

# On The Rate Equations Used For Analyzing The So-called Zero-order Desorption

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## Abstract

There has been a controversy on rate equations with a factor  $(1 - \theta)^{-1}$  in analyzing the "zero-order" desorption. In order to resolve this, we will show and discuss the assumptions involved in the derivations of rate equations within the framework of absolute rate theory. The factor  $(1 - \theta)^{-1}$  will be eliminated at higher coverages of adsorbates under the conditions used.

## 1. Introduction

Recently, J. -H. He<sup>1)</sup> has proposed and discussed a model for Phase-transition-related zero-order thermal desorption<sup>2)</sup>. He has employed the method and procedure adopted by Nagai<sup>3)</sup>. This has been criticized by Zhdanov<sup>4)</sup>, and subsequently by Cassuto<sup>5)</sup>. However, Nagai has provided rebuttals for them<sup>6)</sup>. On the other hand, Kreuzer and Payne<sup>7)</sup> have considered the rate equations from a different aspect, i. e., on the basis of non-equilibrium thermodynamics.

The rate equations (presented by the desputants, Zhdanov<sup>4)</sup> or Cassuto<sup>5)</sup> and Nagai<sup>6)</sup>) for non-associated desorption with ideal localized model are

$$R = \nu N \theta e^{-E_{des}/kT} \quad (A)$$

$$= \nu N \frac{\theta}{1 - \theta} e^{-E_{des}/kT} \quad (B)$$

where  $\nu = kT/h$  has the usual meaning,  $N$  is the number of sites per unit area,  $\theta$  is the relative coverage and  $E_{des}$  is the activation energy for desorption. The transmission coefficient is omitted for simplicity. Equations (A) and (B) are sufficient for the discussion of this subject.

Nagai<sup>3)</sup> has derived the rate equation (B) for desorption within the framework of the absolute rate theory (ART) with two layers of the two-dimensional lattice gas theory. Considering the assumptions involved in his treatment, Zhdanov<sup>4)</sup> has concluded that the derived equation is identical to that of the precursor theory<sup>7)</sup>. More recently a similar comment has been made by Cassuto<sup>5)</sup>, who has stated that one of the relations of eqs. (A) and (B) has to be wrong.

The essential point at issue is the derivation of the factor  $1/(1 - \theta)$  in (B), since this factor has appeared in the expression of the rate equation for desorption in the precursor theory<sup>7)</sup>. In this manuscript, we shall only consider the rate equations in controversy, not the mechanism of the so-called zero-order desorption<sup>2)</sup>. The aim of this article is to show that both equations (A) and (B) can be derived under different assumptions in terms of the ART. Thus we have to examine assumptions used to derive the rate equations (A) and (B) in terms of the ART.

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## 2. Preliminary considerations

It is known that the form of eq. (B) can be derived by means of the precursor theory<sup>8)</sup>. Let us compare the rate equations deduced from the precursor theory as well as Nagai's treatments in terms of simple kinematical theory, as discussed by Zhdanov<sup>4)</sup>.

The rate of desorption is written as

$$R = k_d^i \theta^i \quad i = * \text{ or } \ddagger \quad (2.1)$$

where the  $k_d$  is the rate constant of desorption from the state of  $i$ , the superscript  $i$  of  $k$  and  $\theta$  refers to  $*$  for the precursor or to  $\ddagger$  for the activated state. The problem is how to evaluate  $\theta^i$ ? The  $\theta^*$  is determined with the assumption of the steady state in the precursor state, denoted as (I), while the  $\theta^\ddagger$  is determined with that of complete equilibrium between the initial and the activated states, denoted as (II).

Case (I). Let  $\theta^*$  be

$$\theta^* = \frac{k_+ \theta}{k_d + k_- (1 - \theta)} \quad (2.2)$$

with the steady state assumption for (I);

$$\frac{d\theta^*}{dt} = k_+ \theta - k_- (1 - \theta) \theta^* - k_d \theta^* \quad (2.3)$$

Here  $k_+$  and  $k_-$  are the rate constants of the forward and backward steps between the precursor and the adsorbate states, respectively.

