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## Eyring Equation

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**German version**

*"If the Lord Almighty had consulted me before embarking upon the Creation,  
I should have recommended something simpler."*

Alphonso X, the Wise of Spain (1223-1284)

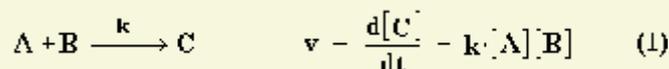
*"Everything should be made as simple as possible, but not simpler."*

Albert Einstein



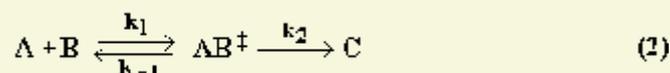
Both the **Arrhenius** and the **Eyring equation** describe the temperature dependence of reaction rate. Strictly speaking, the **Arrhenius equation** can be applied only to the kinetics of gas reactions. The **Eyring equation** is also used in the study of solution reactions and mixed phase reactions - all places where the simple **collision model** is not very helpful. The Arrhenius equation is founded on the empirical observation that rates of reactions increase with temperature. The **Eyring equation** is a theoretical construct, based on **transition state** model.

The bimolecular reaction



is considered by 'transition state theory'.

According to the **transition state** model, the reactants are getting over into an unsteady intermediate state on the reaction pathway.



There is an '**energy barrier**' on the pathway between the reactants (A, B) and the

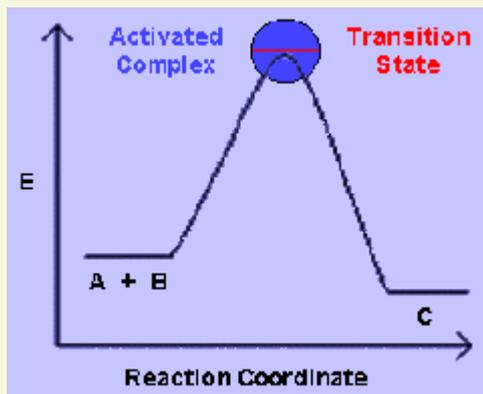


Figure 1: Energy profile

E: Potential energy

Reaction coordinate: parameter changing during the course of the reaction (as bond length or bond angle)

Transition state: Maximum of energy in the path way

product (C). The barrier determines a 'threshold energy' or minimum of energy necessary to permit the reaction to occur. It is called 'activation enthalpy' ('activation energy').

Fig. 1 shows the energy of the molecules along the reaction coordinate which measures the progress of the reaction. Along the flat region at the left, the particles are approaching each other. They possess kinetic energy and their potential energy is constant. The beginning of the rise in the curve signifies that the two molecules have enough energy to have an effect on each other. During the approach, the particles slow down as their kinetic energies furnish the potential energy to climb the curve. If the reacting particles possess sufficient energy they can ascend the left side of the 'barrier' all the way up to the summit. Attaining of the summit can be interpreted as follows: The approaching reactant molecules had sufficient kinetic energy to overcome the mutual repulsive forces between the electron clouds of their constituent atoms and thus come very close to each other.

An 'activated complex'  $AB^\ddagger$  or 'transition state' is formed at the potential energy maximum. The high-energy complex represents an unstable molecular arrangement, in which bonds break and form to generate the product C or to degenerate back to the reactants A and B. Once the energy barrier is surmounted, the reaction proceeds downhill to the product.

Principles of the transition state theory:

- There is a thermodynamic equilibrium between the transition state and the state of reactants at the top of the energy barrier.

- The rate of chemical reaction is proportional to the concentration of the particles in the high-energy transition state.

The process if the reaction (1) can be divided into two stages (2):

- a direct step downhill from the transition state to the product
- the equilibrium between the reactants and the transition state.

The change in the concentration of the complex  $AB^\ddagger$  over time can be described by the following equation:

$$\frac{d[AB^\ddagger]}{dt} = k_1 \cdot [A] \cdot [B] - k_{-1} \cdot [AB^\ddagger] - k_2 \cdot [AB^\ddagger] \quad (3)$$

- Due to the equilibrium between the 'activated complex'  $AB^\ddagger$  and the reactants A and B, the components  $k_1 \cdot [A] \cdot [B]$  and  $k_{-1} \cdot [AB^\ddagger]$  cancel out. Thus the rate of the direct reaction is proportional to the concentration of  $AB^\ddagger$ :

$$\frac{d[C]}{dt} = k_2 \cdot [AB^\ddagger] \quad (4)$$

$k_2$  is given by statistical mechanics:

$$k_2 = \frac{k_B \cdot T}{h} \quad (5)$$

$k_B$  = Boltzmann's constant [ $1.381 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$ ]

T = absolute temperature in degrees Kelvin (K)

h = Plank constant [ $6.626 \cdot 10^{-34} \text{ J} \cdot \text{s}$ ]

$k_2$  is called 'universal constant for a transition state' ( $\sim 6 \cdot 10^{12} \text{ sec}^{-1}$  at room temperature).

