Generalized model for state-resolved chemical reaction rate coefficients in high-temperature air

E Kustova and A Savelev
Saint Petersburg State University, 7/9 Universitetskaya nab., St. Petersburg, 199034, Russia
E-mail: e.kustova@spbu.ru and aleksey.schumacher@gmail.com

Abstract. In the present study, we propose a general model for state-resolved reaction rate coefficients. The model combines the main advantages of several theoretical models for preferential dissociation and exchange reactions coupled to vibrational relaxation. Vibrational and electronic excitation of all species participating in the reaction is taken into account. The complete set of parameters for state-resolved chemical reactions in five-component air is obtained by fitting the results of the most reliable quasi-classical trajectory simulations in the temperature range 2000–15000 K.

1. Introduction
Detailed studies of coupled chemical and vibrational kinetics are of importance for accurate predictions of fluid-dynamic parameters and heat transfer in non-equilibrium high-temperature gas mixture flows, such as flows around spacecrafts entering planetary atmospheres. There are several degrees of detail in the non-equilibrium flow description. The most simple and numerically efficient is the one-temperature description, which is based on the fluid-dynamic equations coupled with the equations of one-temperature chemical kinetics governed by the Arrhenius law. More complex and accurate are multi-temperature models taking into account coupling of vibrational relaxation and chemical reactions through the dependence of reaction rate coefficients on the vibrational temperatures; in this case, the fluid-dynamic equations are solved together with the equations of chemical kinetics and relaxation equations for specific vibrational energies [1, 2]. The most detailed approach is the completely coupled state-to-state model, which requires data on the state-resolved rate coefficients specifying the production terms in the master equations for the vibrational level populations [2]. Several theoretical models for the state-to-state reaction rate coefficients have been proposed earlier, among them the Marrone–Teanor [3], Aliat [4], Warnatz [5], Polak [6], Macheret-Fridman [7], Starik [8, 9] and other models.

Despite the diversity, the existing models have certain disadvantages and limitations. Thus, the Marrone–Teanor model does not take into account the vibrational excitation of the reaction products and the second reagent. The Starik model overcomes this issue, but at the same time does not allow taking into account preferential reactions from high energy states. In our previous works [10, 11], we proposed generalizations of the Marrone–Teanor and Aliat models by introducing temperature- and vibrational energy-dependent parameters to ensure good agreement of theoretical calculations with quasi-classical trajectory (QCT) results. Although providing close agreement with the QCT results, our earlier models have some shortcomings: (1) they do not take into account electronically excited states and excitation of all species.
participating in the reaction; 2) some of the rate coefficients, when being averaged with the thermal equilibrium Boltzmann distribution, do not reduce to the Arrhenius ones; 3) the dependence of the model parameters on the vibrational energy complicates its implementation; it was shown [12] that the temperature dependence is more important; this has to be checked.

The objectives of the present study are: 1) to overcome the above issues; 2) to derive a universal model for the state-resolved rate coefficients of dissociation and exchange reactions taking into account vibrational and electronic excitation of all species involved to the reaction; and 3) to derive the set of best-fit model parameters suitable for all reactions in the five-component high-temperature air mixture.

2. Reactions Rate Coefficients

We consider dissociation and exchange reactions in collisions of diatomic and polyatomic molecules with atoms and molecules in the state-to-state and multi-temperature approaches [2]. The energy corresponding to each internal state may include the vibrational and electronic energy of a molecule, \( e^{\text{el}} + e^{\text{vibr}} = \varepsilon_n + \varepsilon_k \), and the electronic energy of atomic species \( e^{\text{el}} = \varepsilon_n \); \( n \), \( i \) stand for the electronic and vibrational level, correspondingly. Similarly to [9], we denote the sets of quantum states of all reactants \( r \) and reaction products \( p \) as \( V_r \) and \( V_p \). For instance, for reactants, \( V_r = \{ i, k, n, m \} \) with \( i, k \) denoting vibrational levels, and \( n, m \) electronic levels. Further, for polyatomic species, the vibrational quantum number is a set of quantum numbers of vibrational modes; thus, for CO\(_2\), \( i = \{ i_1, i_2, i_3 \} \) with \( i_1, i_2, i_3 \) associated to symmetric, bending and asymmetric vibrations. The energy of the reagents \( E_r = \varepsilon_n + \varepsilon_k \); if one of the reactants is atom, only its electronic energy contributes to this expression. The same notations are used for the product quantum states \( V_p \) and energies \( E_p \). For the dissociation reaction, \( V_p \) and \( E_p \) include quantum states and energies of three particles.

