

## Is the $\lambda$ in Marcus Equation a Constant or a Function of $\Delta G^\circ$ ?

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### Abstract

The fundamental errors of Marcus equation have been discovered for more than 6 years and many literatures on the fundamental errors of Marcus equation have been published, but till now many people have continued to make articles using the incorrect Marcus equation despite the fundamental errors of Marcus equation. Why? In this review article, the main reasons of their mistakes are pointed out.

**Keywords:** Marcus equation; Intrinsic barrier; Reaction of Lewis acids with Lewis bases; Inverted region; Zhu equation

### Introduction

As well known, Marcus equation (Eq. 1) was initially proposed by Rudolph A. Marcus in 1956 to describe the kinetics of the outer sphere electron transfer reactions according to the solvent polarization [1,2]. In Marcus equation,  $\Delta G^\circ$  is the free energy change of chemical reactions,  $\Delta G^\ddagger$  is the activation free energy of chemical reactions,  $\lambda$  is the reorganization energy of chemical reactions. After the extension by many chemists [3-7] Marcus equation has been widely used in various chemical reactions. However, If the relationship of  $\Delta G^\ddagger$  with  $\Delta G^\circ$  in Marcus equation is examined, it is found that  $\Delta G^\ddagger$  is a quadratic function of  $\Delta G^\circ$  for a chemical reaction. Because the quadratic function has two solutions (i.e., two roots) at the same time, a chemical reaction should have one  $\Delta G^\ddagger$  value and two different  $\Delta G^\circ$  values under given conditions according to Marcus equation. It is clear that Marcus equation is incorrect because every chemical reaction has only one  $\Delta G^\ddagger$  value and one  $\Delta G^\circ$  value under given conditions. In order to find the fundamental error of Marcus equation, in 2013 we re-examined the premise assumptions of Marcus equation and found that the most important premise assumption of Marcus equation (i.e., the energy parabola of the reactant system and the production system have the same rate of change) directly violates the law of energy conservation [8]. Although the fundamental error of Marcus equation has been discovered for more than 6 years and many papers about the fundamental error of Marcus equation have been reported [8-18], there are still many chemists who use Marcus equation to make papers today [19-32]. Why? After examining the publications made using Marcus equation, we found that the authors of these publications not only did not read our articles on the fundamental errors of Marcus equation but also did not understand Marcus equation. In this short review article, we take an article entitled “Which Factors Control the Nucleophilic Reactivities of Enamines?” by Daria S. Timofeeva,

Robert J. Mayer, Peter Mayer, Armin R. Ofial, and Herbert Mayr in Chem Eur J (hereafter referred to as the Mayr's paper) [19] as an example for reviewing. In the Mayr's paper, the authors calculated the intrinsic barriers ( $\Delta G_0^\ddagger$ ) of 20 reactions of Lewis acids with Lewis bases in acetonitrile using Marcus equation in order to explain the special nucleophilic reactivities of some enamines. The main mistake of the Mayr's paper is that the authors took the  $\lambda$  in Marcus equation as a function of the thermodynamic driving force ( $\Delta G^0$ ) of reactions rather than a constant, which directly violates the nature of the  $\lambda$  in Marcus equation. Since this error first appeared in Marcus own article [1,2,36], it is necessary to reconfirm the nature of the  $\lambda$  in Marcus equation firstly.

$$\Delta G^\ddagger = \frac{\lambda}{4} \left( 1 + \frac{\Delta G^0}{\lambda} \right)^2 \quad (1)$$

### The Nature of the $\lambda$ in Marcus Equation

To reconfirm the nature of the  $\lambda$  in Marcus equation, we first need to know the derivation of Marcus equation. Marcus equation was derived originally for the outer sphere electron transfer reactions [1,2]. There are a lot of methods to derive Marcus equation containing the complicated and cumbersome original derivation method reported by Marcus himself [1,2] and some simplified derivation methods reported later [33-35]. By examining the reported methods, it is clear that both the original method and the subsequently simplified methods contain two essential assumptions: the first assumption is that the free (or potential) energy changes of reactant system (reactants plus surrounding medium) and product system (products plus surrounding medium) as a function of the reaction coordinate can be described by using two harmonic oscillators (or parabolas), respectively. The other assumption is that whether the product system and the reactant system are the same or different, the two harmonic oscillators have the same frequency [i.e., the constants ( $k$ ) of the two parabolas are the same]. **FIG. 1** is a typical Marcus kinetic model for a chemical reaction described by two parabolas with the same constant ( $k$ ). In **FIG. 1**, the left parabola (red) refers to the reactant system (symbolized by R), the right parabola (black) refers to the product system (symbolized by P), the intersecting point refers to the transition state (TS).  $\Delta G^\ddagger$  is the activation free energy of reactions;  $\Delta G^0$  is the thermodynamic driving force of reactions;  $a$  is the change of reaction coordinates between reactants system and product system at the ground state (In general,  $a=1e$  charge for electron transfer reactions).  $G=kr^2$  is the parabola equation of reactant system (Eq. 2),  $G=k(a-r)^2 + \Delta G^0$  is the parabola equation of product system (Eq. 3).

