

On Rate Constants: Simple Collision Theory, Arrhenius Behavior, and Activated Complex Theory

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0.1 Introduction

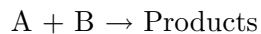
Up to now, we haven't said much regarding the rate constant k . It should be apparent from the discussions, however, that:

- k is constant at a specific temperature, T and pressure, P
- thus, $k = k(T,P)$ (rate constant is temperature and pressure dependent)
- bear in mind that the rate constant is *independent* of concentrations, as the *reaction rate*, or *velocity* itself is treated explicitly to be concentration dependent

In the following, we will consider how the physical, microscopic details of reactions can be reasoned to be embodied in the rate constant, k .

1 Simple Collision Theory

Let's consider the following **gas-phase elementary reaction**:



The reaction rate is straightforwardly:

$$\begin{aligned}
& \text{Rate} = k[A]^\alpha[B]^\beta \\
& = k[A]^1[B]^1 \qquad \alpha = 1 \quad \beta = 1 \\
& = k \frac{N_A}{V} \frac{N_B}{V} \qquad V = \text{volume}
\end{aligned}$$

Recall previous discussions of the total collisional frequency for heterogeneous reactions:

$$Z_{AB} = \sigma_{AB} \sqrt{\frac{8kT}{\pi\mu}} n_A^* n_{B^*}$$

where the $n_A^* = \frac{N_A}{V}$, $n_{B^*} = \frac{N_B}{V}$ are number of molecules/particles per unit volume. We can see the following:

$$Z_{AB} = \underbrace{\sigma_{AB} \sqrt{\frac{8kT}{\pi\mu}}}_k \frac{N_A}{V} \frac{N_B}{V}$$

Here we see that the concepts of collisions from simple kinetic theory can be fundamentally related to ideas of reactions, particularly when we consider that elementary reactions (only for which we can write rate expressions based on molecularity and order mapping) can be thought of proceeding due to collisions (or interactions of some sort) of monomers (unimolecular), dimers (bimolecular), trimers (trimolecular), etc.

If we are to naively say that reactions occur due only to collisions of particles (keep in mind the nature of the system – gas-phase, elementary reaction), then we can at the zero'th order equate the maximum reaction rate to the total collisional frequency for heterogeneous pairs:

$$R^{max} = Z_{AB}$$

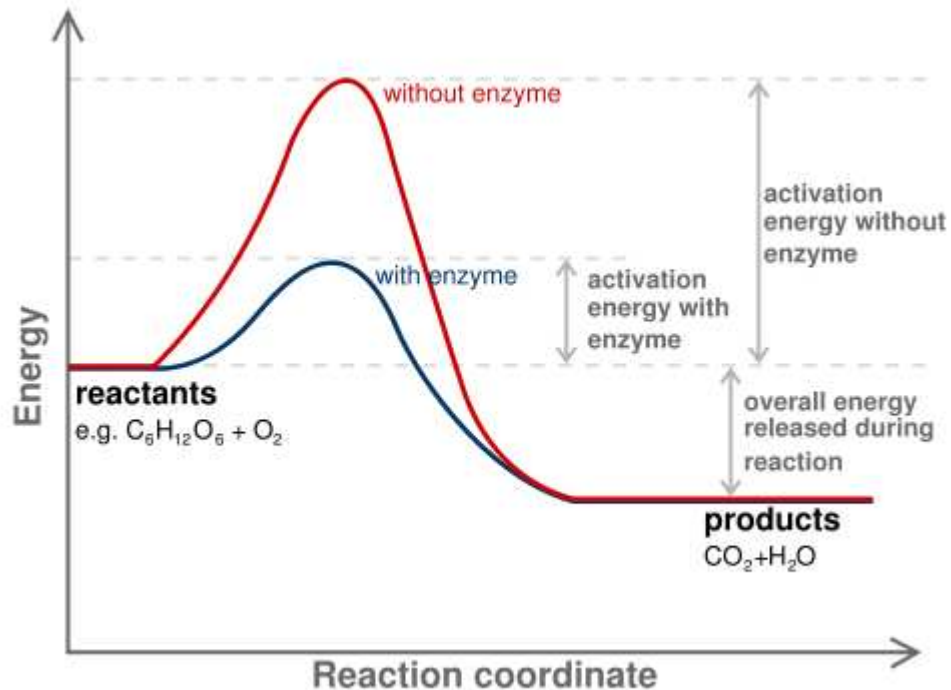
$$k^{max} [A]^1 [B]^1 = \underbrace{\sigma_{AB} \sqrt{\frac{8kT}{\pi\mu}}}_k \frac{N_A}{V} \frac{N_B}{V}$$

$$k^{max} \equiv \sigma_{AB} \sqrt{\frac{8kT}{\pi\mu}}$$

1.1 Simple Collision Theory: Caveats

Simple collision theory (SCT), we see from above, remarkably predicts an expression for the microscopic rate constant that relates to the dimensions of the reactive species, their mass, and temperature. The form we determined above assumes two things:

- All collisions are of sufficient energy that chemical transformation can occur



- Steric/orientational nature of collision is always correct/accommodating

Thus, we need to consider the effects of **collision energy** and **collision sterics and/or orientation** in our discussion of simple collision theory and its application to defining the rate constant, k .

- For energetic considerations, we can empirically add a factor to account for the **probability** of a collision having a sufficient energy, *vis-a-vis*, E_{min} , for collision. When we multiply the total collisional frequency by this probability, we can describe the fraction of collisions that will energetically be able to progress from reactants to products. The energy probability is taken to be Boltzmann-like:

$$Probability(E_{min}) \propto e^{\frac{-E_{min}}{RT}}$$

- For steric/orientational nature of collision, we introduce a steric factor (empirically), p
- $p < 1$ generally

Thus, we can write a more general expression for the collision theory based reaction rate as:

$$\begin{aligned} \text{Rate} &= Z_{AB} p e^{-\frac{E_{min}}{RT}} \\ &= p \sigma_{AB} \sqrt{\frac{8kT}{\pi\mu}} e^{-\frac{E_{min}}{RT}} \frac{N_A}{V} \frac{N_B}{V} \end{aligned}$$

Thus we arrive at a corrected Simple collision theory expression for the rate constant:

$$\begin{aligned} k_{SCT} &= p \sigma_{AB} \sqrt{\frac{8kT}{\pi\mu}} e^{-\frac{E_{min}}{RT}} \\ \ln(k_{SCT}) &= \ln \left[p \sigma_{AB} \sqrt{\frac{8kT}{\pi\mu}} \right] - \frac{E_{min}}{RT} \end{aligned}$$

Note the temperature dependence of the rate constant with SCT:
 $k_{SCT} \propto T^{\frac{1}{2}}$.

In general, we can write this expression for the rate constant as:

$$k_{general} = c T^m e^{-E_{min}/RT} \quad (1)$$

2 Arrhenius Temperature Dependence

In general, experiments do not suggest a $T^{\frac{1}{2}}$ temperature dependence of the rate constant. Moreover, experiments demonstrate for most reactions that the temperature dependence of $\ln(k)$ is linear with $\frac{1}{T}$. Thus, Arrhenius proposed the following relation between temperature and the rate constant:

$$k_{Arr} = A e^{-\frac{E_{activation}}{RT}} \quad (2)$$

Thus,

$$\ln(k_{Arr}) = \ln(A) - \frac{E_{activation}}{R} \frac{1}{T} \quad (3)$$

The energy is the activation energy (as discussed above) and the A value is a temperature-independent frequency factor, or pre-exponential factor.

Plotting $\ln(k)$ versus T^{-1} will yield a straight line with slope equal to $-\frac{E_{activation}}{R}$ and y intercept of $\ln(A)$.

The pre-exponential factor in this case is **independent** of temperature, contrasted with the SCT result from above. Though many reactions (across the spectrum of reaction orders, mechanisms, etc.) follow Arrhenius behavior, there are exceptions (as always).

3 Activated Complex Theory; Transition State Theory

In this section, we will consider a further refinement of our formulation of a reaction on the atomic level. Up to now, we have not entertained the possibility of **short-lived, highly unstable intermediates** appearing/being generated upon the initial "collision" of reactive species. Eyring and co-workers postulated the presence of these **highly unstable, fleeting, transition states**, and furthermore suggested an equilibrium between this transition state and the reactive species. The transition state is also considered an **activated complex**, hence the nomenclature Activated Complex Theory (as well as Transition State Theory).

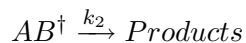
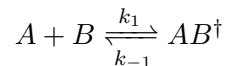
A further important aspect of invoking the activated complex is that for a reaction such as $AB + C \rightarrow A + BC$, the path the reaction follows (if depicted on a three-dimensional potential energy surface) is the **minimum energy path**. That is, the reaction will not follow along a **reaction coordinate** that requires any higher energetic cost than is minimally necessary. See Figure 36.19 in Engell and Reid for a representation of a representative 3-D potential energy surface.