Following the ideas proposed by Knab [13] and further developed in [4, 14, 10, 11] we derive the general expression for the state-resolved reaction rate coefficient taking into account vibrational and electronic excitation of both reagents and products. The main steps are reported in [15] although in the latter study electronic excitation is not considered. In the present study, we choose the representation of the rate coefficients proposed in [9], which is based on the Heaviside function and thus has a compact form. The state-resolved rate coefficients of dissociation or exchange reaction \( k_{V_r \rightarrow V_p}^{\text{ex,dis}} \) are obtained in the form:

\[
k_{V_r \rightarrow V_p}^{\text{ex,dis}} = B \cdot \exp \left( -\frac{\Delta E_{V_r \rightarrow V_p}}{k} \Theta \left( \frac{\Delta E_{V_r \rightarrow V_p}}{W} \right) \left( \frac{1}{T} + \frac{1}{U} \right) \right), \quad \Delta E_{V_r \rightarrow V_p} = E_a + E_p - E_r, \tag{1}\]

where \( k \) is the Boltzmann constant, \( T \) is the gas temperature, \( U \) is a model parameter which takes into account preferential reactions from high energy states, \( E_a \) is the forward reaction activation energy, \( \Theta(x) \) is a Heaviside function. Function \( B \) is introduced by the formula:

\[
B(T) = \frac{k^{\text{eq}}(T)}{\sum_{V_r^* \rightarrow V_p^*} \exp \left( -\frac{\Delta E_{V_r^* \rightarrow V_p^*}}{k} \Theta \left( \frac{\Delta E_{V_r^* \rightarrow V_p^*}}{W} \right) \left( \frac{1}{T} + \frac{1}{U} \right) \right) \prod_{l=1}^{M_r} m_{V_r^* l}}, \tag{2}\]

\( k^{\text{eq}}(T) \) is the thermal equilibrium rate coefficient in the Arrhenius form, \( M_r \) is a number of reagents, \( m_{V_r^* l} \) is the reduced equilibrium Boltzmann distribution (dimensionless) of the \( l \)th reagent over electronic and vibrational energy at a temperature \( T \).

The present general model combines the advantages of existing models, while eliminating the main known disadvantages. The proposed model, due to the choice of the \( E_a \) parameter, can be used both for dissociation and exchange reactions. The use of the \( U \) parameter allows
one to describe the preferential reactions from high energy states (in this work we consider only the temperature dependence of $U$) and to fit the rate coefficients to existing QCT data. The proposed formula can be used for both molecule–molecule and molecule–atom collisions (including polyatomic molecules), and takes into account vibrational and electronic excitation of molecules and electronic excitation of atoms, for all species participating in the reaction.

Let us consider particular cases of Eq. (1). First of all, one can see that the expression is very similar to that given in [9]. There are, however, two differences: 1) in model [9], in the definition of $E_a$ there is a maximum function, which is absent in our model; 2) in our model, the parameter $U$ appears, which is responsible for the preferential reactions from high energy states. In the limit $U = \infty$, our formula reduces to that from [9] with the only exception in the maximum in $E_a$. It is worth noting that both models, although having a compact and convenient form, are rather computationally expensive compared to the form given in [11, 15].

