

# The effect of the affinity on the equilibrium behavior of a reactive system

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**Abstract.** Nonequilibrium effects, induced by a bimolecular reaction of type  $A_1 + A_2 \rightleftharpoons A_3 + A_4$  in a dilute gas system close to chemical equilibrium, are investigated within the frame of macroscopic equations derived from the chemical kinetic Boltzmann equation. The main objective of the present paper is to analyze the trend to thermodynamical equilibrium for the Hydrogen-Chlorine system, emphasizing the role of the affinity on the asymptotic behavior of the reactive flow. Assuming elastic and inelastic cross-sections for hard spheres and linearized Maxwellians as input distributions, a first-order perturbation solution technique is applied to the macroscopic field equations for the spatially uniform gas system. The forward and backward reaction rates, diffusion fluxes and partial number densities for each constituent, as well as the temperature of the mixture, are explicitly computed and the perturbations to the macroscopic fields are represented for different equilibrium temperatures of the mixture and initial conditions.

**Keywords:** Boltzmann equation, chemical reactions, reactive mixture

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## INTRODUCTION

The nonequilibrium effects associated with reactive gaseous systems [1, 2] have been investigated in literature by many authors for a long period [3]-[7] as a fundamental topic of kinetic theory extended to chemical processes. Several approximate solution techniques of the chemical kinetic Boltzmann equation have been improved during many years of research, in order to examine the effects induced by different chemical reactions [4, 8, 9] on the equilibrium velocity distributions. The perturbative Chapman-Enskog methods [3, 10, 11], the Grad moments method [12], Monte Carlo [4, 13] and molecular dynamics simulations [14, 15] are the methods most commonly employed. Their range of validity has been widely discussed [4, 6, 8] as well as the separation of the elastic and reactive time scales [16].

In this frame, a quaternary gaseous mixture undergoing an elementary reaction of type  $A_1 + A_2 \rightleftharpoons A_3 + A_4$  is studied with the main objective of describing the role of the constituents and the effect of the affinity with regard to the macroscopic picture of the reactive system and its trend to mechanical, thermal and chemical equilibria. The deviations induced by the chemical reaction on the macroscopic hydrodynamic variables are investigated in a flow regime close to the final stage of the reaction, when the mixture is near the chemical equilibrium and all constituents have the same temperature. A first-order perturbation technique is applied to the balance equations of number density and momentum of each constituent, and temperature of the whole mixture. The corresponding production rates are evaluated assuming the hard-spheres model for the elastic collisions and the line-of-centers energy model for the inelastic collisions which refer to the reactions [17]. The input distribution functions, required for the explicit computation of the production terms, are Maxwellians in the constituents' rest frame which are then linearized in the mixture rest frame with respect to diffusion velocities. Assuming a spatially uniform evolution of the gas system, the macroscopic fields are considered as small perturbations of their equilibrium values whose deviations are time dependent only. The resulting linearized differential equations are numerically solved, for the Hydrogen-Chlorine system, under initial data corresponding to both positive and negative values of the affinity. The profiles of the perturbations corresponding to partial number densities, reaction rates, diffusion fluxes and temperature of the whole mixture show, as expected, an asymptotic behavior with respect to the trend to mechanical, thermal and chemical equilibria.

## REACTIVE BASIC EQUATIONS

In absence of external body forces, the extended Boltzmann equation for a reacting mixture of four constituents in the unknown one-particle distribution function  $f_\alpha$ ,  $f_\alpha \equiv f(\mathbf{x}, \mathbf{c}_\alpha, t)$ ,  $\alpha = 1, \dots, 4$ , reads

$$\frac{\partial f_\alpha}{\partial t} + c_i^\alpha \frac{\partial f_\alpha}{\partial x_i} = \sum_{\beta=1}^4 \mathcal{Q}_{\alpha\beta}^E + \mathcal{Q}_\alpha^R. \quad (1)$$

