumb tells us that a temperature rise of 10 K doubles the rate of reaction. This rule is valid for slow reactions that take between 1 s and 1 a, at not too high temperatures. The actual factor lies between 1.5 and 4.

As we hinted at in Sect. 16.5, the influence of temperature upon the reaction rate is included in the rate coefficient k. Toward the end of the nineteenth century, the Swedish chemist Svante Arrhenius proposed after comparing the experimental kinetic data available at that time that in most reactions, the rate coefficient changes exponentially with the reciprocal of temperature:

$$k(T) = A\mathrm{e}^{-B/T}. \tag{18.1}$$

The parameters A and B that Arrhenius considered to be independent of temperature are characteristic of a reaction.

Arrhenius was also the first to interpret this result, especially the parameter B. In a chemical reaction, the arrangement of atoms in the starting substances must be transformed into that of the products. In this process, preexisting bonds are broken in order to form new ones. One can imagine that a certain minimum energy, the molar (Arrhenius) *activation energy* W_A of the given reaction, is necessary for this. By expanding the exponent by the gas constant R, Eq. (18.1) can be rewritten as follows:

$$k(T) = k_\infty \mathrm{e}^{-W_\mathrm{A}/RT} \quad \text{(Arrhenius equation)}. \tag{18.2}$$

(k_∞ corresponds to the parameter A and W_A/R corresponds to the parameter B [in all, the exponent is then dimensionless, as it should be]).

The *pre-exponential factor* k_∞ (also called the *frequency factor*) mathematically represents the limiting value of the rate coefficient for very high (and in practice impossible to realize) temperatures above 10^4 K ($T \to \infty$) (Fig. 18.1a).

In order to get an impression of the magnitude of activation energy in chemical reactions, let us return to the rule of thumb mentioned above. According to this rule, a temperature increase of 10 K from, for example, $T_1 = 298$ K to $T_2 = 308$ K, should result in a doubling of the rate coefficient. This means that

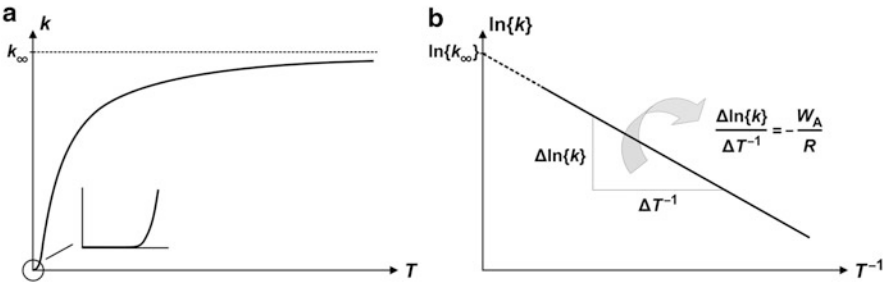


Fig. 18.1 (**a**) Temperature dependency of the rate coefficient k, (**b**) Determination of the activation energy W_A from the Arrhenius diagram.

$$2 \approx \frac{k_2}{k_1} = \frac{k_\infty e^{-W_A/RT_2}}{k_\infty e^{-W_A/RT_1}} = \exp \frac{W_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

Taking the logarithm and solving for W_A yields:

$$W_A = \frac{\ln\frac{k_2}{k_1} \cdot R}{\frac{1}{T_1} - \frac{1}{T_2}} \approx \frac{\ln 2 \times 8.314\ \text{J mol}^{-1}\,\text{K}^{-1}}{\frac{1}{298\ \text{K}} - \frac{1}{308\ \text{K}}} \approx 53\ \text{kJ mol}^{-1}.$$

In fact, the values for molar activation energies of many common reactions lie between 30 and 100 kJ mol^{-1}.

In order to find the molar activation energy for a certain reaction from experimental data, it is a good idea to first take the logarithm of Eq. (18.2):

$$\ln\frac{k}{k^\dagger} = \ln\frac{k_\infty}{k^\dagger} - \frac{W_A}{R} \cdot \frac{1}{T}.$$

$k^\dagger$ represents an arbitrarily chosen reference value with the same dimension as k or k_∞, which is introduced because the argument of a logarithm must be dimensionless. We will try to keep the equation from becoming unnecessarily complicated by using curly brackets to indicate the division by the reference value (compare Sect. 16.5):

$$\ln\{k\} = \ln\{k_\infty\} - \frac{W_A}{R} \cdot \frac{1}{T}. \tag{18.3}$$

If $\ln\{k\}$ is now plotted as a function of $1/T$ (Arrhenius diagram) (Fig. 18.1b), we obtain a straight line from whose slope $-W_A/R$, the molar activation energy results. The value of $\ln\{k_\infty\}$ and, therefore, k_∞ can be determined from the axis intercept after extrapolation to $1/T = 0$.

