

2.2 TEMPERATURE-DEPENDENT TERM OF A RATE EQUATION

Temperature Dependency from Arrhenius' Law

For many reactions, and particularly elementary reactions, the rate expression can be written as a product of a temperature-dependent term and a composition-dependent term, or

$$\begin{aligned} r_i &= f_1(\text{temperature}) \cdot f_2(\text{composition}) \\ &= k \cdot f_2(\text{composition}) \end{aligned} \quad (33)$$

For such reactions the temperature-dependent term, the reaction rate constant, has been found in practically all cases to be well represented by Arrhenius' law:

$$k = k_0 e^{-E/RT} \quad (34)$$

where k_0 is called the frequency or pre-exponential factor and E is called the activation energy of the reaction.* This expression fits experiment well over wide temperature ranges and is strongly suggested from various standpoints as being a very good approximation to the true temperature dependency.

At the same concentration, but at two different temperatures, Arrhenius' law indicates that

$$\ln \frac{r_2}{r_1} = \ln \frac{k_2}{k_1} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (35)$$

provided that E stays constant.

Comparison of Theories with Arrhenius' Law

The expression

$$k = k_0' T^m e^{-E/RT}, \quad 0 \leq m \leq 1 \quad (36)$$

summarizes the predictions of the simpler versions of the collision and transition state theories for the temperature dependency of the rate constant. For more complicated versions m can be as great as 3 or 4. Now, because the exponential term is so much more temperature-sensitive than the pre-exponential term, the variation of the latter with temperature is effectively masked, and we have in effect

$$k = k_0 e^{-E/RT} \quad (34)$$

* There seems to be a disagreement in the dimensions used to report the activation energy; some authors use joules and others use joules per mole. However, joules per mole are clearly indicated in Eq. 34.

But what moles are we referring to in the units of E ? This is unclear. However, since E and R always appear together, and since they both refer to the same number of moles, this bypasses the problem. This whole question can be avoided by using the ratio E/R throughout.

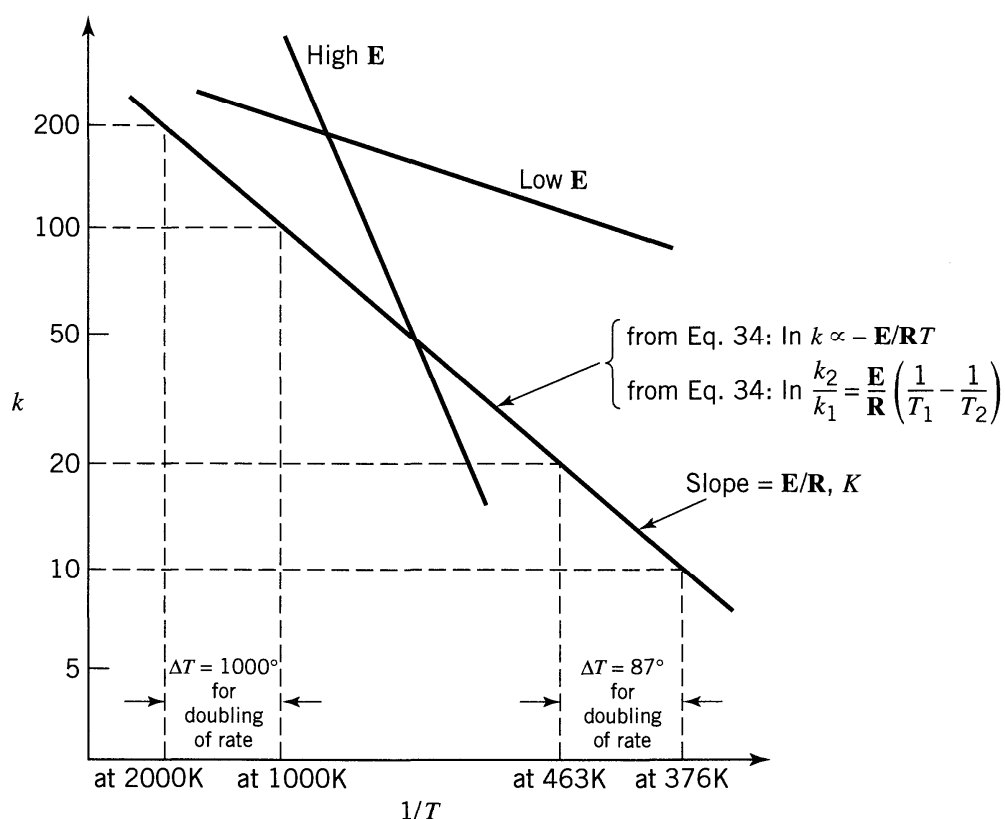


Figure 2.2 Sketch showing temperature dependency of the reaction rate.

