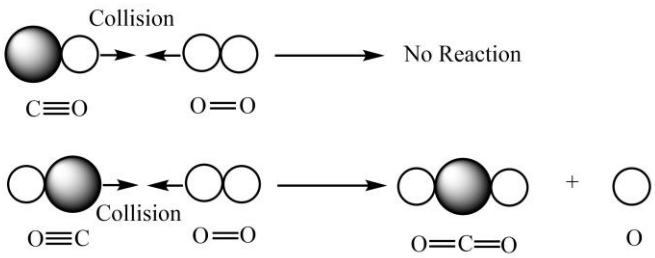
❖ Steric Factor

One of the most glaring limitations of the collision is that the predicted values of rate constants for many reactions were found to be considerably different from the values obtained experimentally. Moreover, it was also noticed that more the complexity, the higher was the deviation. This happened because the collision theory supposed that the particles participating in the chemical reaction are completely spherical, and thus, are able to react in every direction. However, this is far from the truth since the orientation of the collisions is not always appropriate to result in the chemical change. For instance, in the hydrogenation of ethylene, the dihydrogen molecule must approach the bonding zone between the atoms, and not all the possible collisions would be able to satisfy this requirement. For more clear view, consider the formation of CO_2 as shown below.



To solve this problem, the concept of steric factor (ρ) was introduced, which is simply the ratio of experimental value to the predicted value of the rate constant. In other words, the steric factor may be defined as the ratio between the frequency factor and the collision frequency i.e.

$$\rho = \frac{A_{observed}}{Z_{calculated}} \tag{171}$$

It is worthy to note that the value of the steric factor most of the cases is less than unity. Typically, it has been seen that more the complex the reactant molecules are, the lower is the steric factor. However, some reactions do have steric factors higher than unity; for instance, the harpoon reactions in which atoms involved exchange electrons generating ions. The deviation from unity may arise due to different reasons such as non-spherical shape of reacting molecules, or the partial delivery of kinetic energy, the presence of a solvent when applied to solutions.

In order to derive the expression for modified collision theory that does consider the reactants steric, recall the rate constant calculated from simple collision theory first i.e.

$$Rate = Ze^{-E_a/RT} \tag{172}$$

For experimental rate, multiply the equation (172) by the probability or steric factor i.e.

$$Rate = \rho Ze^{-E_a/RT} \tag{173}$$

Now considering both the possibilities i.e. whether the reacting species are the same or different, we can simplify the above equation in two ways:

i) For dissimilar molecules:

If the colliding molecules are not the same, the exponential part in equation (173) takes the form

$$A = \rho \frac{N}{10^3} \sigma_{AB}^2 \sqrt{\frac{8\pi RT(M_A + M_B)}{M_A M_B}} \tag{174}$$

Substituting the values of different constants, we get

$$A = 2.753 \times 10^{29} \times \rho \times \sigma_{AB}^2 \sqrt{\frac{T(M_A + M_B)}{M_A M_B}} \tag{175}$$

ii) For similar molecules:

If the colliding molecules are the same, the exponential part in equation (173) takes the form

$$A = \rho \frac{N}{10^3} 4\sigma^2 \sqrt{\frac{\pi RT}{M_A}} \tag{176}$$

$$A = 3.893 \times 10^{29} \times \rho \times \sigma^2 \sqrt{\frac{T}{M_A}} \tag{177}$$

