

# On the Influence of Vibrational Distributions on Dissociation Rates

E.A. Nagnibeda, K.A. Sinitsyn and S.S. Bazilevich

*Saint-Petersburg State University, Mathematics and Mechanics Dept.  
Universitetsky prospekt, 28, 198504, Peterhof, Saint-Petersburg, Russia.*

**Abstract.** The paper presents the results of theoretical study of two-temperature dissociation rate coefficients in five gases N<sub>2</sub>, O<sub>2</sub>, NO, CO, H<sub>2</sub>. Non-equilibrium dissociation rate coefficients are calculated using four quasi-stationary vibrational distributions: Treanor distribution, Boltzmann distribution with the vibrational temperature different from the gas temperature, generalized Treanor distribution for the case of strong vibrational excitation and thermal equilibrium Boltzmann distribution described by Arrhenius formula. Comparison of the results obtained using different distributions is presented and a role of vibrational non-equilibrium in a dissociation process is demonstrated. Non-monotonous dependence of rate coefficients and non-equilibrium factor on the gas temperature is found for all considered gases. Peculiarities of vibrational distributions and dissociation coefficients in different gases are discussed.

**Keywords:** Dissociation rate coefficients, non-equilibrium factor, vibration distribution.

**PACS:** 51.10.+y, 82.20.-w.

## INTRODUCTION

Modeling of reaction rate coefficients is important for many problems of chemical kinetics and non-equilibrium gas dynamics. In thermal equilibrium gas mixture these coefficients are described by Arrhenius law whereas under non-equilibrium conditions global reaction rates are defined by the state-to-state coefficients averaging with vibrational distributions [1]. Global reaction rates in various flows have been widely studied in the literature using different kinetic models. The most rigorous results have been obtained using the state-to-state vibrational populations in a flow [1], [2], [3]. This approach gives a rather good accuracy for reaction rates. However it appears too complicated for applications, particularly if many cases should be considered. Indeed, for each case one has to solve, first, the equations of state-to-state kinetics and gas dynamics, and then calculate global reaction rate coefficients for this case using found distributions. Multi-temperature models based on quasi-stationary distributions are much more suitable for applications. These models permit to obtain analytical expressions for reaction rate coefficients and investigate their behavior for many particular cases in different gases. The important question is how to construct an adequate multi-temperature model for reaction rate coefficients which would satisfy the requirements of both accuracy and simplicity.

In the present paper two-temperature dissociation rate coefficients are studied in five diatomic gases (N<sub>2</sub>, O<sub>2</sub>, CO, NO, H<sub>2</sub>) using different quasi-stationary approaches. The comparison of the results obtained using different models, shows the influence of vibrational distributions on dissociation rate coefficients.

## BASIC EQUATIONS

We consider dissociation reactions of diatomic molecules



Where  $A_2(i)$ ,  $AB(i)$  are diatomic molecules at vibrational level  $i$ , the partner  $M$  can be a molecule or an atom. The rate coefficient  $k_{\text{diss}}^{(M)}$  of reaction (1) is defined as

$$k_{diss}^{(M)} = \frac{1}{n_{mol}} \sum_{i=0}^L n_i k_{i,diss}^{(M)} \quad (2)$$

Here  $n_i$  is the population of  $i$ th vibrational level,  $n_{mol} = \sum_{i=0}^L n_i$  is the total number of molecules in the unit volume,  $k_{i,diss}^{(M)}$  is the state-dependent dissociation rate coefficient depending on the vibrational level of a dissociating molecule.