If we consider vibrational-electronic excitation of only one reagent ($r_1$) and neglect electronic excitation of atoms, then $\Delta E_{V_r \rightarrow V_p} = E_a - E_{r_1}$, and Eq. (1) can be easily reduced to the state-dependent reaction rate coefficient from [4], with the correction of the normalizing factor discussed in work [11]. Finally, if we consider a dissociation reaction taking into account only vibrational excitation of the dissociating molecule, then 1) $E_a = D$ (D is the dissociation energy); 2) $\Delta E_{V_r \rightarrow V_p} = \Delta E_i = D - \varepsilon_i$; 3) all $\Theta(\Delta E_i) = 1$; 4) the summation is carried out only over the vibrational states of the dissociating molecule; 5) only the distribution of the dissociating molecule is taken into account. After these simplifications, one easily gets the well-known Marrone–Treanor [3] formula.

In order to derive the multi-temperature reaction rate coefficients, we average Eq. (1) multiplying it by the nonequilibrium vibrational distributions of both reagents and make summation over all the vibrational states of the reagents and products. Note that hereafter we do not take into account electronic excitation.

### 3. Results and discussion

#### 3.1. Dissociation reaction in air

Let us consider state-resolved reactions in a five-component air mixture. As noted above, for dissociation of diatomic molecules taking into account the vibrational excitation of only the decaying molecule, Eq. (1) is identical to the Marrone–Treanor model [3]. In our previous studies [14, 10], we proposed its modification introducing the parameter $U$ depending on temperature and vibrational energy; the parameter was fitted using the QCT data. One of the fundamental problems of those early studies was the lack of QCT data which were given only for 15-20% of the vibrational states. Recent studies provide data for all vibrational states and, in addition, the relative error of QCT simulations. This can help to significantly improve the accuracy of our model.

Based on the QCT data provided by D. Andrienko [16], we performed calculations of NO molecules dissociation rate coefficients in collisions with atoms. The model assessment for the NO+N reaction is presented in Figure 1. The left plot shows the relative error of the QCT simulations whereas the right one — the relative error of our calculations with respect to the QCT data, $(k - k_{QCT})/k_{QCT}$. One can see that the trajectory simulations have a significant error for the low vibrational states at low temperatures. At the same time, the use of the Marrone–Treanor model with our set of parameters yields agreement with the results of trajectory calculations within the error of the QCT data in the entire range of temperatures and vibrational states. The same result is obtained for NO+O dissociation.

Thorough analysis based on the complete data set shows that the dependence of the parameter $U$ on the vibrational energy is redundant, and a good accuracy can be obtained taking into account only its temperature dependence. On the other hand, eliminating the vibrational energy dependence noticeably reduces the computational cost of the model. Therefore, we have decided...
to upgrade the sets of parameters obtained in our previous studies [14, 10, 11]. The new sets of parameters for dissociation reactions in air are summarized in Table 1. For all the reactions presented in the Table 1, except the reactions O$_2$+N$_2$, O$_2$+NO, N$_2$+O$_2$, N$_2$+NO and NO+NO, the recommended values of the parameters of the Arrhenius law and parameter $U$ are based on the best fit of the QCT data [17, 18, 19, 20, 21, 22]. Due to the lack of QCT data on the above indicated reactions, we recommend the parameters of the Arrhenius law from [23], and the parameter $U$ is chosen based on the analysis of the remaining reactions. It is important to note that fitting of the parameter $U$ was carried out in the temperature range from 1000 K to 15000 K; the model was not assessed outside this range.

It is worth noting that, despite the fact that these parameters can be used for any oscillator model, the best agreement with the QCT data is achieved when using the same vibrational energy levels as in the trajectory calculations. When using an oscillator models with a smaller number of vibrational states, the values of the corresponding rate coefficients are greater than when using the same energy levels.