The steeper the straight line is, meaning the higher the activation energy of the reaction, the stronger its temperature dependency will be. When the temperatures of reactions with low activation energies (around 10 kJ mol^{-1}) are raised, they only accelerate a little. The rates of reactions with high activation energies (around 60 kJ mol^{-1}) increase strongly with rising temperatures.

If $\ln\{k\}$drawn as a function of $1/T$ is not properly straight, the activation energy can be determined from the slope of the tangent for a section of the curve. W_A is then no longer constant but changes with temperature. In general, reactions with complex reaction mechanisms such as chain reactions, enzyme reactions, and heterogeneous catalytic reactions exhibit non-Arrhenius behavior. In the following, however, we will avoid such complications.

The Arrhenius equation is important for its development of the idea that when reactants convert into products, they must go through an activated state that requires a characteristic energy. This was the basis of two of the most important theories of reaction rates, collision theory and transition state theory.

18.2 Collision Theory

A deeper understanding of what the Arrhenius parameters mean can be developed from the *collision theory* of bimolecular gas phase reactions, which itself is based upon kinetic gas theory. The requirement for two particles like H_2 and I_2 or two HI particles to react with each other is that they encounter each other, i.e., that they collide. It has been found, however, that the frequency of collisions in an ideal gas (which is of the order of 10^{35} m^{-3} s^{-1} at standard conditions) by far surpasses the number of particles present so that any gas phase reaction should actually occur in fractions of a microsecond. However, this is not the case. Experimentally determined half-lives are much longer. For example, the reaction of H_2 and I_2 has a half-life of $t_{1/2} = 2 \times 10^{-2}$ s and that of 2 HI has a half-life of $t_{1/2} = 5 \times 10^{-3}$ s. Obviously not all collisions lead to reactions, but only those where the collision energy has exceeded a certain minimum value necessary for rearranging the bonds (Fig. 18.2).

Let us now consider a bimolecular gas phase reaction between particles of types A and B from this point of view. The more particles of one type there are, the more often collisions will occur between the different particles A and B. The *collision frequency* or "*collision density*" Z_{AB}, meaning the number of collisions between A and B (given in mol) per volume and time is directly proportional to the concentrations of both types of particles:

$$Z_{AB} \sim c_A \cdot c_B \quad \text{or} \quad Z_{AB} = \text{const.} \cdot c_A \cdot c_B. \tag{18.4}$$

The amount of energy available at collision for breaking the bonds of two particles A and B does not depend upon their speed v, but upon their speed relative to each other. The way in which they encounter each other (centrally or grazingly) and how

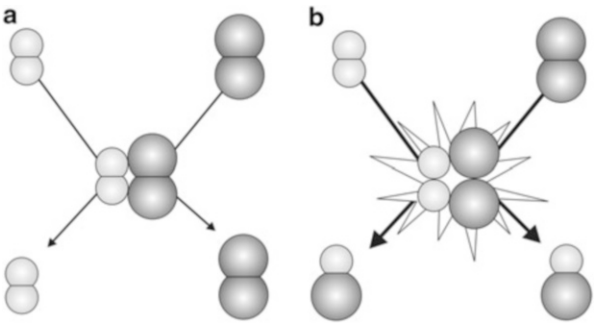


Fig. 18.2 (**a**) Absence of reaction due to too little collision energy, (**b**) Successful reaction in a collision with high enough energy (for the sake of simplicity, we will imagine that all colliding particles—despite their differences in size—are equally heavy and equally fast).

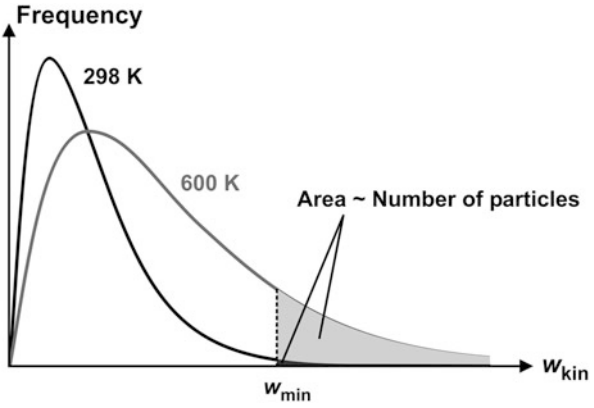


Fig. 18.3 Frequency of gas particles per energy interval dw as a function of kinetic energy w_{kin} at various temperatures. The factor $e^{-w/k_B T}$ with $w = w_{kin}$ stemming from Maxwell's distribution is responsible for the rapid fall of the distribution curve as energy increases.

they rotate or oscillate in the process also plays a role. It is plausible to note that as v increases, the other velocities also increase. We were introduced to Maxwell's distribution of speeds in Sect. 10.4. It indicates the frequency of gas particles per velocity interval dv as a function of velocity v. It is relatively easy to now convert the velocity distribution into a distribution of kinetic energy $w_{kin} = \frac{1}{2}mv^2$ (Fig. 18.3).