In the present paper dissociation rate coefficients (2) are studied using different distributions  $n_i$ : non-equilibrium Boltzmann distribution with the vibrational temperature different from the gas temperature, two-temperature Treanor distribution [4], and generalized Treanor distribution for dissociating gas with strong vibrational excitation [5], [6]. Two-temperature Treanor distribution is valid only until the vibrational level  $i_*$ , which can be found as the minimum of the function  $n_i$ . If  $T \gg T_1$ , the level  $i_*$  is close to the last vibrational level  $L$ , and Treanor distribution is valid almost at all vibrational levels. For strongly excited gas with high vibrational energy ( $T \ll T_1$ ) the minimum of Treanor distribution is reached at low levels, and its increasing branch is not realized. In this case level populations can be described by generalized Treanor distribution, which has a form of Treanor distribution at low levels, slopping plateau at intermediate levels and Boltzmann distribution at upper levels [6]:

$$n_i = \begin{cases} \frac{N_1}{Z_{vibr}^{Tr}} \exp\left(-\frac{\varepsilon_i - i\varepsilon_1}{kT} - \frac{i\varepsilon_1}{kT_1}\right), & 0 \leq i \leq i_* \\ n_{mol} \frac{\Gamma}{i+1}, & i_* \leq i \leq i_{**} \\ \frac{N_3}{Z_{vibr}^B} \exp\left(-\frac{\varepsilon_i}{kT}\right), & i_{**} \leq i \leq L \end{cases} \quad (3)$$

coefficients  $N_1$ ,  $\Gamma$ ,  $N_3$  are found using normalizing conditions and distribution continuity;  $i_{**}$  was calculated using the comparison of probabilities of VV and VT transitions (the probabilities of VV and VT transitions are equal when  $i > i_{**}$ ). The value  $L$  was calculated by equating vibrational energy of an anharmonic oscillator to the dissociation energy  $D$ .

Two-temperature dissociation rate coefficients were presented in such a form:

$$k_{diss}^{(M)}(T, T_1) = Z(T, T_1, U) k_{diss,eq}^{(M)} \quad (4)$$

Here  $Z(T, T_1, U)$  is the non-equilibrium factor:

$$Z(T, T_1, U) = \frac{1}{n_{mol}} \sum_{i=0}^L n_i Z_i(T, U) \quad (5)$$

$Z_i$  is the state-dependent non-equilibrium factor [6]:

$$Z_i(T, U) = \frac{Z_{vibr}^{(T)}}{Z_{vibr}^{(-U)}} \exp\left[\frac{\varepsilon_i}{k} \left(\frac{1}{T} + \frac{1}{U}\right)\right] \quad (6)$$

According to the Treanor-Marrone model dissociation may happen from any vibrational level. The state-to-state rate coefficient  $k_{i,diss}^{(M)}$  may be connected with the thermal equilibrium rate coefficient  $k_{diss}^{eq(M)}$ , by the expression:

$$k_{i,diss}^{(M)} = Z_i(T) k_{diss,eq}^{(M)}(T) \quad (7)$$

Calculations were presented with usual values of parameter  $U$ :  $U = \infty, U = D/6k, U = 3T$ . The thermal equilibrium rate coefficient  $k_{diss}^{eq(M)}$  is expressed by the generalized Arrhenius law:

$$k_{diss,eq}^{(M)}(T) = AT^n \exp\left(-\frac{D}{kT}\right) \quad (8)$$

Empirical quantities  $A$ ,  $n$  for considered gases are given in the Table 1 ([7], [8]).