According to the formalism of paper [18], when the reaction is of type  $A_1 + A_2 \rightleftharpoons A_3 + A_4$ , the collision operators  $\mathcal{Q}_{\alpha\beta}^E$  for elastic scattering and  $\mathcal{Q}_{\alpha\gamma}^R$  for chemical interactions are defined by

$$\mathcal{Q}_{\alpha\beta}^E = \int (f'_\alpha f'_\beta - f_\alpha f_\beta) g_{\beta\alpha} \sigma_{\beta\alpha} d\Omega_{\beta\alpha} d\mathbf{c}_\beta, \quad (2)$$

$$\mathcal{Q}_{1(2)}^R = \int \left[ f_3 f_4 \left( \frac{m_1 m_2}{m_3 m_4} \right)^3 - f_1 f_2 \right] \sigma_{12}^* g_{21} d\Omega d\mathbf{c}_{2(1)}, \quad (3)$$

$$\mathcal{Q}_{3(4)}^R = \int \left[ f_1 f_2 \left( \frac{m_3 m_4}{m_1 m_2} \right)^3 - f_3 f_4 \right] \sigma_{34}^* g_{43} d\Omega' d\mathbf{c}_{4(3)}. \quad (4)$$

Above,  $g_{\beta\alpha} = |c_\beta - c_\alpha|$  represents a relative velocity,  $d\Omega$ 's elements of solid angle which characterize the scattering processes,  $\sigma_{\alpha\beta}$  the differential elastic cross section,  $\sigma_{12}^*$  and  $\sigma_{34}^*$  the differential reactive ones for forward and backward reaction, respectively, related by the micro-reversibility principle in the form  $(m_3 m_4)^2 (g_{43})^2 \sigma_{34}^* = (m_1 m_2)^2 (g_{21})^2 \sigma_{12}^*$ . Masses, momenta and energies of constituents are arranged by

$$m_1 + m_2 = m_3 + m_4, \quad m_1 \mathbf{c}_1 + m_2 \mathbf{c}_2 = m_3 \mathbf{c}_3 + m_4 \mathbf{c}_4, \quad \varepsilon_1 + \frac{1}{2} m_1 c_1^2 + \varepsilon_2 + \frac{1}{2} m_2 c_2^2 = \varepsilon_3 + \frac{1}{2} m_3 c_3^2 + \varepsilon_4 + \frac{1}{2} m_4 c_4^2,$$

where  $\varepsilon_\alpha$  is the formation energy of constituent  $\alpha$  and  $(\mathbf{c}_1, \mathbf{c}_2)$  and  $(\mathbf{c}_3, \mathbf{c}_4)$  are the velocities of reactants and products, respectively. Mass, momentum and total energy are preserved during both elastic and reactive collisions so that

$$\sum_{\alpha=1}^4 \sum_{\beta=1}^4 \int \psi_\alpha \mathcal{Q}_{\alpha\beta}^E d\mathbf{c}_\alpha = 0, \quad \sum_{\alpha=1}^4 \int \psi_\alpha \mathcal{Q}_\alpha^R d\mathbf{c}_\alpha = 0$$

hold, where  $\psi_\alpha = m_\alpha$ ,  $\psi_\alpha = m_\alpha c_i^\alpha$  and  $\psi_\alpha = \frac{1}{2} m_\alpha c_\alpha^2 + \varepsilon_\alpha$  alternatively.

The balance laws for number densities and momentum of each constituent, and energy of the mixture are classically derived from Eq.(1) in the form

$$\frac{\partial \rho_\alpha}{\partial t} + \frac{\partial}{\partial x_i} (\rho_\alpha u_i^\alpha + \rho_\alpha v_i) = \int m_\alpha \left( \sum_{\beta=1}^4 \mathcal{Q}_{\alpha\beta}^E + \mathcal{Q}_\alpha^R \right) d\mathbf{c}_\alpha \equiv \pi_\alpha, \quad (5)$$