This shows that Arrhenius' law is a good approximation to the temperature dependency of both collision and transition-state theories.

Activation Energy and Temperature Dependency

The temperature dependency of reactions is determined by the activation energy and temperature level of the reaction, as illustrated in Fig. 2.2 and Table 2.1. These findings are summarized as follows:

1. From Arrhenius' law a plot of $\ln k$ vs $1/T$ gives a straight line, with large slope for large E and small slope for small E .
2. Reactions with high activation energies are very temperature-sensitive; reactions with low activation energies are relatively temperature-insensitive.

Table 2.1 Temperature Rise Needed to Double the Rate of Reaction for Activation Energies and Average Temperatures Shown^a

Average Temperature	Activation Energy E			
	40 kJ/mol	160 kJ/mol	280 kJ/mol	400 kJ/mol
0°C	11°C	2.7°C	1.5°C	1.1°C
400°C	65	16	9.3	6.5
1000°C	233	58	33	23
2000°C	744	185	106	74

^a Shows temperature sensitivity of reactions.

- Any given reaction is much more temperature-sensitive at a low temperature than at a high temperature.
- From the Arrhenius law, the value of the frequency factor k_0 does not affect the temperature sensitivity.

EXAMPLE 2.3 *SEARCH FOR THE ACTIVATION ENERGY OF A PASTEURIZATION PROCESS*

Milk is pasteurized if it is heated to 63°C for 30 min, but if it is heated to 74°C it only needs 15 s for the same result. Find the activation energy of this sterilization process.

SOLUTION

To ask for the activation energy of a process means assuming an Arrhenius temperature dependency for the process. Here we are told that

$$t_1 = 30 \text{ min} \quad \text{at a} \quad T_1 = 336 \text{ K}$$

$$t_2 = 15 \text{ sec} \quad \text{at a} \quad T_2 = 347 \text{ K}$$

Now the rate is inversely proportional to the reaction time, or rate $\propto 1/\text{time}$ so Eq. 35 becomes

$$\ln \frac{r_2}{r_1} = \ln \frac{t_1}{t_2} = \frac{\mathbf{E}}{\mathbf{R}} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

or

$$\ln \frac{30}{0.25} = \frac{\mathbf{E}}{8.314} \left(\frac{1}{336} - \frac{1}{347} \right)$$

from which the activation energy

$$\underline{\underline{\mathbf{E} = 422\,000 \text{ J/mol}}}$$

2.3 SEARCHING FOR A MECHANISM

The more we know about what is occurring during reaction, what the reacting materials are, and how they react, the more assurance we have for proper design. This is the incentive to find out as much as we can about the factors influencing a reaction within the limitations of time and effort set by the economic optimization of the process.

There are three areas of investigation of a reaction, the *stoichiometry*, the *kinetics*, and the *mechanism*. In general, the stoichiometry is studied first, and when this is far enough along, the kinetics is then investigated. With empirical rate expressions available, the mechanism is then looked into. In any investigative

program considerable feedback of information occurs from area to area. For example, our ideas about the stoichiometry of the reaction may change on the basis of kinetic data obtained, and the form of the kinetic equations themselves may be suggested by mechanism studies. With this kind of relationship of the many factors, no straightforward experimental program can be formulated for the study of reactions. Thus, it becomes a matter of shrewd scientific detective work, with carefully planned experimental programs especially designed to discriminate between rival hypotheses, which in turn have been suggested and formulated on the basis of all available pertinent information.

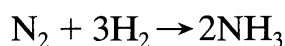
Although we cannot delve into the many aspects of this problem, a number of clues that are often used in such experimentation can be mentioned.

1. Stoichiometry can tell whether we have a single reaction or not. Thus, a complicated stoichiometry



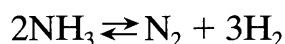
or one that changes with reaction conditions or extent of reaction is clear evidence of multiple reactions.