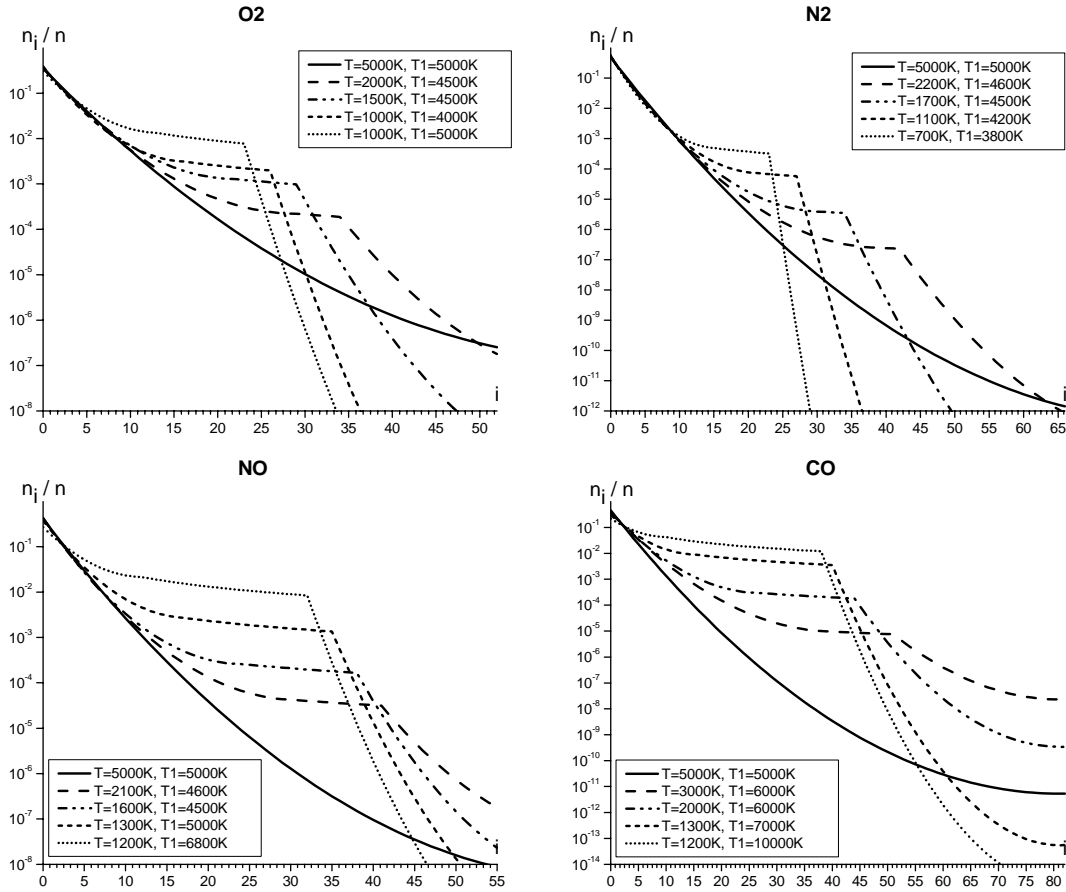
**TABLE 1.**

Element	$A$	$n$
N2	$3,7 * E15$	-1,6
O2	$1,99 * E15$	-1,5
H2	$1,47 * E13$	-1,23
CO	$0,45 * E13$	-1,0
NO	$0,41 * E12$	-1,0

## RESULTS

Let us consider vibrational distributions and their influence on dissociation rate coefficients. Non-equilibrium distributions are highly dependent from the temperatures  $T$  and  $T_1$ . In gas with low vibrational excitation and high gas temperature ( $T > T_1$ ), thermal equilibrium Boltzmann distribution gives overestimated values of level populations in comparison with Treanor distribution. Whereas non-equilibrium Boltzmann distribution, which is valid only for harmonic oscillators underestimates level populations.