In Figures 2 and 3, we present some comparisons of the rate coefficients calculated taking into account the energy dependence of $U$ and neglecting it. For all reactions except O$_2$+O$_2$, the results are similar; the new set of parameter even provides better agreement for some energy ranges. For the O$_2$+O$_2$ reaction, we used the most recent and accurate QCT data from [18], where improved potential energy surfaces were implemented compared to previous simulations of [24]. One can notice (see Figure 3) a significant difference between the present and previous rate coefficients; the new data set is more accurate and thus is recommended for using in high-temperature air kinetics. In addition, it is found that the new QCT data of [18] are described quite well using the Arrhenius parameters from [23] and the parameter $U = 3T$.

3.2. Zeldovich reactions
Let us consider the exchange reactions in air, also known as Zeldovich reactions:

$$\text{N}_2(i) + O \leftrightarrow \text{NO}(j) + \text{N},$$

$$\text{O}_2(i) + \text{N} \leftrightarrow \text{NO}(j) + \text{O}.$$  

Previously, we have already considered these reactions taking into account the excitation of the reaction product [11] and obtained a good agreement with the data of the Stellar database [17].
Table 1. Arrhenius and Marrone–Treanor model parameters for the dissociation reaction rate coefficient, $k_{\text{dis}}$, cm$^3$ s$^{-1}$.

| Reaction          | $A$         | $n$  | $E_a/k$, K | $U(T)$, K                                                                 |
|-------------------|-------------|------|------------|--------------------------------------------------------------------------|
| $\text{O}_2+\text{O}$ | $6.1953 \cdot 10^{-6}$ | -0.55724 | 60496      | $5.5 \cdot T + 14000, T \leq 7000K$                                     |
|                   |             |      |            | $-0.000368 \cdot T^2 + 12.78 \cdot T - 18936, \text{otherwise}$          |
| $\text{O}_2+\text{O}_2$ | $7.085 \cdot 10^{-6}$ | -0.73 | 60496      | $1.1 \cdot T + 13900, T \leq 10000K$                                     |
|                   |             |      |            | $24900, 10000 < T \leq 12000K$                                           |
|                   |             |      |            | $3.3 \cdot T - 14700, T > 12000K$                                         |
| $\text{O}_2+\text{N}_2$ | $1.3 \cdot 10^{-4}$ | -1.0  | 60496      | $\infty$                                                                 |
| $\text{O}_2+\text{NO}$ | $1.1 \cdot 10^{-4}$ | -1.0  | 60496      | $\infty$                                                                 |
| $\text{N}_2+\text{O}$ | $4 \cdot 10^{-6}$ | -0.68 | 115000     | $5 \cdot T - 3000, T \leq 5000K$                                         |
|                   |             |      |            | $-0.000313 \cdot T^2 + 5.5 \cdot T + 2313, T \leq 9000K$                |
|                   |             |      |            | $26000, T > 9000K$                                                       |
| $\text{N}_2+\text{N}$ | $2.67 \cdot 10^{-7}$ | -0.381 | 115000 | $299.4 \cdot T^{0.5248}$                                               |
| $\text{N}_2+\text{N}_2$ | $4.1 \cdot 10^{-6}$ | -0.62 | 115000 | $3T$ or the same as for $\text{N}_2+\text{N}$                           |
| $\text{N}_2+\text{O}_2$ | $1.5 \cdot 10^{-5}$ | -0.68 | 115000 | $3T$ or the same as for $\text{N}_2+\text{N}$                           |
| $\text{N}_2+\text{NO}$ | $1.5 \cdot 10^{-5}$ | -0.68 | 115000 | $3T$ or the same as for $\text{N}_2+\text{N}$                           |
| $\text{NO}+\text{O}_2$ | $7.097 \cdot 10^{-4}, T \leq 4000K$ | -1.46295, $T \leq 4000K$ | 76885 | $1.6 \cdot T - 2500, T > 5000K$                                          |
|                   | $1.5425 \cdot 10^{-6}, T > 4000K$ | -0.72385, $T > 4000K$ |          | $T + 500, \text{otherwise}$                                              |
| $\text{NO}+\text{N}_2$ | $1.9 \cdot 10^{-4}, T < 4000K$ | -1.3066, $T < 4000K$ | 76885 | $17770 - 3.1 \cdot T + 2.7 \cdot 10^{-4} \cdot T^2, T > 8000K$         |
|                   | $7.865 \cdot 10^{-7}, T > 4000K$ | -0.6451, $T > 4000K$ |          | $-667 + 1.33 \cdot T, 2000K < T \leq 8000K$                            |
|                   |             |      |            | $0.5 \cdot T + 1500, T \leq 2000K$                                       |
| $\text{NO}+\text{O}$ | $5.59 \cdot 10^{-7}$ | -0.447 | 76885 | $22455 + 1.41 \cdot T, T < 18000K$                                       |
|                   |             |      |            | $42500 + 0.25 \cdot T, \text{otherwise}$                                 |
| $\text{NO}+\text{N}$ | $1.5038 \cdot 10^{-6}$ | -0.5468 | 76885 | $2.07 \cdot 10^{-4} \cdot T^2 - 1.452 \cdot T + 15907$                 |
| $\text{NO}+\text{NO}$ | $1.0 \cdot 10^{-4}$ | -1.0  | 76885 | $1.5 \cdot T$                                                           |
Figure 2. State-to-state reaction rate coefficients as functions of the reagent vibrational energy. $T=10000$ K. Comparison with QCT data from [19, 21].