Putting eq. (2.2) into eq. (2.1), we get

$$R = \frac{k_d k_+ \theta}{k_d + k_- (1 - \theta)} \quad (2.4)$$

By the use of two different conditions, eq. (2.4) may be written into ways:

$$R = k_+ \theta \quad \text{for} \quad k_d \gg k_- (1 - \theta) \quad (2.5)$$

$$R = \frac{k_d k_- \theta}{k_- (1 - \theta)} \quad \text{for} \quad k_d \ll k_- (1 - \theta) \quad (2.6)$$

From these, it should be noted that in the extreme case when  $\theta = 1$  the application of equation (2.6) breaks down.

Case (II). On the other hand, the  $\theta^\ddagger$  is taken as

$$\theta^\ddagger = \frac{k_+ \theta}{k_- (1 - \theta)} \quad (2.7)$$

with the equilibrium assumption for (II);

$$k_+ \theta = k_- (1 - \theta) \theta^\ddagger \quad (2.8)$$

Putting eq. (2.7) into eq. (2.1), then we have

$$R = \frac{k_d k_+ \theta}{k_- (1 - \theta)} \quad (2.9)$$

Eq. (2.9) is similar to eq. (2.6). As Zhdanov<sup>4)</sup> has pointed out, the assumption that (initial) adsorbed and activated particles are in thermodynamic equilibrium is not correct at  $\theta \rightarrow 1$ .

## 3. Derivation of rate equations (A) and (B) by ART

In order to derive the rate equations (A) and (B) in terms of the ART as developed by Horiuti<sup>9)</sup>, (although there are several points of view in formulated the rate equation by ART)<sup>10)</sup> we need certain functions for describing the rate equation for desorption. First of all we shall define and explain these functions.

C represents a macroscopic system. Let  $\delta$  be a single particle and  $C^\delta$  is a system transferring  $\delta$  from its standard state into C without specifying the whereabouts of the  $\delta$  within C.  $QC$  and  $QC^\delta$  are the partition functions of C and  $C^\delta$ , respectively. Similarly C and  $C^\delta$  are particular states such that definite sites represented by  $\sigma$  are unoccupied and occupied by  $\delta$  with certainty.  $QC_{\sigma(o)}$  and  $QC_{\sigma(\delta)}$  are the partition functions of  $C_{\sigma(o)}$  and  $C_{\sigma(\delta)}$  respectively. A  $\ddagger$  means the symbol of the activated state. Then  $\delta^\ddagger$  and  $\sigma^\ddagger$  represent an activated complex and its site, respectively.

We shall define two particular functions p and q by

$$p^\delta = \frac{QC^\delta}{QC} \quad (3.1)$$

and

$$q = \frac{QC_{\sigma(\delta)}^\delta}{QC_{\sigma(o)}} \quad (3.2)$$

Let us consider physical meaning of the functions of  $p^\delta$  and  $q^\delta$  briefly. The Helmholtz free energy F is written as

$$F = -kT \ln(p.f.) \quad (3.3)$$

where the p.f. means the partition function. From the eq. (3.3)

$$\begin{aligned} -kT \ln p^\delta &= -kT (\ln QC^\delta - \ln QC) \\ &= \Delta F^\delta \end{aligned} \quad (3.4)$$

$\Delta F^\delta$  is the increment of F, i. e., the reversible work required to transfer  $\delta$  from its standard state into C without specifying the whereabouts of the  $\delta$  within C. Thus,  $\Delta F^\delta$  (eq. (3.4)) may be identified with the chemical potential in thermodynamics, so that

$$-kT \ln p = \mu \quad \text{or} \quad p = e^{-\mu/kT} \quad (3.5)$$

Similar as in eq. (3.4)

$$\begin{aligned} -kT \ln q^\delta &= -kT (\ln QC_{\sigma(\delta)}^\delta - \ln QC_{\sigma(o)}) \\ &= \Delta F_{\sigma}^\delta \end{aligned} \quad (3.6)$$

$\Delta F_{\sigma}^\delta$  is the increment of F and  $C_{\sigma}^\delta$  caused by the addition of a  $\delta$  to a definite, previously vacant site  $\sigma$  on C.