The shaded area underneath the corresponding curve indicates the number of gas particles having at least the kinetic energy w_{min}. As the temperature rises, the proportion of particles capable of reacting strongly increases. This is mainly due to the so-called "Boltzmann factor" $e^{-w/k_B T}$ in the energy distribution (compare Sect. 10.5). This factor remains when we integrate over the distribution between $w = w_{min}$ and $w = \infty$. Neglecting the modifying prefactors which enter into this, we obtain a surprising result. The fraction q of all particles having a minimum energy of w_{min} at temperature T equals

$$q = \frac{N(w \geq w_{\min})}{N_{\text{ges}}} \approx \mathrm{e}^{-w_{\min}/k_{\text{B}}T} \quad \text{or} \tag{18.5}$$

$$q \approx \mathrm{e}^{-W_{\min}/RT}, \tag{18.6}$$

where the energy $W_{\min}$ refers to one mol of particles.

We obtain the rate density r by multiplying the collision density by the fraction of collisions having sufficient energy:

$$r = q \cdot Z_{\text{AB}} = \mathrm{e}^{-W_{\min}/RT} \cdot \text{const.} \cdot c_{\text{A}} \cdot c_{\text{B}}. \tag{18.7}$$

When this expression is compared to the second-order rate law (Eq. 16.17),

$$r = k \cdot c_{\text{A}} \cdot c_{\text{B}},$$

the rate coefficient k turns out to be:

$$k = \text{const.} \cdot \mathrm{e}^{-W_{\min}/RT}. \tag{18.8}$$

This relation has exactly the same form as the Arrhenius equation (18.2). The Arrhenius parameters can then be interpreted as follows:

- The activation energy W_{A} corresponds to a minimum energy necessary for breaking existing bonds and forming new bonds when two gas particles collide.
- The pre-exponential factor k_{∞} is the maximum possible rate coefficient that could be attained if all collisions were successful.

To illustrate this, we will take a look at what fraction of gas particles would even be capable of reacting at room temperature when we assume a typical activation energy of 50 kJ mol^{-1}:

$$q = \exp\left(-\frac{W_{\text{A}}}{RT}\right) = \exp\left(-\frac{50 \times 10^3 \ \text{J mol}^{-1}}{8.314 \ \text{J mol}^{-1}\,\text{K}^{-1} \times 298 \ \text{K}}\right) = 1.7 \times 10^{-9},$$

meaning that fewer than two collisions in a billion can lead to a reaction.

The magnitudes of pre-exponential factors k_{∞}, which can be calculated with the help of kinetic gas theory, generally agree with empirically determined values. However, experiments can also show values that are smaller by one or two orders of magnitude than the ones that are calculated. Obviously, a collision of two gas particles with sufficient energy alone, does not guarantee a successful conversion. The particles must be favorably oriented toward each other in order to make a bond between particular atoms possible (Fig. 18.4).

We introduce the so-called *steric factor* $p \leq 1$ in order to correct for this effect. Its numeric value indicates the fraction of collisions having favorable orientation. The more complicated the particles participating in the reaction are,

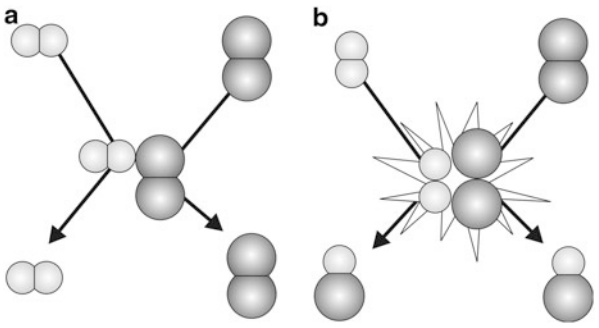


Fig. 18.4 Collision with (**a**) unfavorable orientation, (**b**) favorable orientation.

the higher the requirements for orientation will be and therefore the smaller p will be.

Let us summarize: There are essentially three things necessary for a chemical reaction:

- Collisions of gas particles A and B,
- Excess energy for rearrangement of bonds (activation),
- Favorable mutual orientation at collision (orientation).

18.3 Transition State Theory

Collision theory, which only suffices for simple gas reactions, essentially views reactants as if they were particles with a certain kinetic energy. Matter dynamic considerations play no role here. In the following, we will get to know a more comprehensive theory that can, in principle, be applied to every possible type of reaction.