$$\frac{\partial \rho_\alpha v_i^\alpha}{\partial t} + \frac{\partial}{\partial x_j} (p_{ij}^\alpha + \rho_\alpha u_i^\alpha v_j + \rho_\alpha u_j^\alpha v_i + \rho_\alpha v_i v_j) = \int m_\alpha c_i^\alpha \left( \sum_{\beta=1}^4 \mathcal{Q}_{\alpha\beta}^E + \mathcal{Q}_\alpha^R \right) d\mathbf{c}_\alpha \equiv \theta_i^\alpha, \quad (6)$$

$$\frac{\partial}{\partial t} \left( \frac{3}{2} nkT + \sum_{\alpha=1}^4 n_\alpha \varepsilon_\alpha + \frac{1}{2} \rho v^2 \right) + \frac{\partial}{\partial x_i} \left[ q_i + p_{ij} v_j + \left( \frac{3}{2} nkT + \sum_{\alpha=1}^4 n_\alpha \varepsilon_\alpha + \frac{1}{2} \rho v^2 \right) v_i \right] = 0. \quad (7)$$

The macroscopic observables can be written [18] in terms of  $f_\alpha$  by the usual definitions in kinetic theory, i.e.,

$$\rho_\alpha = m_\alpha n_\alpha = \int m_\alpha f_\alpha d\mathbf{c}_\alpha, \quad \rho = \sum_{\alpha=1}^4 \rho_\alpha, \quad \rho_\alpha v_i^\alpha = \int m_\alpha c_i^\alpha f_\alpha d\mathbf{c}_\alpha, \quad \rho v_i = \sum_{\alpha=1}^4 \rho_\alpha v_i^\alpha, \quad (8)$$

$$p_{ij}^\alpha = \int m_\alpha \xi_i^\alpha \xi_j^\alpha f_\alpha d\mathbf{c}_\alpha, \quad p_{ij} = \sum_{\alpha=1}^4 p_{ij}^\alpha, \quad q_i = \sum_{\alpha=1}^4 \left( \int \frac{1}{2} m_\alpha \xi_\alpha^2 \xi_i^\alpha f_\alpha d\mathbf{c}_\alpha + n_\alpha \varepsilon_\alpha u_i^\alpha \right), \quad T = \frac{1}{3nk} \sum_{\alpha=1}^4 \int m_\alpha \xi_\alpha^2 f_\alpha d\mathbf{c}_\alpha. \quad (9)$$

Above,  $\rho_\alpha$  denotes the mass density,  $\rho_\alpha v_i^\alpha$  the momentum density,  $\xi_i^\alpha = c_i^\alpha - v_i$  a peculiar velocity,  $u_i^\alpha = v_i^\alpha - v_i$  the diffusion velocity,  $p_{ij}^\alpha$  the components of the pressure tensor,  $q_i$  the components of the heat flux,  $\pi_\alpha$  and  $\theta_i^\alpha$  production terms of mass and momentum densities, respectively,  $\mathbf{v}$  and  $T$  mean velocity and temperature of the whole mixture.

## REACTION MODEL

The main features of the chemical kinetics for the considered system with reversible bimolecular reaction, in absence of internal degrees of freedom, can be now outlined.

- The chemical potential of each constituent,  $k$  and  $h$  being the Boltzmann and the Planck constants, is expressed by

$$\mu_\alpha = \varepsilon_\alpha - kT \left[ \frac{3}{2} \ln T - \ln n_\alpha + \frac{3}{2} \ln \left( \frac{2\pi m_\alpha k}{h^2} \right) \right]. \quad (10)$$

- The affinity of the reaction is defined in terms of chemical potentials [19] as  $\mathcal{A} = -\sum_{\alpha=1}^4 \nu_\alpha \mu_\alpha$ , where the stoichiometric coefficients are such that  $\nu_1 = \nu_2 = -\nu_3 = -\nu_4 = -1$ . The quantity  $\mathcal{A}$  is an indicator of how far the system is from the equilibrium, being  $\mathcal{A} = 0$  in chemical equilibrium conditions. The mass action law reads

$$E^* \equiv \frac{E}{kT} = \frac{3}{2} \ln \left( \frac{m_3 m_4}{m_1 m_2} \right) + \ln \left( \frac{n_1^{\text{eq}} n_2^{\text{eq}}}{n_3^{\text{eq}} n_4^{\text{eq}}} \right), \quad (11)$$