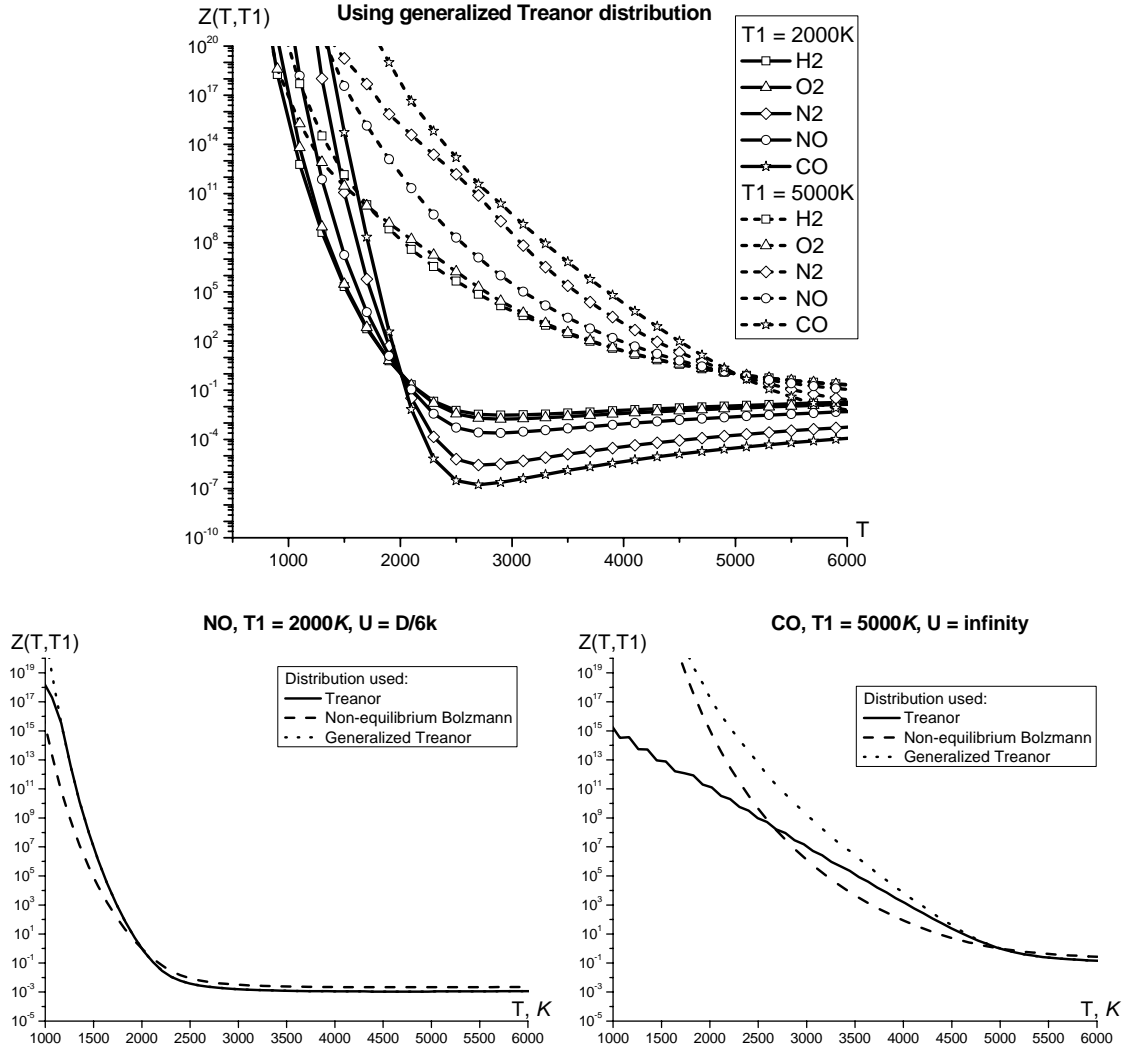
In the case of strong vibrational excitation ( $T < T_1$ ) Treanor distribution does not describe correctly populations of intermediate and high levels and complex distribution (3) is needed. Boltzmann non-equilibrium distribution as well as thermal equilibrium one underestimates level populations. Vibrational level populations of O2, N2, NO, CO and H2 were calculated using generalized Treanor distribution (3) for different values of  $T_1/T$ . Results are presented in Fig. 1.



**FIGURE 1.** Generalized Treanor distribution for O2, N2, NO and CO molecules.

One can see that the length of plateau at intermediate levels decreases with the reduction of  $T_1/T$ . Calculations show a very short plateau in  $N_2$  whereas it is rather long in  $NO$  and  $H_2$ .