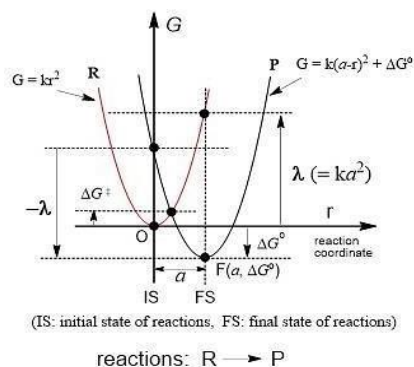


FIG. 1. A typical Marcus kinetic model for a chemical reaction ( $R \rightarrow P$ ).

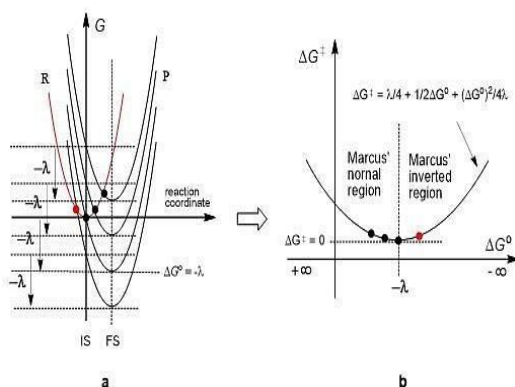


FIG. 2. Relationship between  $\Delta G^\ddagger$  and  $\Delta G^\circ$  derived from the Marcus kinetic model in which  $\lambda$  is a constant when  $\Delta G^\ddagger$  and  $\Delta G^\circ$  change.

$$G = kr^2 \quad (2)$$

$$G = k(a-r)^2 + \Delta G^\circ \quad (3)$$

When Eq. 2 and Eq. 3 are solved jointly, we can derive Marcus equation (Eq. 1).

In Eq. 1,

$$\lambda = ka^2 \quad (4)$$

Since  $k$  and  $a$  in Eq. 4 all keep constant when  $\Delta G^\circ$  changes, the  $\lambda$  in Marcus equation, as the  $\alpha$  and  $\beta$  in Brønsted equation ( $\Delta G^\ddagger = \alpha\Delta G^\circ + \beta$ ), is a constant rather than a function of  $\Delta G^\circ$ .

In addition, when  $\Delta G^\circ$  in FIG. 1 moves from positive infinity to negative infinity (shown in FIG. 2a), we can get a parabolic line for the relationship of  $\Delta G^\ddagger$  with  $\Delta G^\circ$  (shown in FIG. 2b), in which  $\lambda$  is constant when  $\Delta G^\ddagger$  and  $\Delta G^\circ$  change. If  $\Delta G^\circ$  of a chemical reaction is greater than  $-\lambda$ , the reaction is in the normal region; if  $\Delta G^\circ$  of a chemical reaction is smaller than  $-\lambda$ , the reaction is in the Marcus inverted region.

From the derivation of Marcus equation and FIG. 2, it is clear that the  $\lambda$  in Marcus equation has been reconfirmed to be a constant rather than a function of  $\Delta G^\circ$ . It is true that if the  $\lambda$  in Marcus equation were not a constant, there would not be Marcus equation and the Marcus' inverted region.