2. Stoichiometry can suggest whether a single reaction is elementary or not because no elementary reactions with molecularity greater than three have been observed to date. As an example, the reaction



is not elementary.

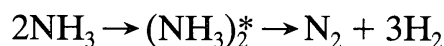
3. A comparison of the stoichiometric equation with the experimental kinetic expression can suggest whether or not we are dealing with an elementary reaction.
4. A large difference in the order of magnitude between the experimentally found frequency factor of a reaction and that calculated from collision theory or transition-state theory may suggest a nonelementary reaction; however, this is not necessarily true. For example, certain isomerizations have very low frequency factors and are still elementary.
5. Consider two alternative paths for a simple reversible reaction. If one of these paths is preferred for the forward reaction, the same path must also be preferred for the reverse reaction. This is called the *principle of microscopic reversibility*. Consider, for example, the forward reaction of



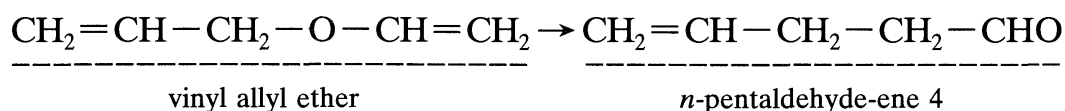
At a first sight this could very well be an elementary bimolecular reaction with two molecules of ammonia combining to yield directly the four product molecules. From this principle, however, the reverse reaction would then also have to be an elementary reaction involving the direct combination of three molecules of hydrogen with one of nitrogen. Because such a process is rejected as improbable, the bimolecular forward mechanism must also be rejected.

6. The principle of microreversibility also indicates that changes involving bond rupture, molecular syntheses, or splitting are likely to occur one at a

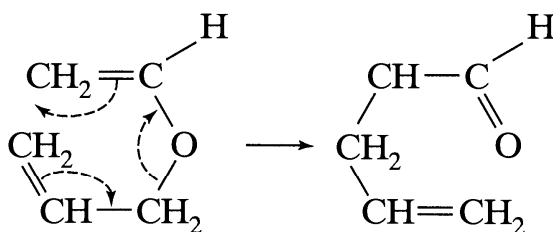
time, each then being an elementary step in the mechanism. From this point of view, the simultaneous splitting of the complex into the four product molecules in the reaction



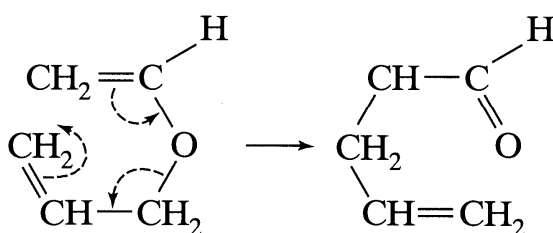
is very unlikely. This rule does not apply to changes that involve a shift in electron density along a molecule, which may take place in a cascade-like manner. For example, the transformation



can be expressed in terms of the following shifts in electron density:



or



7. For multiple reactions a change in the observed activation energy with temperature indicates a shift in the controlling mechanism of reaction. Thus, for an increase in temperature E_{obs} rises for reactions or steps in parallel, E_{obs} falls for reactions or steps in series. Conversely, for a decrease in temperature E_{obs} falls for reactions in parallel, E_{obs} rises for reactions in series. These findings are illustrated in Fig. 2.3.

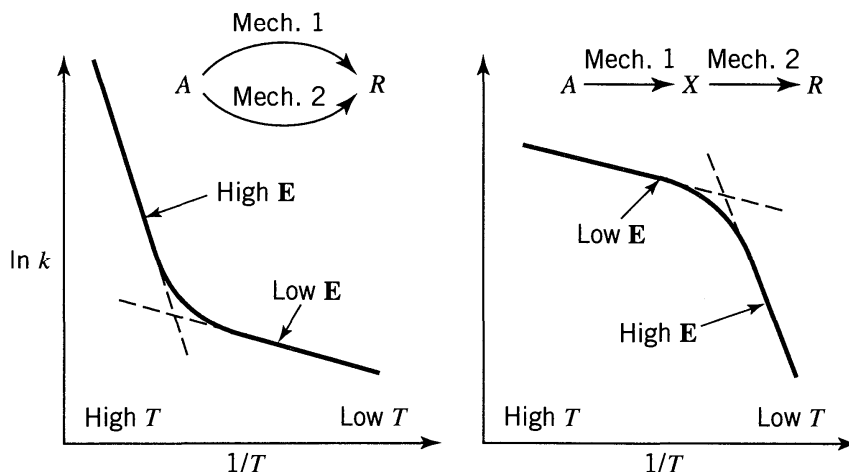


Figure 2.3 A change in activation energy indicates a shift in controlling mechanism of reaction.