$-kT \ln q^\delta$  can also be expressed as

$$-kT \ln q^\delta = -kT \ln q_{\sigma,o}^\delta + W \quad (3.7)$$

where  $q_{\sigma,o}^\delta$  is the particular case of  $q^\delta$  in the absence of the interaction and thus can be represented with a single particle partition function,  $q_{\sigma,o}^\delta = e^{-\epsilon/kT}$ , where  $\epsilon$  is adsorbate enthalpy.

$-kT \ln q_{\sigma,o}^\delta$  means the increment of F in the absence of the interaction and W is a part of the change of F due to the interaction between ad-particles. But the evaluation of W is not the aim of this article.

The ratio of  $q_{\sigma}^\delta$  to  $p^\delta$  is, with the help of the equations (3.1) and (3.2)

$$\frac{q_{\sigma}^\delta}{p^\delta} = \frac{QC_{\sigma(\delta)}^\delta / QC_{\sigma(o)}}{QC^\delta / QC} = \frac{QC_{\sigma(\delta)}^\delta / QC^\delta}{QC_{\sigma(o)} / QC} = \frac{\Theta_{\sigma(\delta)}}{\Theta_{\sigma(o)}} \quad (3.8)$$

The function  $QC_{\sigma(\delta)}^\delta / QC_{\sigma(o)}$  and  $QC^\delta / QC$  are equal to the probability that  $C^\delta$  and C assume the particular state  $C^\delta$  and  $C_{\sigma(o)}$ , respectively. Hence we have

$$QC_{\sigma(\delta)}^\delta / QC_{\sigma(o)} + QC^\delta / QC = 1$$

admitting that the  $\sigma$  is either occupied by  $\delta$  or totally unoccupied and that the probability is practically unaffected by the addition of a single adatom to macroscopic assembly C. Denoting the probability  $QC_{\sigma(\delta)}^\delta / QC_{\sigma(o)}$  by  $\theta$  we have

$$\frac{p^\delta}{q_{\sigma}^\delta} = \frac{\theta}{1 - \theta} \quad (3.8)'$$

We shall start from the familiar expression of the rate equation with the ART

$$R = \nu \frac{QC^{\delta^*}}{QC^{\delta^I}} \quad (3.9)$$

The expressions of eqs. (A) and (B) can be derived from eq. (3.9) in terms of different conditions, as seen below. It should be mentioned that the derivation of eq. (3.9) has nothing to do with some equilibrium relations between the initial (I) and the activated ( $\delta^*$ ) states<sup>9)</sup>.

Now, eq. (3.9) may be transferred by the use of eqs. (3.1) and (3.8)

$$\begin{aligned} R &= \nu \frac{QC^{\delta^*}}{QC^{\delta^I}} = \nu \frac{QC^{\delta^*}/QC}{QC^{\delta^I}} = \nu \frac{p^{\delta^*}}{p^{\delta^I}} \\ &= \nu \frac{\Theta_{\sigma^*(o)}/\Theta_{\sigma^*(\delta^*)}}{(1-\theta)/\theta} \frac{q_{\sigma^*}^{\delta^*}}{q_{\sigma^I}^{\delta^I}} \end{aligned} \quad (3.10)$$