Assumptions of activated complex theory:

- Equilibrium exists between reactants and activated complex

- Reaction coordinate can be mapped onto a single energetic degree of freedom of the activated complex (i.e., a vibrational degree of freedom corresponding to bond-stretching)

The kinetic mechanism incorporating the activated complex is now:



The differential rate expression for A becomes:

$$\frac{d[A]}{dt} = 0 = -k_{-1}[A][B] + k_{-1}[AB^\ddagger]$$

$$[AB^\ddagger] = \frac{k_1}{k_{-1}}[A][B] = \frac{K_c^\ddagger}{c^\circ} [A][B]$$

Note the dependence of the equilibrium constant on the standard state concentration, c° :

$$K_c^\ddagger = \frac{\frac{[AB^\ddagger]}{c^\circ}}{\frac{[A]}{c^\circ} \frac{[B]}{c^\circ}} = \frac{[AB^\ddagger] c^\circ}{[A][B]}$$

The rate of product, P, formation (equal to the reaction rate) is:

$$\text{Rate} = \frac{d[P]}{dt} = k_2[AB^\ddagger]$$

and since we know what $[AB^\ddagger]$ is from equilibrium of the reactants with the activated complex:

$$\text{Rate} = \frac{d[P]}{dt} = \frac{k_2 K_c^\ddagger}{c^\circ} [A][B]$$

Now, we will consider how to refine our understanding of k_2 . Consider:

- We have formulated our discussion with the assumption that there is a single reaction coordinate mapped onto a vibrational degree of freedom
- Let this vibrational degree of freedom be a **weak** bond
- Rate of product formation = Rate of reaction = Frequency of vibration of **weak** bond (inverse seconds) (Maximum rate since we are taking every initial motion along that vibration coordinate to lead to product formation) ($k_2 = \nu$).
- If every κ of the vibrational cycles leads to product formation, then $k_2 = \kappa\nu$

Thus, the reaction rate can be written as:

$$\text{Rate} = \frac{d[P]}{dt} = \frac{\kappa \nu K_c^\ddagger}{c^\circ} [A][B]$$

Using elements of statistical mechanics (the details of which are outside the current scope, but are covered in: Moore and Pearson, **Kinetics and Mechanism**, John Wiley, 1981, pp. 159-186)

$$k_2 = \frac{\kappa k_B T K_c^\ddagger}{h c^\circ}$$

where the h in the denominator is Planck's constant. Finally, if we recall that we can relate the equilibrium constant to the **free energy** change from reactant to activated complex,

$$\Delta G^\ddagger = -RT \ln(K_c^\ddagger)$$

Thus, the rate constant becomes (taking $\kappa = 1$, which is a good approximation for most situations (exceptions include surface reactions)):

$$k_2 = \frac{k_B T}{h c^\circ} e^{-\Delta G^\ddagger / RT}$$

Since:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

we finally obtain the **Eyring Equation**:

$$k_2 = \frac{k_B T}{hc^\circ} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}$$

In the most general sense:

$$k(T) = \frac{k_B T}{hc^\circ} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}$$

We see that activated complex theory allows us to incorporate free energy as a metric for determining the rate constant. In this sense, **entropic** factors come into play as well. In the next section, we will discuss the relation between the parameters of Arrhenius theory and ΔS^\ddagger and ΔH^\ddagger .

4 Connection to Arrhenius Parameters

The quantities ΔH^\ddagger and ΔS^\ddagger are now related to the Arrhenius pre-exponential factor and activation energy, E_a .

Table 1. Relation Between Arrhenius and Eyring Parameters.

Phase / Molecularity	Activation Energy, E_a	Pre-Exponential, A
Solution/Bimolecular	$E_a = \Delta H^\ddagger + RT$	$A = \frac{e k_B T}{hc^\circ} e^{\Delta S^\ddagger/R}$
Solution/Unimolecular	$E_a = \Delta H^\ddagger + RT$	$A = \frac{e k_B T}{h} e^{\Delta S^\ddagger/R}$
Gas/Unimolecular	$E_a = \Delta H^\ddagger + RT$	$A = \frac{e k_B T}{h} e^{\Delta S^\ddagger/R}$
Gas/Bimolecular	$E_a = \Delta H^\ddagger + 2RT$	$A = \frac{e^2 k_B T}{hc^\circ} e^{\Delta S^\ddagger/R}$
Gas/Trimolecular	$E_a = \Delta H^\ddagger + 3RT$	$A = \frac{e^3 k_B T}{h(c^\circ)^2} e^{\Delta S^\ddagger/R}$