2.4 PREDICTABILITY OF REACTION RATE FROM THEORY

Concentration-Dependent Term

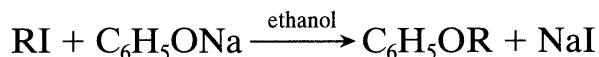
If a reaction has available a number of competing paths (e.g., noncatalytic and catalytic), it will in fact proceed by all of these paths, although primarily by the one of least resistance. This path usually dominates. Only a knowledge of the energies of all possible intermediates will allow prediction of the dominant path and its corresponding rate expression. As such information cannot be found in the present state of knowledge, a priori prediction of the form of the concentration term is not possible. Actually, the form of the experimentally found rate expression is often the clue used to investigate the energies of the intermediates of a reaction.

Temperature-Dependent Term

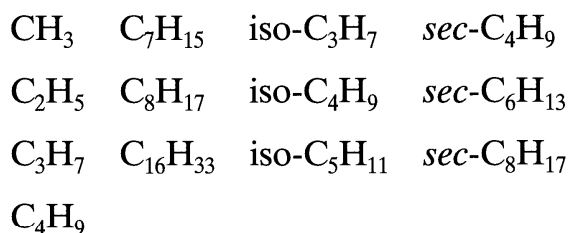
Assuming that we already know the mechanism of reaction and whether or not it is elementary, we may then proceed to the prediction of the frequency factor and activation energy terms of the rate constant.

If we are lucky, frequency factor predictions from either collision or transition-state theory may come within a factor of 100 of the correct value; however, in specific cases predictions may be much further off.

Though activation energies can be estimated from transition-state theory, reliability is poor, and it is probably best to estimate them from the experimental findings for reactions of similar compounds. For example, the activation energies of the following homologous series of reactions



where R is



all lie between 90 and 98 kJ.

Use of Predicted Values in Design

The frequent order-of-magnitude predictions of the theories tend to confirm the correctness of their representations, help find the form and the energies of various intermediates, and give us a better understanding of chemical structure. However, theoretical predictions rarely match experiment by a factor of two. In addition, we can never tell beforehand whether the predicted rate will be in the order of magnitude of experiment or will be off by a factor of 10⁶. Therefore, for engi-

neering design, this kind of information should not be relied on and experimentally found rates should be used in all cases. Thus, theoretical studies may be used as a supplementary aid to suggest the temperature sensitivity of a given reaction from a similar type of reaction, to suggest the upper limits of reaction rate, etc. Design invariably relies on experimentally determined rates.

RELATED READING

Jungers, J. C., et al., *Cinétique chimique appliquée*, Technip, Paris, 1958.

Laidler, K. J., *Chemical Kinetics*, 2nd ed., Harper and Row, New York, 1987.

Moore, W. J., *Basic Physical Chemistry*, Prentice-Hall, Upper Saddle River, NJ, 1983.

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Lindemann, F. A., *Trans. Faraday Soc.*, **17**, 598 (1922).

Michaelis, L., and Menten, M. L., *Biochem. Z.*, **49**, 333 (1913). This treatment is discussed by Laidler (1987), see Related Readings.

PROBLEMS

- 2.1.** A reaction has the stoichiometric equation $A + B = 2R$. What is the order of reaction?
- 2.2.** Given the reaction $2NO_2 + \frac{1}{2} O_2 = N_2O_5$, what is the relation between the rates of formation and disappearance of the three reaction components?
- 2.3.** A reaction with stoichiometric equation $\frac{1}{2} A + B = R + \frac{1}{2} S$ has the following rate expression

$$-r_A = 2C_A^{0.5}C_B$$

What is the rate expression for this reaction if the stoichiometric equation is written as $A + 2B = 2R + S$?

- 2.4.** For the enzyme-substrate reaction of Example 2, the rate of disappearance of substrate is given by

$$-r_A = \frac{1760[A][E_0]}{6 + C_A}, \quad \text{mol/m}^3 \cdot \text{s}$$

What are the units of the two constants?