As what follows, it will be shown how eq. (3.10) reduces to the expressions of eqs. (A) and (B). At first we have to make some approximations on  $\Theta_{\sigma^*}$ . For the first approximation the probability that the site  $\sigma^*$  is occupied by a single  $\delta^*$  is replaced by the reciprocal of the number of per unit area

$$N\Theta_{\sigma^*(\delta^*)} = 1 \quad \text{or} \quad \Theta_{\sigma^*(\delta^*)} = 1/N \quad (3.11)$$

Then it follows,

$$R = \nu N \frac{\Theta_{\sigma^*(o)}}{(1-\theta)/\theta} \frac{q_{\sigma^*}^{\delta^*}}{q_{\sigma^I}^{\delta^I}} \quad (3.12)$$

To modify eq. (3.12) further, suppose that the site  $\sigma^*$  is identical with the  $\sigma$  ( $\sigma^* = \sigma$  for simplicity) and that  $\Theta_{\sigma^*(o)} = 1 - \theta$ , which means the probability that a site of  $\delta^*$  is vacant. Eq. (3.12) becomes

$$R = \nu N \frac{1-\theta}{(1-\theta)/\theta} \frac{q_{\sigma^*}^{\delta^*}}{q_{\sigma^I}^{\delta^I}} = \nu N \theta \frac{q_{\sigma^*}^{\delta^*}}{q_{\sigma}^{\delta}} \quad (3.13)$$

which is to be compared with eq. (A). By replacing  $q_{\sigma^*}^{\delta^*}/q_{\sigma}^{\delta}$  by  $e^{-(\epsilon^* - \epsilon)/kT} = e^{-E_{des}/kT}$  which is the case for the non-interaction between ad-particles, eq. (3.13) can be simplified to the familiar form, eq. (A).

We now consider a particular case: If  $\Theta_{\sigma^*(o)} = 1$  with  $\sigma^* = \sigma$ , which is the extreme case corresponding to lower coverage, eq. (3.13) reduces to

$$R = \nu N \frac{1}{(1-\theta)/\theta} \frac{q_{\sigma^*}^{\delta^*}}{q_{\sigma^I}^{\delta^I}} \quad (3.14)$$

Furthermore when  $\theta \rightarrow 0$ , eq. (3.14) is expanded as

$$R = \nu N \theta \frac{q_{\sigma^*}^{\delta^*}}{q_{\sigma^I}^{\delta^I}} \quad (3.15)$$

On the other hand, if the site is independent of  $\sigma$  ( $\sigma^* = \sigma$ ) and  $\Theta_{\sigma^*(o)} = 1$ , then eq. (3.12) becomes

$$R = \nu N \frac{1}{(1-\theta)/\theta} \frac{q_{\sigma^*}^{\delta^*}}{q_{\sigma^I}^{\delta^I}} = \nu N \frac{\theta}{1-\theta} \frac{q_{\sigma^*}^{\delta^*}}{q_{\sigma^I}^{\delta^I}} \quad (3.16)$$

Apart from notations eq. (3.16) is equivalent to eq. (B). The assumption used here may be identified with Nagai's assumption. He assumed that the condition  $\Theta_{\sigma^*(o)} = 1$  is applicable at all cover-

ages of adsorbates. This assumption is not realistic as has been pointed out by Zhdanov<sup>4)</sup>. A desorption rate equation used by He<sup>1)</sup> (eq. (8) in ref. 1)) is essentially identical to eq. (3.14) with  $A \Theta_{\sigma^*}(\delta^*) = 1$  in place of eq. (3.11), where  $A$  is the area occupied by  $\delta^*$  in one layer lattice gas model. Since He's treatment is almost a parallel to that of Nagai's this is also open to criticism.

In summary, the rate equations (A) and (B) ((3. 13) and (3. 16) respectively) can be derived on equal footing, but under different assumptions. As a matter of fact it is not correct to state that one of the relations (A) or (B) has to be wrong. Therefore the important point is that when analyzing the desorption rate, one has to take into account the applicability of the assumptions used in the derivations of the rate equation.

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