- Additionally,  $[AB^\ddagger]$  can be derived from the pseudo equilibrium between the transition state molecule  $AB^\ddagger$  and the reactant molecules:

$$[AB^\ddagger] = K^\ddagger \cdot [A] \cdot [B] \quad (6)$$

$K^\ddagger$  = thermodynamic equilibrium constant

Due to the equilibrium that will be reached rapidly, the reactants and the activated complex decrease at the same rate. Therefore, considering both equation (5) and (6), equation (4) becomes:

$$\frac{d[C]}{dt} = \frac{k_B \cdot T}{h} \cdot K^\ddagger \cdot [A] \cdot [B] \quad (7)$$

Comparing the derived rate law (1) and the expression (7) yields for the rate constant of the overall reaction

$$k = \frac{k_B \cdot T}{h} \cdot K^\ddagger \quad (8)$$

• Additionally, thermodynamics gives a further description of the equilibrium constant:

$$\Delta G^\ddagger = -R \cdot T \cdot \ln K^\ddagger \quad (9)$$

Furthermore  $\Delta G^\ddagger$  is given by

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad (10)$$

R = Universal Gas Constant = 8.3145 J/mol K

$\Delta G^\ddagger$  = free activation enthalpy [kJ · mol<sup>-1</sup>]

$\Delta S^\ddagger$  = activation entropy [J · mol<sup>-1</sup> · K<sup>-1</sup>]

$\Delta H^\ddagger$  = activation enthalpy [kJ · mol<sup>-1</sup>]

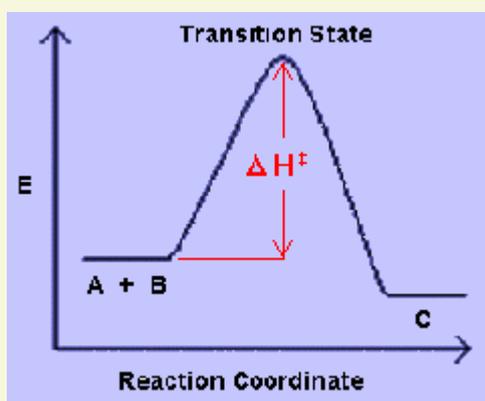


Figure 2: Enthalpy of activation

$\Delta H^\ddagger$  is the difference between the enthalpy of the transition state and the sum of the enthalpies of the reactants in the ground state. It is called **activation enthalpy** (Fig. 2).

S is for the entropy, the extent of randomness or disorder in a system. The difference between the entropy of the transition state and the sum of the entropies of the reactants is called **activation entropy**  $\Delta S^\ddagger$ .

$\Delta G^\ddagger$  is the **free activation enthalpy** (Gibb's free energy). According to equation (10)  $\Delta G^\ddagger$  is equal to the **change in enthalpy**

$\Delta H^\ddagger$  minus the **product of temperature T** (which is in kelvin) and the **change in entropy**  $\Delta S^\ddagger$  of the chemical system.

$\Delta G^\ddagger$  may be considered to be the **driving force** of a chemical reaction.  $\Delta G^\ddagger$  determines the extent and spontaneity of the reaction.

$\Delta G^\ddagger < 0 \Rightarrow$  reaction is spontaneous

$\Delta G^\ddagger = 0 \Rightarrow$  system at equilibrium, no net change occurs

$\Delta G^\ddagger > 0 \Rightarrow$  reaction is not spontaneous

Combining equation (9) with expression (10) and solving for  $\ln k$  yields:

$$\ln k = -\frac{\Delta H^\ddagger}{R \cdot T} + \frac{\Delta S^\ddagger}{R} \quad (11)$$

The *Eyring equation* is found by substituting equation (11) into equation (8):

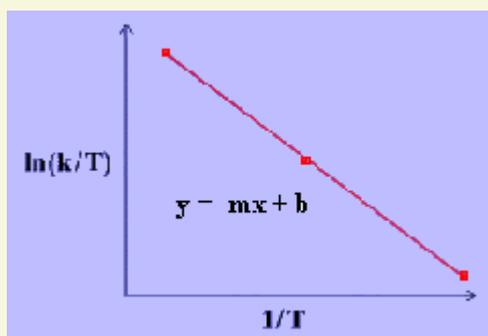
$$k = \frac{k_B \cdot T}{h} \cdot e^{-\frac{\Delta H^\ddagger}{R \cdot T}} \cdot e^{\frac{\Delta S^\ddagger}{R}} \quad (12)$$

$$\ln k = \ln \frac{k_B}{h} \cdot T - \frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} + \frac{\Delta S^\ddagger}{R} \quad (13)$$

$$\ln \frac{k}{T} = -\frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} + \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} \quad (14)$$

A plot of  $\ln(k/T)$  versus  $1/T$  produces a straight line with the familiar form  $y = -mx + b$  (Fig. 3), where

$x = 1/T$   
 $y = \ln(k/T)$



$$m = -\Delta H^\ddagger / R$$

$$b = y(x = 0)$$

$\Delta H^\ddagger$  can be calculated from the slope  $m$  of this line:  $\Delta H^\ddagger = -m \cdot R$ .