We can imagine breaking up even single-step reactions into still smaller partial steps. A chemical reaction, as we imagine in atomic models, is a rearrangement of certain molecular components. Atoms making up a certain kind of molecule can be rearranged and combined into new kinds of molecules. For this to happen, existing bonds between atoms must be loosened or broken to form new ones. In a single-step process, all the participating atoms must be present at the same time. They form a so-called "*transition complex*" where the rearrangement takes place. This "complex" is a labile entity, a kind of *transition state* that has a well-defined composition and its own chemical potential, just like any substance. The configuration in the transition state is richer in energy than the particles at the beginning or end of the reaction. The atoms or molecules need to be in an "activated" (energy rich) state in order to form this configuration of higher energy. Therefore, the transition complex is also called *activated complex*.

It takes a certain amount of time to pass through the transition state. This can be regarded as a finite but extremely short lifetime. Despite their short lifetime, these complexes behave like a kind of particle and the ensemble of these labile "transition particles" behaves like a substance that is present in very small concentration in the reaction mixture. In order to emphasize this aspect, we will call the ensemble of such short-lived particles a *transition substance* and mark it by the symbol ‡. Formation of a transition substance can be expressed by the following formula:

$$\underbrace{\mathrm{A} + \mathrm{BC} \rightleftarrows \overbrace{\mathrm{A} \cdots \mathrm{B} \cdots \mathrm{C}}^{\ddagger}}_{\text{Activation}} \rightarrow \mathrm{AB} + \mathrm{C}.$$

The first half-step of this transformation, which requires energy input, is called the *activation* or *activation reaction*. We will use the index ‡ for the quantities belonging to this process as we do with all quantities related to the transition substance. In the second half-step, the transition substance decays into the products (this latter step is monomolecular).

The extremely short lifetime and maximum energy distinguish between this transition substance and the unstable intermediate substance of a consecutive reaction (compare Sect. 17.4). The latter has "normal" bonds and can be isolated and investigated, while the former cannot.

An optimally realistic description of transition substances based upon quantum mechanics form the core of the theory developed in the 1930s by Henry Eyring, Meredith Gwynne Evans, and Michael Polanyi.

A transformation of the starting substances into the final products must always proceed over a transition substance whose instantaneous amount $n_\ddagger$ as well as lifetime $\tau_\ddagger$ will determine the rate of the reaction:

$$\omega = \dot{\xi} = \frac{n_\ddagger}{\tau_\ddagger}. \tag{18.9}$$

In a homogeneous reaction, we obtain the rate density r from ω, as usual, by dividing the equation above by volume V (where $c_\ddagger = n_\ddagger/V$ is the concentration of the transition substance):

$$r = \frac{c_\ddagger}{\tau_\ddagger}. \tag{18.10}$$

According to considerations stemming most likely from Eyring in 1935, it can be assumed approximately that the amount of the short-lived transition substance present in a reaction mixture will reach a value that would form in equilibrium

with the reactants. (This assumption is not strictly valid because there is no classical chemical equilibrium when the transition substance constantly decays into the products. We therefore also speak from the quasi-equilibrium assumption.)

However, if we proceed on the assumption that the transition substance exists in close to equilibrium concentration, this quantity can easily be calculated using the mass action law. For the reaction above we have:

$$\overset{\circ}{\mathcal{K}}_{\ddagger} = \frac{c_{\ddagger}/c^{\ominus}}{(c_{\mathrm{A}}/c^{\ominus}) \cdot (c_{\mathrm{BC}}/c^{\ominus})} \cdot \tag{18.11}$$

If we solve the equation for the concentration $c_{\ddagger}$ of the transition substance, we obtain

$$c_{\ddagger} = \overset{\circ}{\mathcal{K}}_{\ddagger} \cdot c^{\ominus} \cdot \frac{c_{\mathrm{A}}}{c^{\ominus}} \cdot \frac{c_{\mathrm{BC}}}{c^{\ominus}}. \tag{18.12}$$

Eyring used quantum mechanics to derive a very simple expression for the lifetime of the transition state:

$$\tau_{\ddagger} = \frac{h}{k_{\mathrm{B}}T}. \tag{18.13}$$

Here, h is Planck's constant with $h = 6.626 \times 10^{-34}$ J s and k_{B} is Boltzmann's constant with $k_{\mathrm{B}} = 1.381 \times 10^{-23}$ J K^{-1}.

Equation (18.13) only deals with the decay of the transition substance into the products, because the reverse decay into the reactants is compensated for by constant formation.