Figure 3. State-to-state reaction rate coefficients as functions of the $O_2$ vibrational energy. $O_2+O_2$ dissociation. Comparison with [18, 23].

The rate coefficients proposed in [11] have some specific features. For each NO vibrational state, we used different Arrhenius law parameters: the constant $A$ and the activation energy $E_a$ were vibrational state-dependent. This provides perfect accuracy but essentially complicates the model implementation and leads to some inconsistency: when averaged with the thermal equilibrium distributions, the rate coefficients do not reduce to the one-temperature Arrhenius coefficients. In the present study, we use the generalized expression (1) which does not suffer of this issue.

First, consider reaction (3). Similarly to the previous studies, it was found that the best fit to the QCT results [17] is obtained when using the parameter $U=\infty$. However, for the modified model, the use of the Arrhenius law parameters proposed earlier in [11] for the NO ground vibrational state provides satisfactory agreement only for temperatures below 4000 K. For higher temperatures, the use of this set of parameters yields underestimated reaction rate coefficients, the error exceeds one order of magnitude for 15000 K. To overcome this problem, we have upgraded the Arrhenius parameters, see Table 2; the results are compared in Figure 4 (left plot). Note that although the model [11] provides slightly better agreement with [17], its implementation is much less straightforward with respect to the present model.

At the next step, reaction (4) is considered. As in the case of reaction (3), the slope of the
rate coefficients is reproduced in the best way when we use the value $U = \infty$. But, in contrast to the previous reaction, there is a discrepancy for the $O_2$ excited vibrational states at low vibrational energy of the product. The reason is that the QCT results for reaction (4) show the shift in the point where the plateau part is attained. From the theoretical point of view, this point has to correspond to the vibrational excitation energy of the product. This issue requires additional investigation. Otherwise, the situation is similar to the previous reaction: for the product ground vibrational state, the Arrhenius parameters from [11] adequately describe the results; for temperatures above 4000 K, some additional improvement is needed, see Table 2. The comparison is shown in Figure 4 (right plot).

The sets of parameters for reactions (3) and (4) recommended for air flows in the temperature range 2000–15000 K are presented in Table 2. For lower temperatures, it is preferable to use the Arrhenius law parameters proposed earlier in [11]; they provide better accuracy although are more difficult to implement.