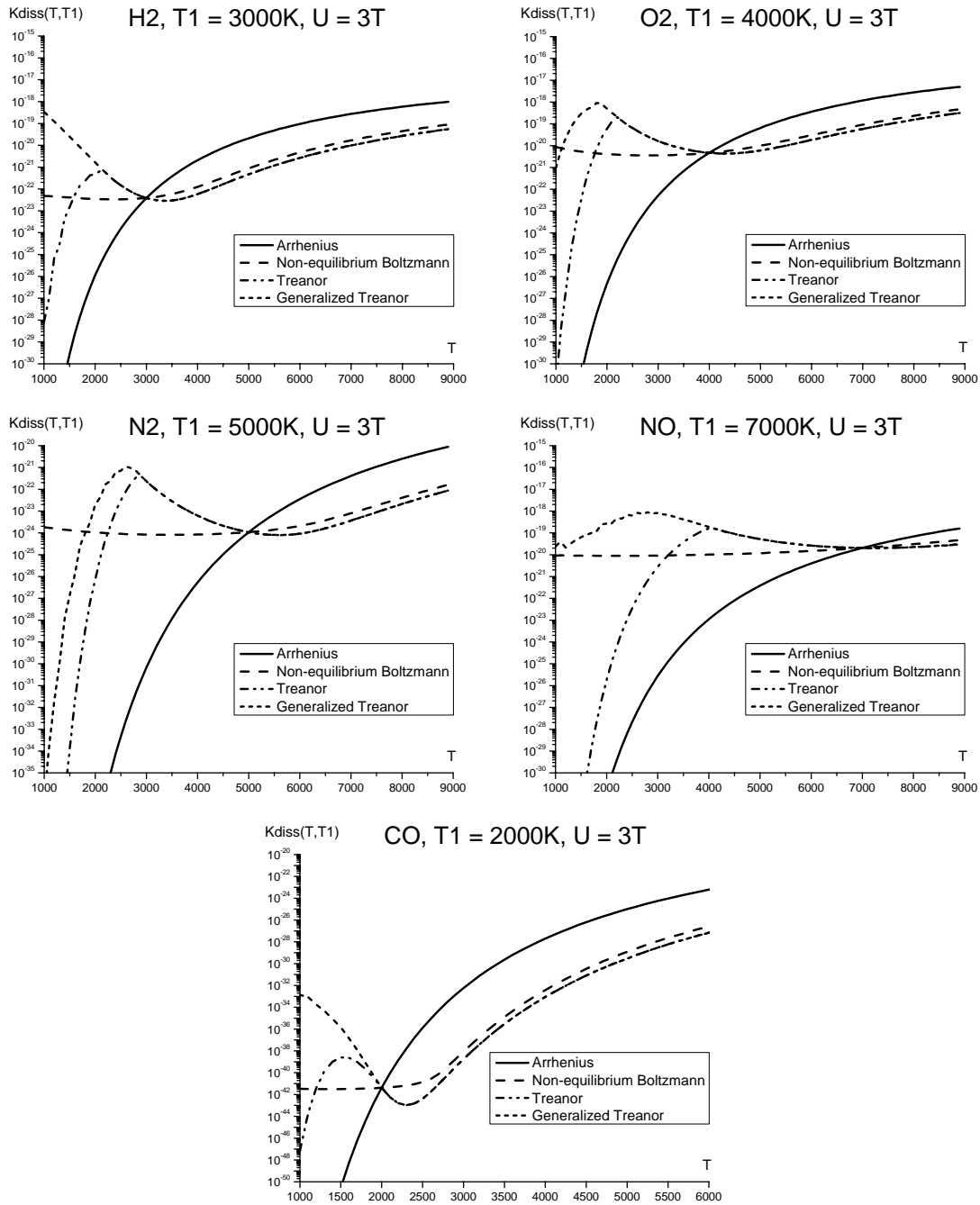
Two-temperature non-equilibrium factors were found on the basis of three quasi-stationary vibrational distributions: Treanor distribution, non-equilibrium Boltzmann distribution and generalized Treanor distribution. Fig.2 presents the temperature dependence of  $Z$  for different gases calculated for fixed  $T_1$  values. A general tendency is that  $Z$  for all distributions and gases increases with  $T_1/T$  rising;  $Z > 1$  at  $T_1/T > 1$  and  $Z < 1$  at  $T_1/T < 1$ . Use of both Treanor distribution and distribution (3) give higher values of  $Z$  in comparison with use of Boltzmann distribution. The role of distribution is high at  $T_1 > T$  and diminishes with  $T_1/T$  decreasing. It is obvious that  $Z=1$  when  $T=T_1$  for all distributions.