The resulting order of magnitude of $\tau_{\ddagger}$ at room temperature is $\tau_{\ddagger}$ [$= 6.626 \times 10^{-34}$ J s/$(1.381 \times 10^{-23}$ J K$^{-1} \times 298$ K)] $\approx 10^{-13}$ s. The lifetime is, indeed, very short. As temperature rises, it gets even shorter. One of the reasons is that, on average, the transition state will be passed through more quickly because of greater particle velocity in a warmer environment. The best aspect of this equation is that all transition substances behave identically, *independent of their type*.

Because we lack the theoretical background to reason in detail about the two Eyring assumptions—namely those concerning concentration and lifetime of transition substances—we treat them as basic assumptions that can be justified by comparing their conclusions in retrospect with those of experience. But what are these conclusions?

By combining the equations for $c_{\ddagger}$ and $\tau_{\ddagger}$, we obtain the desired rate density r, which we will contrast with the corresponding rate law for a second-order reaction:

$$r = \boxed{\frac{k_B T}{h} \cdot \overset{\circ}{\mathcal{K}}_{\ddagger} \cdot c^{\ominus} \cdot \frac{c_A}{c^{\ominus}} \cdot \frac{c_{BC}}{c^{\ominus}}} = k \cdot c_A \cdot c_{BC} \,. \tag{18.14}$$

In the framed expression, the equilibrium number $\overset{\circ}{\mathcal{K}}_{\ddagger}$ is the only quantity that is dependent upon the *type* of reaction. As usual, this can be calculated from the relation

$$\overset{\circ}{\mathcal{K}}_{\ddagger} = \exp\left(\frac{\overset{\circ}{\mathcal{A}}_{\ddagger}}{RT}\right) = \exp\left(\frac{\overset{\circ}{\mu}_A + \overset{\circ}{\mu}_{BC} - \overset{\circ}{\mu}_{\ddagger}}{RT}\right) = \exp\left(-\frac{\Delta_{\ddagger}\overset{\circ}{\mu}}{RT}\right). \tag{18.15}$$

The rate coefficient k then results in

$$k = \kappa_{\ddagger} \frac{k_B T}{h} \cdot \exp\left(\frac{\overset{\circ}{\mathcal{A}}_{\ddagger}}{RT}\right) = \kappa_{\ddagger} \frac{k_B T}{h} \cdot \exp\left(-\frac{\Delta_{\ddagger}\overset{\circ}{\mu}}{RT}\right) \tag{18.16}$$

with the dimensional factor $\kappa_{\ddagger} = (c^{\ominus})^{-1}$. We will call the quantity $-\mathcal{A}_{\ddagger} = \Delta_{\ddagger}\mu = \mu_{\ddagger} - \mu_A - \mu_{BC}$ the *activation threshold* of the reaction and its special value $-\overset{\circ}{\mathcal{A}}_{\ddagger} = \Delta_{\ddagger}\overset{\circ}{\mu}$ its basic value. Note that because we assume equilibrium, we have $\mathcal{A}_{\ddagger} = 0$. However, the basic value $\overset{\circ}{\mathcal{A}}_{\ddagger}$ is not equal to zero.

This conclusion is rather remarkable. It tells us that the reaction resistance and therefore the individual differences in the rates of different reactions are solely dependent upon the height of the potential threshold $\Delta_{\ddagger}\overset{\circ}{\mu}$ between the starting substances and the transition substance. In order to clarify this statement, the potentials, i.e., the basic values $\overset{\circ}{\mu}$ and the actual values μ, will be represented graphically (Fig. 18.5).

Only in the case of basic potentials does an activation threshold $\Delta_{\ddagger}\overset{\circ}{\mu}$ appear in the form of a step ascending from the left toward the transition substance. The threshold is equal to zero in the case of actual potentials because of the assumed equilibrium:

$$A + BC \rightleftarrows \ddagger \qquad\qquad \Delta_{\ddagger}\mu = 0.$$

The potential threshold $\Delta_{\ddagger}\overset{\circ}{\mu}$ determines the conversion rate of the reaction proceeding from left to right. The higher the activation threshold is, the lower the rate coefficient, and the slower the reaction. The rate decreases very quickly, i.e., exponentially, with the height of the activation threshold.