### The Errors of the Mayr's Paper

For the Mayr's paper, our focus is on the method by which the authors calculated the intrinsic barriers ( $\Delta G_o^\ddagger$ ) of the 20 reactions of Lewis acid with Lewis bases in acetonitrile. From the method applied, we found that the authors took the  $\lambda/4$  in Marcus equation as the intrinsic barrier of chemical reaction ( $\Delta G_o^\ddagger$ ) and directly introduced the values of  $\Delta G^\ddagger$  and  $\Delta G^\circ$  of the 20 reactions into Marcus equation to yield the corresponding intrinsic barriers of the reactions shown in the Table 7 in the Mayr's paper [19]. This method evidently is incorrect, because it is not in line with the nature of the  $\lambda$  in Marcus equation. As well known, the intrinsic barrier ( $\Delta G_o^\ddagger$ ) of a reaction is the activation free energy ( $\Delta G^\ddagger$ ) of the reaction when the thermodynamic driving force ( $\Delta G^\circ$ ) of the reaction is equal to zero [36]. According to this definition, the  $\lambda/4$  in Marcus equation is  $\Delta G_o^\ddagger$ . Since the  $\lambda$  in Marcus equation is a constant rather than a function of  $\Delta G^\circ$ , the 20 reactions should have the same intrinsic barrier value according to Marcus equation. The only method to derive the intrinsic barrier value ( $\lambda/4$ ) of the 20 reactions is to fit the plot of  $\Delta G^\ddagger$  against  $\Delta G^\circ$  for the 20 reactions using Marcus equation [37,38], which is like the derivation of the values of the  $\alpha$  and  $\beta$  in Brønsted equation ( $\Delta G^\ddagger = \alpha\Delta G^\circ + \beta$ ) by fitting using Brønsted equation. The  $\Delta G^\circ$  value

corresponding to the inflection point of the Marcus fitting curve line is the value of  $4\Delta G_o^\ddagger$  ( $\lambda$ ) of the 20 reactions shown in **FIG. 2b**. Evidently, the method that the authors used in their paper to get  $\Delta G_o^\ddagger$  of the 20 reactions is incorrect.

If the  $\lambda/4$  in Marcus equation were a function of  $\Delta G^\circ$  as the authors hold, when the values of  $\Delta G^\ddagger$  and  $\Delta G^\circ$  for the 20 reactions were introduced into Marcus equation, we should obtain two different values of  $\Delta G_o^\ddagger$  for each reaction at the same time ( $\Delta G_o^\ddagger_1$  and  $\Delta G_o^\ddagger_2$ ) (**TABLE 1**) rather than only one  $\Delta G_o^\ddagger_1$  value that the authors provided (shown in Table 7 in the Mayr's paper [19]). The two different values in **TABLE 1** means that each reaction among the 20 reactions all would have two different intrinsic barriers ( $\Delta G_o^\ddagger_1$  and  $\Delta G_o^\ddagger_2$ ) under given conditions at the same time. This is impossible. Therefore, the  $\lambda$  in Marcus equation is not a function of  $\Delta G^\circ$  and  $\Delta G^\ddagger$ . We do not know why the authors deleted a set of original data ( $\Delta G_o^\ddagger_2$ ) in their paper [19]? If the authors did not delete the original data ( $\Delta G_o^\ddagger_2$ ), we believe that the authors could find the mistakes of Marcus equation.

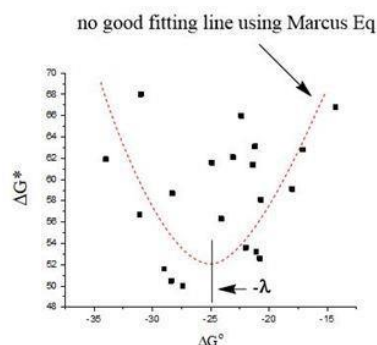
**TABLE 1. The intrinsic barriers ( $\Delta G_o^\ddagger_1$  and  $\Delta G_o^\ddagger_2$ ) for the reactions of the enamines 1-8 with benzhydrylium ions in MeCN at 20°C (KJ/mol).**

				Using Marcus Equation	
Nu	E	$\Delta G^\circ$	$\Delta G^\ddagger$	$\Delta G_o^\ddagger_1$	$\Delta G_o^\ddagger_2$
1H	E5	-28.3	58.7	72.1	0.69
	E6	-21.4	61.4	71.7	0.4
1-OMe	E5	-31.1	56.7	71.4	0.85
	E7	-23.1	62.1	73.2	0.46
1-CN	E4	-20.7	58.1	68.2	0.39
	E5	-17.1	62.8	71.1	0.26
1-NO <sub>2</sub>	E3	-24.1	56.3	67.8	0.54
	E4	-18	59.1	67.8	0.3
2	E4	-24.9	61.6	73.5	0.53
	E5	-22.4	66	76.7	0.41
3	E3	-21.2	63.1	73.3	0.43
	E4	-14.3	66.8	73.8	0.17
4	E5	-28.4	50.5	63.9	0.79
	E6	-20.8	52.6	62.6	0.43
5	E5	-29	51.6	65.3	0.81
	E5	-22	53.6	64	0.47
6	E3	-27.4	50	63	0.75
	E4	-21.1	53.2	63.3	0.44