where  $E = \varepsilon_3 + \varepsilon_4 - \varepsilon_1 - \varepsilon_2$  is the binding energy difference,  $E^*$  is given in units of  $kT$ , “eq” denotes equilibrium, so that a detailed expression of  $\mathcal{A}$  can also be derived from the above equalities in the form

$$\mathcal{A} = kT \ln \left( \frac{n_1 n_2 n_3^{\text{eq}} n_4^{\text{eq}}}{n_3 n_4 n_1^{\text{eq}} n_2^{\text{eq}}} \right). \quad (12)$$

- The cross sections for elastic collisions are those for which  $\sigma_{\alpha\beta} = \frac{1}{4} d_{\alpha\beta}^2$ ,  $d_{\alpha\beta} = \frac{1}{2} (d_\alpha + d_\beta)$ ,  $d_\alpha$  and  $d_\beta$  being the diameters of the colliding spheres. The model for the reactive cross sections is that of line-of-centers with activation energy [17] and is independent of the scattering angle [8],

$$\sigma_{\alpha\beta}^* = \begin{cases} 0, & \gamma_{\alpha\beta} \leq \varepsilon_\sigma^* \\ \frac{1}{4} d_\sigma^2 \left( 1 - \frac{\varepsilon_\sigma^*}{\gamma_{\alpha\beta}} \right), & \gamma_{\alpha\beta} > \varepsilon_\sigma^* \end{cases} \quad (13)$$

where  $d_\sigma$  is a reactive collision diameter,  $\gamma_{\alpha\beta} = m_{\alpha\beta} g_{\beta\alpha}^2 / 2kT$  the relative translational energy,  $\varepsilon_\sigma^* = \varepsilon_\sigma / kT$  the activation energy in units of  $kT$ . The index  $\sigma$  assumes either the value  $+1$  for the reactants ( $\alpha = 1, 2$ ) or  $-1$  for the products ( $\alpha = 3, 4$ ). Thus,  $\varepsilon_1^*$  and  $\varepsilon_{-1}^* = \varepsilon_1^* - E^*$  denote the forward and backward activation energies. The elastic and reactive diameters are connected by the steric factor  $s_\sigma$ , namely [18]

$$d_\sigma = s_\sigma d_{\alpha\beta}, \quad \text{with} \quad s_{-1} = \sqrt{\frac{m_{12}}{m_{34}}} \frac{d_{12}}{d_{34}} s_1 \quad \text{and} \quad 0 \leq s_1 \leq 1, \quad (14)$$

where  $m_{12} = m_1 m_2 / (m_1 + m_2)$ ,  $m_{34} = m_3 m_4 / (m_3 + m_4)$  are reduced masses.

- The reaction rates  $\pi_\alpha$ , and the production rates  $\theta_i^\alpha$  for momentum of constituent  $\alpha$  can be detailed once the integrations involved in Eqs.(5-6) are performed utilizing the above cross sections and input distributions

$$f_\alpha = n_\alpha \left( \frac{m_\alpha}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m_\alpha \varepsilon_\alpha^2}{2kT}} \left( 1 + \frac{m_\alpha \zeta_i^\alpha}{kT} u_i^\alpha \right), \quad (15)$$

where the partial number densities  $n_\alpha$  are not constrained by the chemical equilibrium condition  $\mu_1 + \mu_2 = \mu_3 + \mu_4$ . The input distributions (15) represent a linearization of local Maxwellians in the mixture rest frame with respect to the diffusion velocities only, since in the present approach the role of the affinity is investigated under the simplified assumption of constituents at the same temperature. The computation leads to

$$\pi_\alpha = \nu_\alpha m_\alpha n_\alpha^{\text{eq}} \zeta_{\alpha\gamma}^R \frac{\mathcal{A}}{kT}, \quad (\alpha, \gamma) = (1, 2), (2, 1), (3, 4), (4, 3), \quad (16)$$