When the chemical potential $\overset{\circ}{\mu}_{\ddagger}$ of the transition substance is at the level $\overset{\circ}{\mu}_A + \overset{\circ}{\mu}_{BC}$ of the reactants, meaning the activation threshold $\Delta_{\ddagger}\overset{\circ}{\mu}$ is zero, and all the substances are present in standard concentration, then our formula will yield

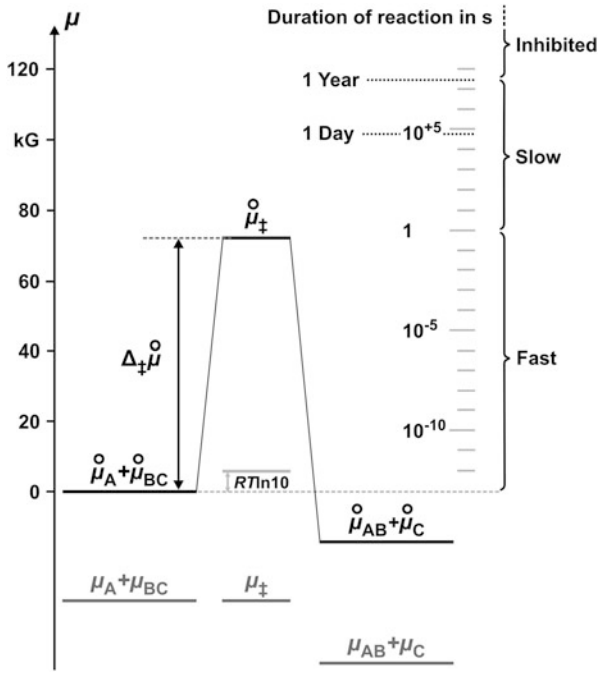


Fig. 18.5 Potential diagram for describing conversion rates. Basic values (*black bars*) and actual values (*gray bars*) are represented for starting substances and final products as well as for the transition substance ‡. (The level of the basic values of μ was arbitrarily chosen as the zero point of the potential scale).

$$r_0 \approx \frac{1}{10^{-13}\ \mathrm{s}} \times 10^3\ \ \mathrm{mol\,m^{-3}} \times \exp(0) \times 1 \times 1 = 10^{16}\ \ \mathrm{mol\,m^{-3}\,s^{-1}}$$

for the rate density r at normal laboratory temperatures. Since there are 10^3 mol of each substance in a cubic meter, they would be used up in 10^{-13} s if these conditions prevailed and the rate were constant.

The conversion rate will slow to one-tenth when $\Delta_\ddagger \overset{\circ}{\mu}$ grows by the decapotential $\mu_\mathrm{d} = RT\ \ln 10 = 5.71$ kG [remember that $\exp(-RT\ \ln 10/RT) = 10^{-1}$] and it will take 10 times as long for the reactants to be used up. Repeatedly elevating the threshold by $RT\ \ln 10$ will lengthen the duration of reaction each time by a factor of 10. After 13 such steps, the duration of reaction will have reached about 1 s which is perceivable under normal laboratory conditions. The dividing line between *fast* and *slow* reactions can be drawn here. Past the twentieth step, the duration of reaction reaches 1 year, sorely taxing the stamina of even the most patient chemists. Such reactions should be considered to be *inhibited* because almost no conversion occurs within the period of observation.

In order to demonstrate the relation with Arrhenius's proposition $k = A\mathrm{e}^{-B/T}$, it is enough to apply the usual linear approximation $\mathcal{A}_\ddagger = \mathcal{A}_{\ddagger,0} + \alpha(T - T_0)$ for $\mathcal{A}_\ddagger(T)$:

$$\overset{\circ}{K}_{\ddagger} = \exp\frac{\overset{\circ}{\mathcal{A}}_{\ddagger}}{RT} = \exp\frac{\overset{\circ}{\mathcal{A}}_{\ddagger,0} + \alpha\cdot(T - T_0)}{RT} = \exp\overbrace{\frac{(\overset{\circ}{\mathcal{A}}_{\ddagger,0} - \alpha\cdot T_0)/R}{T}}^{-B}\cdot\overbrace{\exp\frac{\alpha}{R}}^{A^*} = A^*\mathrm{e}^{-B/T}$$

and consequently,

$$k = \kappa_{\ddagger}\frac{k_{\mathrm{B}}T}{h}A^*\mathrm{e}^{-B/T}.$$

A^* corresponds to Arrhenius's parameter A, except for the factor $\kappa_{\ddagger}\cdot k_{\mathrm{B}}T/h$. B is a constant as assumed by Arrhenius, but A is not. However, compared to the factor $\mathrm{e}^{-B/T}$, this temperature dependency is almost unnoticeable and can be ignored if the temperature range is not too large.

The temperature coefficient α, which we can write more elaborately as $\overset{\circ}{\alpha}_{\ddagger,0}$, agrees numerically with the activation entropy, so $\alpha = \overset{\circ}{\alpha}_{\ddagger,0} = \Delta_{\ddagger}\overset{\circ}{S}_0$. It is negative because the transition state ‡ is better ordered and lower in entropy than what it was formed from: separated, swarming, turbulent particles. When a certain orientation for the colliding particles is required, it is necessary for the transition state to be less arbitrary and have more order so that the activation entropy is more strongly negative. In collision theory, we used the steric factor to describe this characteristic.