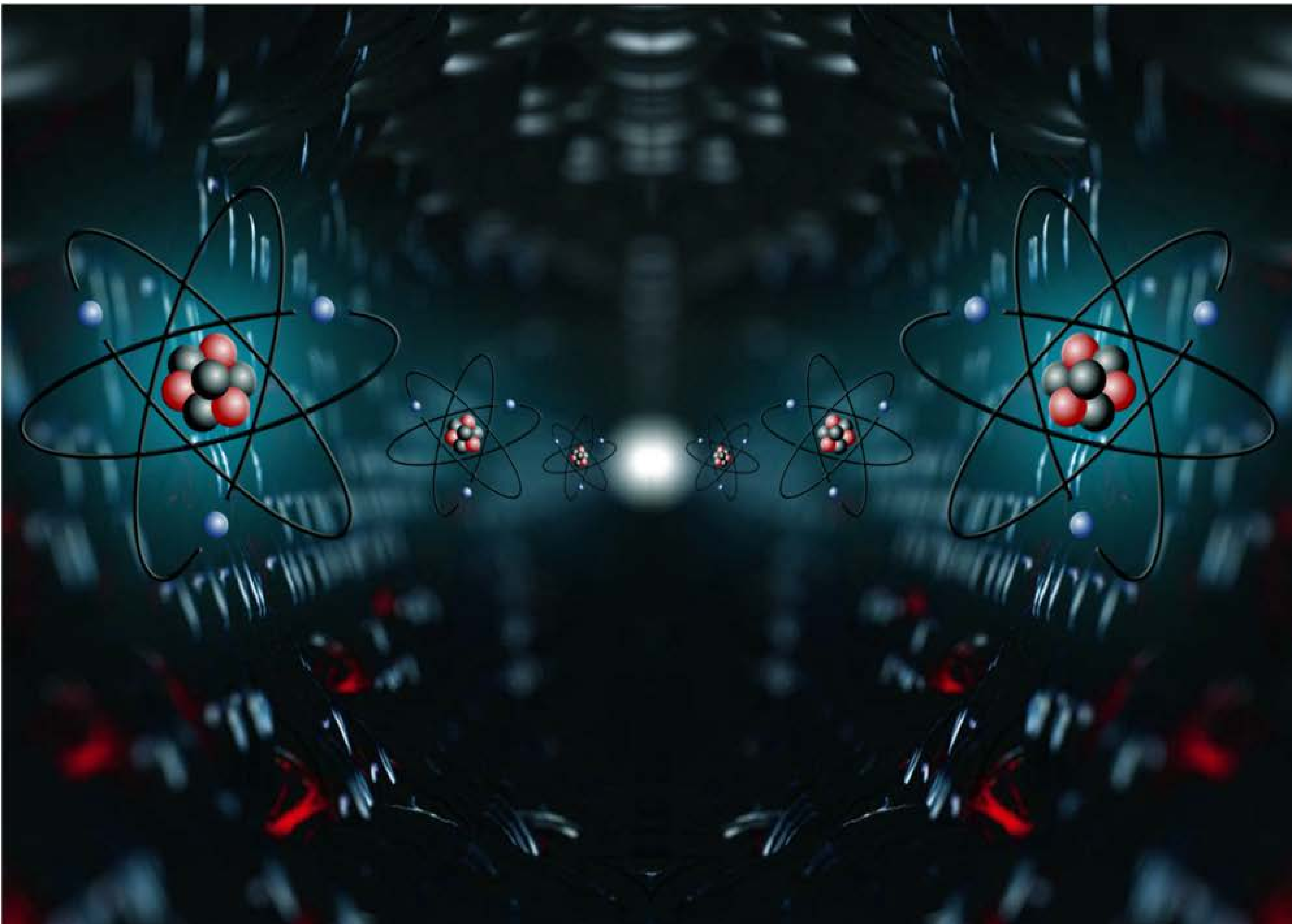
This modified collision theory can account for probability factors up to 10^{-4} but not less than that. This limitation can be overcome by "transition state theory" discussed in the next section.

International
Edition

A TEXTBOOK OF PHYSICAL CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

DALAL INSTITUTE

Table of Contents

Mandeep Dalal
(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)
Founder & Director, Dalal Institute
Contact No: +91-9802825820
Homepage: www.mandeepdalal.com
E-Mail: dr.mandeep.dalal@gmail.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands) .

Other Books by the Author

A TEXTBOOK OF INORGANIC CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF PHYSICAL CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF ORGANIC CHEMISTRY - VOLUME I, II, III, IV

ISBN: 978-81-938720-1-7
9 788193 872017
MRP: Rs 800.00

DALAL INSTITUTE
Main Market, Sector-14, Rohtak, Haryana-124001
(+91-9802825820, info@dalalinstitute.com)
www.dalalinstitute.com