$$\theta_i^\alpha = - \sum_{\beta=1}^4 \zeta_{\alpha\beta}^E n_\alpha^{\text{eq}} m_{\alpha\beta} (u_i^\alpha - u_i^\beta) + \pi_\alpha v_i + m_\alpha n_\alpha^{\text{eq}} \zeta_{\alpha\gamma}^R \left[ \sigma \sum_{\beta=1}^4 \nu_\beta M_\beta u_i^\beta - \frac{2}{3} (\varepsilon_\sigma^* + 2) M_\gamma (u_i^\alpha - u_i^\gamma) \right], \quad (17)$$

where  $M_\alpha = m_\alpha / (m_\alpha + m_\gamma)$ ,  $\zeta_{\alpha\beta}^E$  and  $\zeta_{\alpha\gamma}^R$  are elastic and reactive collision frequencies, respectively, and  $k_\sigma^{(0)}$  represents the first approximation to the rate constant for the forward ( $\sigma = 1$ ) and backward reaction ( $\sigma = -1$ ), namely

$$\zeta_{\alpha\beta}^E = \frac{8}{3} d_{\alpha\beta}^2 \sqrt{\frac{2\pi kT}{m_{\alpha\beta}}} n_\beta^{\text{eq}}, \quad \zeta_{\alpha\gamma}^R = n_\gamma^{\text{eq}} k_\sigma^{(0)}, \quad k_1^{(0)} = \sqrt{\frac{8\pi kT}{m_{12}}} e^{-\varepsilon_1^*} (s_1 d_{12})^2, \quad k_{-1}^{(0)} = \frac{n_1^{\text{eq}} n_2^{\text{eq}}}{n_3^{\text{eq}} n_4^{\text{eq}}} k_1^{(0)}. \quad (18)$$

## SPATIALLY HOMOGENEOUS SOLUTIONS

A perturbation technique is here applied to characterize the extent of the departure from chemical equilibrium of the macroscopic fields of the spatially homogeneous gas. The approximate solution to the balance equations (5-7) provides the long time behavior on the reactive time scale. For processes close to chemical equilibrium, the partial number densities, diffusion velocities and mixture temperature are here expanded around the chemical, mechanical and thermal equilibrium, in the form

$$n_\alpha(t) = n_\alpha^{\text{eq}}[1 + \bar{n}_\alpha(t)], \quad u_x^\alpha(t) = \bar{u}_\alpha(t), \quad T(t) = T_{\text{eq}}[1 + \bar{T}(t)], \quad (19)$$

where  $\bar{n}_\alpha(t), \bar{u}_\alpha(t), \bar{T}(t)$  are small perturbations, and the  $x$ -axis is chosen so that  $u_\alpha^{\text{eq}} = 0$ . Let be

$$x_\alpha^{\text{eq}} = n_\alpha^{\text{eq}}/n, \quad \frac{\mathcal{A}}{kT_{\text{eq}}} = \bar{n}_1(t) + \bar{n}_2(t) - \bar{n}_3(t) - \bar{n}_4(t), \quad \sum_{\alpha=1}^4 m_\alpha n_\alpha^{\text{eq}} \bar{u}_\alpha(t) = 0. \quad (20)$$

Insertion of expressions (19) and (20) into Eqs. (5-7) leads to a linearized system for the perturbations,

$$x_\alpha^{\text{eq}} \frac{d\bar{n}_\alpha}{dt} = v_\alpha x_\alpha^{\text{eq}} \zeta_{\alpha\gamma}^R \frac{\mathcal{A}}{kT_{\text{eq}}} \equiv \tau_\alpha, \quad \alpha = 1, \dots, 4 \quad (21)$$

$$\frac{d\bar{u}_\alpha}{dt} = - \sum_{\beta=1}^4 \zeta_{\alpha\beta}^E M_\beta (\bar{u}_\alpha - \bar{u}_\beta) + \zeta_{\alpha\gamma}^R \left[ \sigma \sum_{\beta=1}^4 v_\beta M_\beta \bar{u}_\beta - \frac{2}{3} (\epsilon_\sigma^* + 2) M_\gamma (\bar{u}_\alpha - \bar{u}_\gamma) \right], \quad \alpha = 1, \dots, 4, \quad (22)$$

$$\frac{d\bar{T}}{dt} = - \frac{2}{3} x_1^{\text{eq}} \zeta_{12}^R E^* \frac{\mathcal{A}}{kT_{\text{eq}}}. \quad (23)$$