7	E6	-31	68	82.8	0.73
8	E6	-34	61.9	78	0.93

In order to examine the validity of Marcus equation to derive the intrinsic barrier value of the 20 reactions of Lewis acids with Lewis bases in acetonitrile, a plot of  $\Delta G^\ddagger$  against  $\Delta G^\circ$  for the 20 reactions was made, the results are shown in **FIG. 3**. From **FIG. 3** it is clear that the 20 reaction points are scattered like the stars in the sky. If we use Marcus equation to fit the 20 reaction points in **FIG. 3**, we cannot get any good Marcus fitting line, which means that Marcus equation is not in line with these experimental results. Why? The reason is quite simple that Marcus equation itself is incorrect because the second assumption to derive Marcus equation that the two harmonic oscillators of the reactants system and the products system have the same frequency directly violates the law of conservation of energy [8]. To point out the fundamental error of Marcus equation, we have published many papers [8-18]. Unfortunately, none of the articles caught Mayr and co-workers' attention. If Mayr and co-workers were to pay more attention to our papers on the fundamental error of Marcus equation, we believe that Mayr and co-workers would not use Marcus equation to calculate the intrinsic barriers of chemical reactions in their paper.

In fact, to estimate the intrinsic barriers ( $\Delta G_o^\ddagger$ ) of chemical reactions, we reported a simple and practical kinetic equation (Eq. 5) that has been named as Zhu equation [10,17,18]. In Eq. 5,  $\Delta G_o^\ddagger$  is a function of  $\Delta G^\circ$  and  $\Delta G^\ddagger$ . The validity of Eq. 5 has been verified by predicting the activation free energies of 59904 hydride transfer reactions [15,18], the activation free energies of 5886 hydrogen atom transfer reactions [16] and the KIEs of 4556 hydride transfer reactions in acetonitrile at 298K [10]. It is regrettable that such a simple and practical equation was not applied by Mayr and coworkers in their paper to get the intrinsic barriers ( $\Delta G_o^\ddagger$ ) of the 20 reactions.



**FIG. 3. The plot of  $\Delta G^\ddagger$  against  $\Delta G^\circ$  for the 20 reactions of the enamines 1-8 with benzhydrylium ions in MeCN at 20°C.**

$$\Delta G_o^\ddagger = \Delta G^\ddagger - 1/2\Delta G^\circ \quad (5)$$

**TABLE 2** summarizes the intrinsic barriers of the 20 reactions in the Mayr's paper that are derived from the calculation using Eq. 5. In **TABLE 2**, each reaction among the 20 reactions has only one value of the intrinsic barrier ( $\Delta G_o^\ddagger$ ), which evidently is reasonable, and at the same time, the data in **TABLE 2** can be also used to well explain the nucleophilic reactivities of the enamines in the Mayr's paper.

TABLE 2. The intrinsic barriers ( $\Delta G_0^\ddagger$ ) for the reactions of the enamines 1-8 with benzhydrylium ions in MeCN at 20°C from a calculation using Eq. 5 (KJ/mol).

Nu	E	$\Delta G^\circ$	$\Delta G^\ddagger$	$\Delta G_0^\ddagger$
1H	E5	-28.3	58.7	72.9
	E6	-21.4	61.4	72.1
1-OMe	E5	-31.1	56.7	72.3
	E7	-23.1	62.1	73.7
1-CN	E4	-20.7	58.1	68.5
	E5	-17.1	62.8	71.4
1-NO <sub>2</sub>	E3	-24.1	56.3	68.4
	E4	-18	59.1	68.1
2	E4	-24.9	61.6	74.1
	E5	-22.4	66	77.2
3	E3	-21.2	63.1	73.7
	E4	-14.3	66.8	74.0
4	E5	-28.4	50.5	64.7
	E6	-20.8	52.6	63.0
5	E5	-29	51.6	66.1
	E5	-22	53.6	64.6
6	E3	-27.4	50	63.7
	E4	-21.1	53.2	63.8
7	E6	-31	68	83.5
8	E6	-34	61.9	78.9

## Conclusion

In the Mayr's paper [19], the method to calculate the intrinsic barriers of the 20 chemical reactions of Lewis acids with Lewis bases in acetonitrile is incorrect. The main reason is that the authors lack a correct understanding of Marcus equation and incorrectly took the  $\lambda$  in Marcus equation as a function of  $\Delta G^\circ$  rather than a constant. Similarly, in the other recent publications made using Marcus equation [24-32] the authors make the same mistakes as the Mayr's mistakes. In addition, the introduction of Zhu's work in the Mayr's paper [19] is incorrect also, because the origin and the nature of Eq. 5 are thoroughly different from that of Marcus equation [10].

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