4. Conclusions
Generalized model of state-resolved dissociation and exchange reaction rate coefficients in high-temperature air is proposed. The general theoretical expression takes into account electronic and vibrational excitation of all species participating in the reaction as well as preferential reactions from high vibrational states. The model is also suitable for polyatomic gases such as $CO_2$. Several shortcomings of previously developed models are corrected. In particular, the state-to-state rate coefficients averaged with the thermal equilibrium Boltzmann distribution are now reduced to the Arrhenius form. It is found that the dependence of the parameter $U$ on the vibrational energy is redundant and can be eliminated; the temperature-dependent parameter provides satisfactory agreement with the quasi-classical trajectory results; this leads
to considerable simplification of the present model implementation. The model parameters are upgraded in the temperature range from 2000 to 15000 K using the recent QCT calculations. Thus, the complete set of parameters is obtained for state-resolved chemical reactions in the five-component air mixture. Recommended parameters can be used for simulations of high-temperature non-equilibrium flows with coupled vibrational relaxation and chemical reactions.

Acknowledgments
This study is supported by the Russian Science Foundation, grant 19-11-00041. The authors are grateful to Dr. D. Andrienko for providing the QCT data on the NO+O and NO+N reactions.

References
[1] Park C 1990 Nonequilibrium Hypersonic Aerothermodynamics (New York, Chichester, Brisbane, Toronto, Singapore: J.Wiley and Sons)
[2] Nagnibeda E and Kustova E 2009 Nonequilibrium Reacting Gas Flows. Kinetic Theory of Transport and Relaxation Processes (Berlin, Heidelberg: Springer Verlag)
[3] Marrone P and Treanor C 1963 Phys. Fluids 6 1215–1221
[4] Aliat A 2008 Physica A 387 4163–4182
[5] Warnatz J, Riedel U and Schmidt R 1992 Advances in Hypersonics: Modeling Hypersonic Flows (Boston: Birkhäuser)
[6] Polak L, Goldenberg M and Levitskii A 1984 Numerical Methods in Chemical Kinetics (Moscow: Nauka) (in Russian)
[7] Macheret S O, Fridman A A, Adamovich I V, Rich J W and Treanor C E 1994 AIAA Paper 94-1984 6th AIAA/ASME Joint Thermophysics and Heat Transfer Conference (Colorado Springs)
[8] Arsentiev I, Loukhovitski B and Starik A 2012 Chem. Phys. 398 73–80
[9] Kadochnikov I and Arsentiev I 2018 J. Phys. D: Appl. Phys. 51 374001
[10] Kunova O, Kustova E and Savelev A 2016 Chem. Phys. Lett. 659 80–87
[11] Kustova E, Savelev A and Kunova O 2018 AIP Conference Proceedings 1959 060010
[12] Pogosbekyan M and Sergievskaya A 2018 Russian Journ. Phys. Chem. B 12 208–218
[13] Knab O, Frühauf H and Messerschmid E 1995 J. Thermophys. Heat Transfer 9 219–226
[14] Kustova E, Nagnibeda E, Oblapenko G, Savelev A and Sharafutdinov I 2016 Chem. Phys. 464 1–13
[15] Kustova E, Savelev A and Armenise I 2019 J. Phys. Chem. A 123 10529–10542
[16] Andrienko D Private communication, paper in preparation
[17] Stellar database http://esther.ist.utl.pt/pages/stellar.html
[18] Baluckram V and Andrienko D 2021 AIAA Paper 2021–0447
[19] Esposito F, Armenise I and Capitelli M 2006 Chem. Phys. 331 1–8
[20] Armenise I, Esposito F and Capitelli M 2007 Chem. Phys. 336 83–90
[21] Esposito F, Armenise I, Capitelli G and Capitelli M 2008 Chem. Phys. 351 91–98
[22] Armenise I and Esposito F 2012 Chem. Phys. 398 104–110
[23] Scanlon T, White C, Borg M, Palharini R, Farbar E, Boyd I, Reese J and Brown R 2015 AIAA Journal 53 1670–1680
[24] Andrienko D and Boyd I 2017 Chem. Phys. 491 74–81