In Eq. (23)<sub>1</sub>  $\tau_\alpha$  represents the reaction rate density of constituent  $\alpha$ , with  $\tau_\alpha = \pi_\alpha/(nm_\alpha)$ . Equations (21) and (23) are coupled whereas Eqs.(22) form a set of three independent equations since the diffusion velocities are constrained by (20)<sub>3</sub>. The system (21-23) will be solved in the next section for the Hydrogen-Chlorine system.

## TREND TO EQUILIBRIUM OF THE HYDROGEN-CHLORINE SYSTEM

The asymptotic behavior of a mixture undergoing the elementary reaction  $\text{H}_2 + \text{Cl} \rightleftharpoons \text{HCl} + \text{H}$  is studied under two sets of initial conditions. **(a)**  $\bar{n}_1 = 0.1, \bar{n}_2 = 0.05, \bar{n}_3 = 0.15, \bar{n}_4 = 0.1, \bar{T} = 0, \bar{u}_1 = 0.1, \bar{u}_3 = \bar{u}_4 = 0$ , the value of  $\bar{u}_2$  follows from (20)<sub>3</sub>. In this case, the initial temperature is the equilibrium one and the affinity is negative,  $\mathcal{A}/kT_{\text{eq}} = -0.1$ , so that the reaction takes place from right to left; a diffusion of  $\text{H}_2$  and  $\text{Cl}$  occurs in the positive and negative  $x$ -direction, respectively, and  $\text{HCl}$ ,  $\text{H}$  are initially at rest. **(b)**  $\bar{n}_1 = 0.1, \bar{n}_2 = 0.15, \bar{n}_3 = 0.05, \bar{n}_4 = 0.1, \bar{T} = 0, \bar{u}_1 = \bar{u}_2 = 0, \bar{u}_3 = 0.1$ , the value of  $\bar{n}_4$  turning out from (20)<sub>3</sub>. Here the initial temperature is again the equilibrium one and the affinity is positive,  $\mathcal{A}/kT_{\text{eq}} = 0.1$ , so that the reaction takes place from left to right; a diffusion of  $\text{HCl}$  and  $\text{H}$  occurs in the positive and negative  $x$ -direction, respectively, and  $\text{H}_2$ ,  $\text{Cl}$  are at rest.

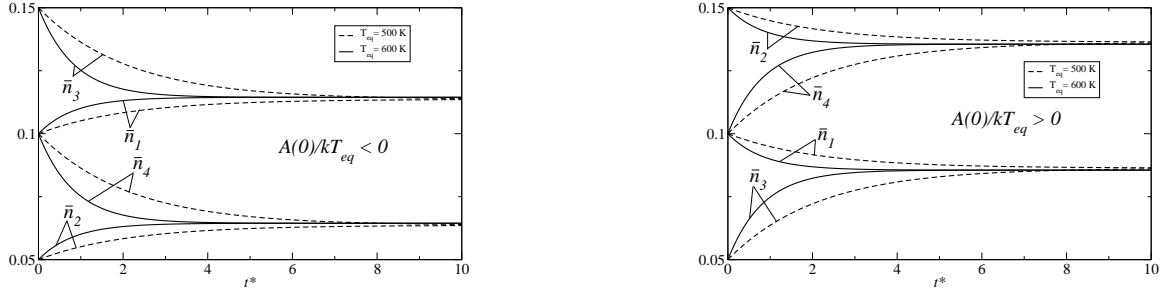
**TABLE 1.** Mass, molecular diameters and formation enthalpy at  $T = 298.15$  K.