18.4 Molecular Interpretation of the Transition State

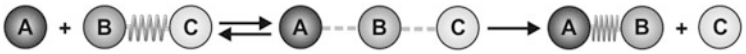
Although the short characterization of the transition state in the last section would basically suffice for our future purposes, a more detailed description is often desired for a deeper understanding.

The rearrangement of atoms during a reaction does not take place all at once but extends over a certain time span. In the process, reactant particles change into product particles. We have seen an example of this in the reaction

$$\mathrm{A} + \mathrm{BC} \rightarrow \mathrm{AB} + \mathrm{C}$$

where it is assumed that the centers of mass of all three atoms always lie in a straight line. During the reaction, when A approaches BC, the bond between B and C is loosened. (A very simple image for this bond might be a spring.) At the same time, a new bond between A and B starts to form. As the reaction progresses, it goes through the aforementioned transition state (activated complex) A···B···C which finally breaks apart forming molecule AB and atom C:

$$A + BC \rightleftarrows \underbrace{A \cdots B \cdots C}_{\ddagger} \rightarrow AB + C.$$



We can imagine both starting substances and final products to be extreme arrangements of the activated complex. In the initial state, atoms B and C are at bonding distance and atom A is far away. Figure 18.6a shows the potential energy W_{pot} as a function of distance r_{BC} between the nuclei in molecule BC (compare Sect. 11.1). It rises sharply when the bond is compressed relative to the equilibrium distance $r_{BC,eq.}$ ($r_{BC} < r_{BC,eq.}$). If the bond is elongated ($r_{BC} > r_{BC,eq.}$), W_{pot} increases as well due to subsiding of attractive forces. It asymptotically approaches a limiting value corresponding to the energy of the completely separated atoms B and C (dissociation energy). The potential energy for various distances between the nuclei of molecule BC can be calculated using quantum mechanics. An analogous diagram can also be created for molecule AB (Fig. 18.6b).

The minimum of potential energy at equilibrium distance $r_{BC,eq.}$ (the always present zero-point energy of the vibrational ground state will not be taken into consideration here) represents the initial state, meaning that atom A is at a great distance from molecule BC. If atom A approaches molecule BC, which will decay during the reaction, then for each instant of this rearrangement, the positions of the molecular components participating in the triatomic stretched "molecule" A···B···C can be characterized. In this way, we end up with a very large number of intermediate states for the reaction. Each possible intermediate state, including the initial and final states, has a certain potential energy assigned to it that is dependent upon the geometry of the given arrangement, meaning the distances r_{AB} and r_{BC} of the atoms. The energy can, in principle, be calculated quantum mechanically. If this energy is plotted in the z direction as a function of the distances of the nuclei (r_{AB} in the x and r_{BC} in the y direction), a three-dimensional representation will result

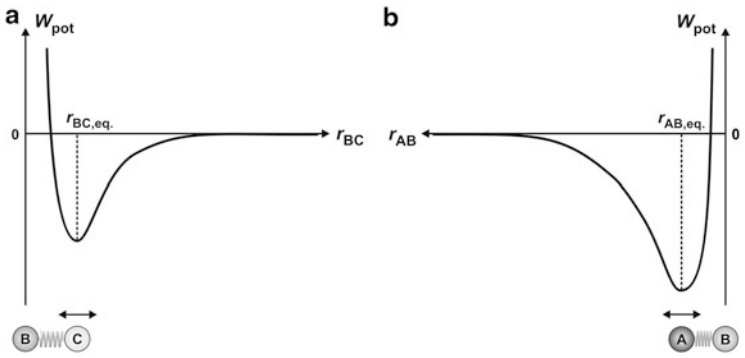


Fig. 18.6 Potential energy W_{pot} of (**a**) molecules BC and (**b**) molecules AB for large distances from the third partners A or C. $r_{BC,eq.}$ and $r_{AB,eq.}$ are the equilibrium distances.

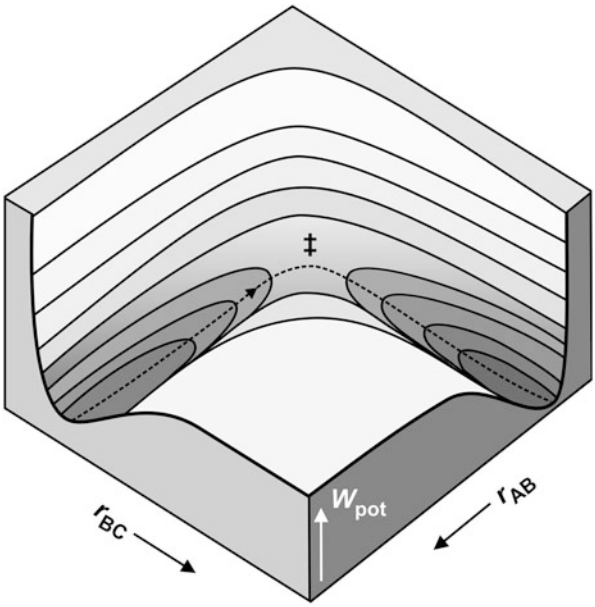


Fig. 18.7 Surface of potential energy for a linear particle system $A \overset{r_{AB}}{\cdots} B \overset{r_{BC}}{\cdots} C$.