Figure 3: Determination of  $\Delta H^\ddagger$

From the y-intercept

$$y(x = 0) = \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} \quad (15)$$

$\Delta S^\ddagger$  can be determined and thus the calculation of  $\Delta G^\ddagger$  for the appropriate reaction temperatures according to equation (10) is allowed.

A comparison between the *Arrhenius equation*

$$\ln k = \frac{E_a}{R \cdot T} + \ln A \quad (16)$$

and the *Eyring equation* (13) shows, that  $E_a$  and  $\Delta H^\ddagger$  or  $\ln A$  and  $\Delta S^\ddagger$  are analogous quantities. These two energies are therefore frequently used interchangeably in the literature to define the activation barrier of a reaction. The activation energy  $E_a$  is related to the activation enthalpy  $\Delta H^\ddagger$  as follows

$$E_a = \Delta H^\ddagger + R \cdot T \quad (17)$$

- low values of  $E_a$  and  $\Delta H^\ddagger \Rightarrow$  fast rate
- high values of  $E_a$  and  $\Delta H^\ddagger \Rightarrow$  slow rate

The typical values of  $E_a$  and  $\Delta H^\ddagger$  lie between 20 and 150 [kJ / mol].

The study of the temperature dependence supplies the above all mechanistically important values  $\ln A$  or  $\Delta S^\ddagger$ , equivalent in their mechanical significance.  $\ln A$ - and  $\Delta S^\ddagger$ -values are sensible sensors. They give informations about the degree of order in the transition state.

- low values of  $\ln A$  correspond to large negative values of  $\Delta S^\ddagger$  (unfavorable)  
The activated complex in the transition state has a more ordered or more rigid structure than the reactants in the ground state. This is generally the case if degrees of freedom (of translation, rotation, vibration) become 'frozen' on the route from the initial to the transition state. The reaction rate is slow.
- high values of  $\ln A$  correspond to positive values (less negative values) of  $\Delta S^\ddagger$  (favorable)  
A positive value for entropy of activation indicates that the transition state is highly disordered compared to the ground state. Translational, rotational and vibrational degrees of freedom are liberated on going from the ground state to the transition state. The reaction proceeds fast.

Although the determination of the activation parameters must be performed accurately, it should not pretend an excessive accuracy. The values of the activation energy and activation enthalpy are rounded to one decimal place. The value of activation entropy is basically written in whole numbers. Values of entropies  $\Delta S^\ddagger \pm 10$  are written to one decimal place of accuracy. The value of  $\ln A$  shall be expressed with an accuracy of two decimal places.

A precise determination of the activation enthalpy (and the other activation parameters) requires at least three different rate constants. This means three kinetic runs at different temperatures are carried out. The temperature intervals should be at least 5°C. If the data points in the plot of  $\ln(k/T)$  versus  $1/T$  (Fig. 3) do not lie exactly on a straight line, a linear regression analysis providing the 'line of best fit' will not increase the accuracy. If the plotted points deviate significantly from the straight line, the rate constant should be determined at a further reaction temperature, since each of the three data points can be 'wrong'. Basically, it recommends to increase the accuracy of the measured values by improvement of the measuring method (accurate thermostating of the reaction mixture).

Sometimes the data points are on a curve concave or convex toward the abscissa axis ( $1/T$  axis) (Fig. 4).

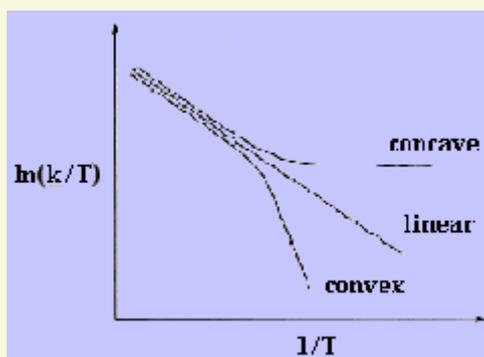


Figure 4: Concave and convex Eyring Plot

In the broad field of kinetics, not restricting consideration to enzyme kinetics, when nonlinear Arrhenius or Eyring plots can be observed, they are almost always concave. A concave Arrhenius or Eyring plot can be attributed to several factors. The most common interpretation is that at least two different rate-limiting reaction steps are involved. Convex Arrhenius and Eyring plots are observed in experiments on enzyme catalyzed reactions involving two competing enzymatic forms, each dominating in a different temperature range. A convex Arrhenius or Eyring plot means that  $E_a$  and  $\Delta H^\ddagger$ , respectively, decreases with increasing temperature.

**References:**

- [Chemical Kinetics](#)
- [Kinetics: Characterization of Transition States](#)
- [Rate Law and Stoichiometry](#)
- [Convex Arrhenius plots and their interpretation](#)

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