

# ONE IMPORTANT ELEMENT FOR THE CALCULATION OF HIGH PRESSURE GAS REACTION RATE

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In the atmospheric condition, the calculated and experimental results accord well. However, in combustion, as the pressure becomes higher, the calculated and experimental results do not accord more than about 40 atm. In this study, using simple assumption, one of causes which affects this deviation was studied.

## Introduction

It is necessary to supply energy to promote the gas reaction. The relationship between the temperature  $T$  and the reaction rate  $k$  is as follows.

$$k = Ae^{-\frac{E_a}{RT}}$$

where  $E_a$  is an activation energy,  $R$  is the gas constant, and  $A$  is a constant. This equation means that the reaction rate becomes larger as the temperature becomes higher. By the way, for promoting the reaction, it is necessary to transfer the translation energy

efficiently to the reaction field.

One report says that the deviation of calculated results from experimental results becomes greater as the reaction pressure becomes higher, especially higher than 40 atm in the methane combustion [1]. In this study, the effect of increasing pressure to reaction field was investigated. And one result was obtained that the translation energy was not transfer easily at the high pressure condition.

## Concept and Simple Calculation

Figure 1 shows the simple

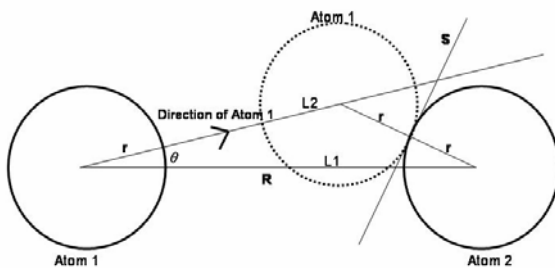


Figure 1

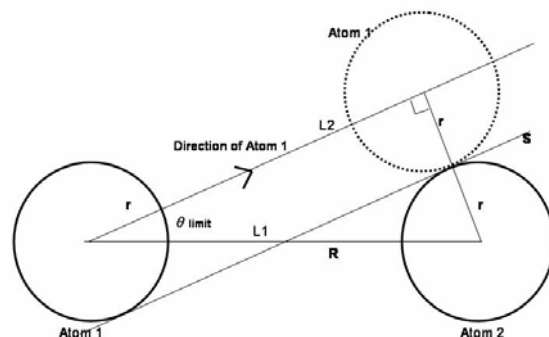


Figure 2

model of a recombination reaction. In this figure,  $r$  represents the radius of molecule, and  $R$  is mean free path. The common tangential plane of two molecules 1 and 2 at the moment of collision is  $S$ .  $L1$  is the line which connects the centers of two molecules.  $L2$  is the direction of atom 1.  $\theta$  is the angles determined by the two lines. Then I suppose that only the vertical element of velocity acts as the energy for promoting reactions. When  $\theta$  is 0, 100% of energy is used to the reaction, but when atom 1 collides slightly, for example figure 2, almost 0% of energy contributes to the reaction.

If the probability of the direction of flight of atom 1 is equal for every direction,  $V_s$ , which means the vertical element to the plane  $S$  of atom 1, is represented as follows.

$$V_s = V \times \sqrt{1 - \frac{R^2}{4r^2} \sin^2 \theta}$$

The vertical element of translation energy  $E_s$  is as follows.

$$\begin{aligned} E_s &= \frac{1}{2} m V_s^2 = \frac{1}{2} m V^2 \left( 1 - \frac{R^2}{4r^2} \sin^2 \theta \right) \\ &= E_0 \left( 1 - \frac{R^2}{4r^2} \sin^2 \theta \right) \end{aligned}$$

where  $m$  is mass of molecule and  $E_0$  is translation energy. And  $0 \leq V_s \leq V$ ,  $0 \leq \theta \leq \theta_{limit}$ .  $\theta_{limit}$  satisfies the condition as follows and seen in figure 2 for easy comprehension.

$$R \sin \theta_{limit} = 2r$$

In this case,  $V_s=0$ m/s and no translation energy contributes the reaction.

If  $E_s$  is replaced with  $E$ , one can represent  $E = \frac{1}{2} m V_s^2$ . In figure 1, the probability that the angle is  $\theta$  is proportional to  $\sin \theta$ . And the probability that vertical element of translation energy is  $E$  is inversely proportional to  $\frac{dE}{d\theta}$ . So the relative probability that the vertical element of translation energy is  $E$  is as follows.

$$\frac{dE}{\sqrt{1 - \frac{4r^2}{R^2} + \frac{2E}{mv^2}}}$$

After integral and normalization of this equation, the probability function of  $E$  is as follows.

$$f(E) = \frac{1}{2E_0 \left( \sqrt{2 - \frac{4r^2}{R^2}} - \sqrt{1 - \frac{4r^2}{R^2}} \right) \times \sqrt{1 - \frac{4r^2}{R^2} + \frac{E}{E_0}}}$$

We can some result from this equation. At low pressure,  $R$  is much larger than  $r$ , so  $f(E)$  can be some value near the mean value where the range of  $E$  is from 0 to  $E_0$ . However when  $R$  approaches to the value of  $2r$ , the probability of  $E=0$  becomes much larger. This means that, in the high pressure condition, the possibility of non efficient transfer of translation energy exists.

The following equation is the result of calculation of expected value of E.

$$\int_0^{E_0} E f(E) dE$$

$$= \frac{1}{2E_0 \left( \sqrt{2 - \frac{4r^2}{R^2}} - \sqrt{1 - \frac{4r^2}{R^2}} \right)} \times \int_0^{E_0} \frac{E}{\sqrt{1 - \frac{4r^2}{R^2} + \frac{E}{E_0}}} dE$$

$$= \frac{E_0}{3} \left\{ \left( 2 - \frac{4r^2}{R^2} \right) + \sqrt{2 - \frac{4r^2}{R^2}} \sqrt{1 - \frac{4r^2}{R^2}} + \left( 1 - \frac{4r^2}{R^2} \right) \right\} - E_0 \left( 1 - \frac{4r^2}{R^2} \right)$$

Figure 3 is a graph representing the influence of pressure to expected value calculated with this equation. Abscissa is  $0 \leq K = \frac{4r^2}{R^2} \leq 1$ . Ordinate is expected value. We see that the expected value goes down abruptly from the point of  $K=0.8$ . This means that, in this model, when the pressure becomes more than 60 atm., non efficient energy transfer occurs.

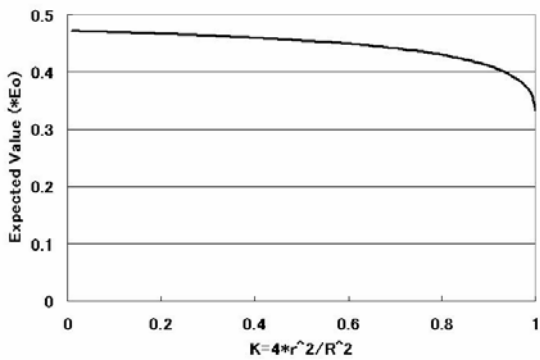


Figure 3

## Conclusion

In this study, I employed very simple model. So I suspect whether this effect truly exists or not. I intend to investigate more minutely with considering the effect of third body problem, reaction potential, heat of

reaction, and so on.

## REFERENCE

1. G.Rozenchan, D. L. Zhu, C. K. Law, and S. D. Tse, Proc. Combust. Inst. 29:1461-1469 (2002)