**FIGURE 2.** Temperature dependence of the averaged non-equilibrium factor  $Z$ .

Now let us consider the influence of distributions on dissociation rate coefficients. Fig. 3 shows the comparison of the average dissociation rate coefficients for four distributions: Treanor distribution, non-equilibrium Boltzmann distribution, distribution (3) and thermal equilibrium distribution.

Calculations show that use of three non-equilibrium distributions give close values of two-temperature dissociation rate coefficients at  $T > T_1$ , whereas thermal equilibrium Boltzmann distribution leads to their overestimation. In the case of strong vibrational excitation ( $T < T_1$ ) at low gas temperature a noticeable discrepancy between dissociation rate coefficients obtained using different distributions can be seen.



**FIGURE 3.** Temperature dependence of the averaged dissociation rate coefficient.

The non-monotonous behavior of dissociation rate coefficients with the temperature rising at  $T < T_1$  was found for all considered gases. Such a character of non-equilibrium factor for bimolecular reactions was found in [9]. Dissociation rate coefficients, calculated using generalized Treanor distribution considerably surpass values of dissociation rate coefficients, found with the usage of Boltzmann non-equilibrium and thermal equilibrium distributions if  $T_1 > T$ . It testifies to an opportunity of dissociation at low temperatures due to the strong vibrational excitation.

## CONCLUSIONS.

The influence of vibrational distributions on dissociation rate coefficients is demonstrated in this paper. Three two-temperature non-equilibrium models are considered and compared with the one-temperature Arrhenius one.

In the case of weak non-equilibrium ( $T_1 < T$ ), all three two-temperature models give resembling results whereas noticeable discrepancy appears in a strongly excited gas ( $T_1 > T$ ). Arrhenius thermal equilibrium approximation leads to overestimation of dissociation rate coefficients at  $T > T_1$  and their underestimation at  $T < T_1$ . The difference between rate coefficients obtained for the case  $T_1 > T$  with the use of the Treanor distribution and more realistic Treanor-plateau-Boltzmann distribution shows the important role of intermediate and upper levels in dissociation process. The non-monotonous dependence of dissociation rate coefficients and non-equilibrium factor on  $T$  in the case  $T_1 > T$  has been found for all gases considered. This effect appears due to intensive dissociation from highly excited levels in this case.

The developed effective algorithms for calculation of reaction rate coefficients can be implemented directly to CFD codes for the prediction of gas dynamic parameters in different non-equilibrium reacting gas flows.

## ACKNOWLEDGMENTS

This work is supported by INTAS (project 03-51-5204).

## REFERENCES

1. E.V. Kustova, E.A. Nagnibeda, in *Proc. of the 22d International Symposium on Shock*, Ed. G.J. Ball, R. Hillier, G.T. Roberts. Vol. 1. Univ. of Southampton, UK, 2000, pp. 783-788.
2. G. Colonna, M. Tuttafesta, M. Capitelli, D. Giordano, in: *Rarefied Gas Dynamics 21*, Ed. R. Brun, Vol.2, CEPADUES, Toulouse, 1999, pp.281-288.
3. E.V. Kustova, E. A. Nagnibeda, T. Yu. Alexandrova, A. Chikhaoui, *Chemical Physics Letters*, vol. 377 (5-6), 663-671 (2003)
4. C. Treanor, I. Rich, and R.J. Rehm, *J. Chem. Phys.*, 48, 1798 (1968).
5. M. Capitelli, C.M. Ferreira, B.F. Gordiets, A.I. Osipov, *Plasma kinetics in atmospheric gases*, Springer-Verlag, Berlin, 2000, 302p.
6. A. Chikhaoui, E.A. Nagnibeda, E.V. Kustova, T.Yu. Alexandrova, *Chem. Phys.* **263**, 111-126 (2001).
7. *International workshop on radiation of high temperature gases in atmospheric entry*. SP-583. Abstracts. 2004. Porquerolles, France. Part II. P. 4-5.
8. Park C. *Nonequilibrium hypersonic aerothermodynamics*. New York, Chichester, Brisbane, Toronto, Singapore: J. Willey and Sons, 1990. 359 p.
9. M.J. Pogosbekian, S.A. Losev, *Chem. Phys.* **22**, 38-46 (2003).