| Gas                                     | H      | H <sub>2</sub> | Cl     | HCl    |
|---|--------|----------------|--------|--------|
| $m_\alpha (\times 10^{-26} \text{ kg})$ | 0.167  | 0.335          | 5.886  | 6.054  |
| $d_\alpha (\times 10^{-10} \text{ m})$  | 1.50   | 2.90           | 1.90   | 3.30   |
| $\Delta_f H_\alpha (\text{kJ/mol})$     | 217.97 | 0              | 121.68 | -92.31 |

Masses, diameters of gas molecules and formation enthalpy are given [3, 20] in table 1. The activation energy and the coefficient  $A$  in the Arrhenius equation,  $k_1^{(0)} = Ae^{-\epsilon_1/kT}$ , are  $\epsilon_1 = 23 \text{ kJ/mol}$  and  $A = 8 \times 10^7 \text{ m}^3/\text{mol s}$ . Thus from Eqs.(14) and (18)<sub>3</sub>, with  $T = 298.15 \text{ K}$ , it follows that the steric factors for the forward and backward reactions are  $s_1 = 0.636$  and  $s_{-1} = 0.888$ . The binding energy difference  $E$  between the products and reactants is related to the enthalpy of the reaction (or reaction heat) by  $E = \Delta_r H = \sum_{\alpha=1}^4 v_\alpha \Delta_f H_\alpha$ . For the forward reaction,  $\Delta_r H = 3.98 \text{ kJ/mol}$ .

One can assume that the enthalpy of the reaction does not change with the temperature, since the difference between the heat capacities at constant pressure vanishes for gases where the internal degrees of freedom of the molecules are neglected. The mixture number density, in equilibrium conditions, consists of one mole of ideal gas,  $n = 2.6 \times 10^{25}$  molecules/m<sup>3</sup>. Assuming  $x_1^{\text{eq}} = x_2^{\text{eq}}$  and  $x_3^{\text{eq}} = x_4^{\text{eq}}$ , being  $\sum_{\alpha=1}^4 x_{\alpha}^{\text{eq}} = 1$ , the only independent molar fraction can be obtained as a function of the temperature from the law of mass action (11).

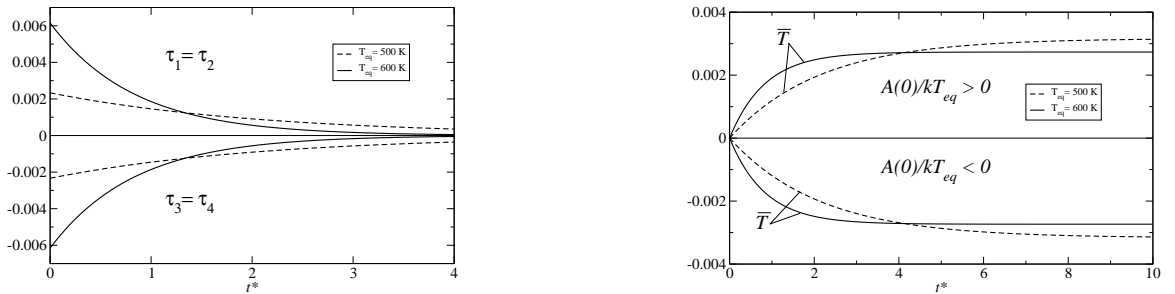
The behavior of particle number density deviations is shown in Fig. 1 versus a dimensionless time  $t^* = t\zeta_R$ , where  $\zeta_R = 10^8$  Hz is a mean frequency of the reactive collisions, for  $x_1^{\text{eq}} = x_2^{\text{eq}} = 0.364$ ,  $x_3^{\text{eq}} = x_4^{\text{eq}} = 0.136$ ,  $T_{\text{eq}} = 500$  K (dot lines), and  $x_1^{\text{eq}} = x_2^{\text{eq}} = 0.355$ ,  $x_3^{\text{eq}} = x_4^{\text{eq}} = 0.145$ ,  $T_{\text{eq}} = 600$  K (solid lines), on the left frame for initial conditions (a) and on the right frame for initial conditions (b).