(potential energy surface; Fig. 18.7). The preceding diagrams 18.6a and b form the vertical side-walls. To make the energy surface clearer, the points of identical energies have been connected at given intervals by lines of constant energy (contour lines).

Initially, when A is still very far away, molecule BC is in a deep energy trough ("bottom of the valley" on the left). If atom A approaches molecule BC, the potential energy rises as a result of loosening of the BC bond ("movement up in the valley") until a maximum ("valley-ridge inflection point" or "saddle" ‡) is obtained that equals the energetically labile transition state A···B···C. As the distance between A and B continues to decrease, W_{pot} will fall again due to formation of the AB bond in the direction of the "bottom of the valley" on the right. At the same time, C moves away from the AB molecule that is forming. In the final state of the reaction, we have the molecule AB in a deep energy trough (equilibrium state $r_{AB,eq.}$) as well as the separated atom C.

A clearer image of this might be gained by imagining the three-dimensional potential energy surface (comparable to a mountainous landscape in which elevation corresponds to potential energy) to be projected upon the plane spanned by the r_{AB} and r_{BC} axes. This produces a two-dimensional contour diagram that is comparable to a topographic contour map (Fig. 18.8a).

Although the initial and the final states of the reaction are uniquely specified, the path by which the rearrangement converts the initial state into the final state is not. It is easy to imagine that the individual molecular components might take very different paths to achieve their stable final arrangements. There are any number of

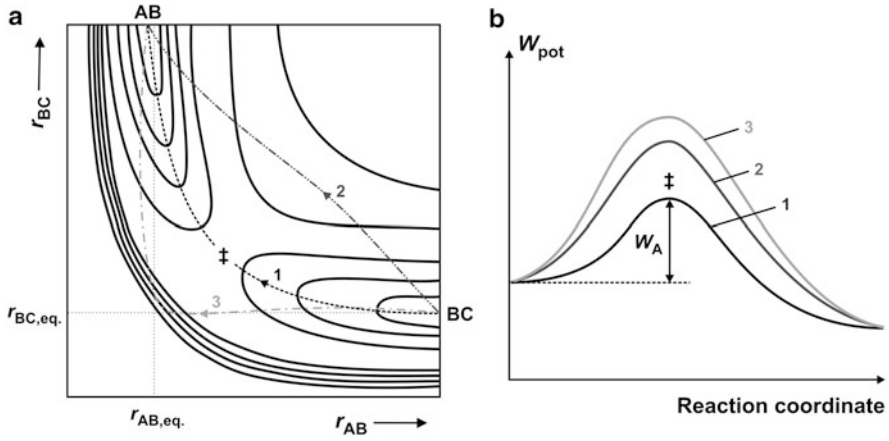


Fig. 18.8 (**a**) Contour map of the energy surface for the linear particle system A···B···C with three possible paths of reaction A + BC → AB + C, (**b**) Corresponding energy profiles.

reaction paths the process of rearrangement may take. In general, there is at least one instantaneous arrangement upon every path whose energy exceeds the energy of the initial and final states. This state is usually called a *transition* or *activated state*. Hence, there is at least one activated state with *maximum energy* on every reaction path. Among all the reaction paths, one path stands out for which the maximum of energy is minimal. The corresponding atomic arrangement is the transition state in the strict sense (for short, *the* transition state).

An image that can make this clearer is a hiker crossing some mountains to reach a destination leaving from a starting point. Upon *each* path the hiker could take, he will find himself at a point of maximum elevation (potential energy) as he crosses the ridge of the mountains. Among these possible paths, there are those that go over a pass. The summit of the pass with the lowest elevation corresponds to the transition state (in the strict sense).

The potential energy contour map (Fig. 18.8a) shows three of the many possible paths leading from BC to AB. If we follow the change of potential energy along these paths with the help of an energy profile (Fig. 18.8b), we see that the path leading over the saddle point (the transition state in the strict sense) is the most economic because it requires the least energy. This special minimum energy path is called *reaction coordinate*. It is important to keep in mind that the transition state (in the strict sense) itself corresponds to an energy maximum along this coordinate, differentiating it from an intermediate product. The course of molecular energies of the reaction is reflected in the course taken by the chemical potentials (compare Fig. 18.5).