**FIGURE 1.** Density deviations versus time for two equilibrium temperatures. Negative affinity (left) and positive affinity (right).

In the left frame, where  $\mathcal{A} < 0$ , the perturbations of H<sub>2</sub> and Cl, namely  $\bar{n}_1$  and  $\bar{n}_2$ , increase and those of HCl and H, namely  $\bar{n}_3$  and  $\bar{n}_4$ , decrease, confirming that the reaction proceeds from right to left. Moreover, the affinity tends to zero for large values of time since the perturbations for H<sub>2</sub> and HCl tend to a same constant value as well as Cl and H. A similar picture is shown in the right frame, where now  $\mathcal{A} > 0$ , and the reaction proceeds from left to right.

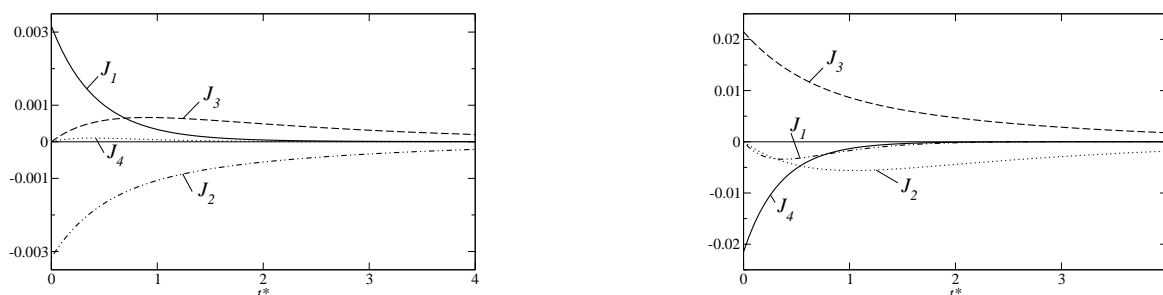
The time decay of the reaction rate densities  $\tau_{\alpha}$  are plotted in the left frame of Fig. 2 for the initial conditions (a) with  $\mathcal{A} < 0$ . For the case with initial conditions (b), where the affinity is positive, the behavior is the same provided that, in the figure,  $\tau_1 = \tau_2$  is substituted by  $\tau_3 = \tau_4$  and *vice-versa*.



**FIGURE 2.** Reaction rate deviations versus time (left) and temperature deviation (right), for two equilibrium temperatures.

As expected, the reaction rate densities become larger for higher equilibrium temperature but they decrease more rapidly with time. The right frame of Fig. 2 represents the behavior of the temperature perturbation, and one can infer from the figure that, for  $\mathcal{A} > 0$ ,  $T$  increases and an exothermic reaction happens, whereas for  $\mathcal{A} < 0$ , an endothermic reaction takes place. The temperature convergence to a constant value is more rapid when  $T_{\text{eq}}$  is higher, since it is connected to the trend to equilibrium of both affinity (see Eq.(20)<sub>2</sub> and Fig. 1) and rate densities (see Fig. 2 left). The trend to equilibrium of the diffusion fluxes  $J_{\alpha} = m_{\alpha} n_{\alpha}^{\text{eq}} \bar{u}_{\alpha}$  is plotted in the left frame of Fig. 3, for case (a), where now the dimensionless time is given by  $t^* = t\zeta_E$  with  $\zeta_E = 4 \times 10^9$  Hz representing a mean frequency of the elastic

collisions. The diffusion of constituent H is very small due to its small mass, and the decay of the lighter components  $H_2$  and H is more rapid with time than the heavier constituents Cl and HCl. The right frame of Fig. 3 represent the time evolution of the diffusion fluxes for case (b). In this case, the same conclusion as in the former case about the trend to equilibrium can be drawn here, i.e., the decay with time of the lighter components  $H_2$  and H is more pronounced than those of the heavier ones Cl and HCl.



**FIGURE 3.** Diffusion fluxes deviations versus time for initial diffusion of reactants (left) and products (right), and  $T_{eq} = 500$  K.

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