

ROTATIONAL RELAXATION OF SPHERICAL TOP GAS MOLECULES

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(Received September 8, 1972)

Collision equations for the Bryan-Pidduck model of molecules α with rotational degrees of freedom are modified by replacement of molecular radii by the effective radii r_α^* and applied to the Sather-Dahler relaxation theory. In collision and relaxation equations the quantity $j_\alpha^* = I_\alpha(r_\alpha^*)^{-2}$ (where I_α is the moment of inertia) plays a similar role in the description of rotation as the molecular mass m_α in the description of translation. The rotational relaxation collision number for molecules α in a mixture with structureless atoms γ for which $r_\gamma^* = 0$, is $Z_{\text{rot}, \alpha\gamma} = \frac{3}{8} \frac{m_\alpha + m_\gamma}{m_\alpha} \frac{(m_{\alpha\gamma} + j_{\alpha\gamma}^*)^2}{m_{\alpha\gamma} j_{\alpha\gamma}^*}$ where the reduced quantity $j_{\alpha\gamma}^*$ is defined similarly to the reduced mass $m_{\alpha\gamma}$. Values calculated from this formula — which is also valid for the pure gas α — are in the experimental range.

1. Introduction

The Bryan-Pidduck model of a perfectly rough and elastic sphere [1, 2] is the simplest model permitting the discussion of collisions of spherical molecules which can exchange their rotational energies. In spite of the defects [3, 4] connected with such a simplified description of collision, the advantage of its simplicity accounts for the fact that this model is still very widely used [5, 6, 7, 8].

The introduction of the roughness factor [9, 10] into the rotational relaxation equations in which this model is applied is inconvenient because it enlarges the discrepancies between theoretical and experimental results [11, 12, 13]. Since the roughness factor is a property of both colliding molecules, it is not appropriate for a discussion of collisions of rotating molecules with structureless atoms which cannot rotate.

Modification of the Bryan-Pidduck model by the introduction of effective radii r_α^* smaller than the molecular radii r_α [14] allows one to overcome the last two difficulties. On applying this to the Sather-Dahler theory of rotational relaxation [9] we were able

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to obtain equations giving the values for rotational relaxation collision numbers within the experimental range. In this paper the idea of such a modification will be discussed more extensively.

2. Simplified collision equations for spherical top molecules

We consider the collisions of spherical top molecules AB_n which consist of a central atom A and n non-central atoms B . Such molecules will be denoted by α . We modify the Bryan-Pidduck model of rough spheres by introducing an effective radius r_α^* instead of the molecular radius r_α .

We write the equations of impact in the following form

$$m_1(\mathbf{c}'_1 - \mathbf{c}_1) = -\mathbf{J} \quad m_2(\mathbf{c}'_2 - \mathbf{c}_2) = \mathbf{J} \quad (1)$$

$$I_1(\boldsymbol{\omega}'_1 - \boldsymbol{\omega}_1) = -r_1^* \mathbf{k} \wedge \mathbf{J} \quad I_2(\boldsymbol{\omega}'_2 - \boldsymbol{\omega}_2) = -r_2^* \mathbf{k} \wedge \mathbf{J} \quad (2)$$

where m_1, m_2 are the masses of colliding molecules and I_1, I_2 their moments of inertia. $\mathbf{c}_1, \mathbf{c}_2, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2, \mathbf{c}'_1, \mathbf{c}'_2, \boldsymbol{\omega}'_1$, and $\boldsymbol{\omega}'_2$ denote their linear and angular velocities before and after collision, respectively, \mathbf{J} is the impulse exerted on the second molecule by the first, and \mathbf{k} is the unit vector along the line from the centre of the first molecule to the second molecule at the moment of their contact.

In Eq. (2) we replace r_α by r_α^* because we assume that the roughness is mainly connected with the existence of non-central atoms. These can be treated as elastic teeth [1] or knobs [9] which are necessary for the exchange of rotational energy. In particular collisions this exchange does not depend on the molecular radius but on some acting radius connected with the mutual positions of the colliding atoms B . These acting radii are no larger than r_α . Thus r_α^* being some average acting radius cannot exceed r_α

$$r_\alpha^* < r_\alpha. \quad (3)$$

As it can be seen from a comparison of the theory presented in this paper with experimental results, the effective radius r_α^* is in general no smaller than r'_α , the distance between the nuclei A and B in the molecule α .

$$r'_\alpha \leq r_\alpha^*. \quad (4)$$

We attempt to describe complicated collisions by a simple model. That is why, following Sather and Dahler [9] who did not intend to calculate the values of the roughness factor, we have discussed here only the possible ranges of r_α^* .

From Eqs (1) and (2), in a similar manner as in reference [3] we get collisional equations in the following form:

$$\mathbf{c}'_1 = \mathbf{c}_1 + 2 \frac{m_1^{-1}}{m_{12}^{-1}} \mathbf{V}_{\parallel} + 2 \frac{m_1^{-1}}{m_{12}^{-1} + (J_{12}^*)^{-1}} \mathbf{V}_{\perp} \quad (5)$$

$$\mathbf{c}'_2 = \mathbf{c}_2 - 2 \frac{m_2^{-1}}{m_{12}^{-1}} \mathbf{V}_{\parallel} - 2 \frac{m_2^{-1}}{m_{12}^{-1} + (J_{12}^*)^{-1}} \mathbf{V}_{\perp} \quad (6)$$

$$\omega'_1 = \omega_1 + 2 \frac{(r_1^* j_1^*)^{-1}}{m_{12}^{-1} + (j_{12}^*)^{-1}} \mathbf{k} \wedge \mathbf{V}_\perp \quad (7)$$

$$\omega'_2 = \omega_2 + 2 \frac{(r_2^* j_2^*)^{-1}}{m_{12}^{-1} + (j_{12}^*)^{-1}} \mathbf{k} \wedge \mathbf{V}_\perp \quad (8)$$

where

$$\mathbf{V}_\parallel = \mathbf{k} \mathbf{k} \cdot (\mathbf{c}_2 - \mathbf{c}_1) \quad (9)$$

$$\mathbf{V}_\perp = (\mathbf{U} - \mathbf{k} \mathbf{k}) \cdot (\mathbf{c}_2 - \mathbf{c}_1) + r_2^* \mathbf{k} \wedge \omega_2 + r_1^* \mathbf{k} \wedge \omega_1 \quad (10)$$

where \mathbf{U} is the unit tensor, m_{12} denotes the reduced mass

$$m_{12}^{-1} = m_1^{-1} + m_2^{-1} \quad (11)$$

and likewise

$$(j_{12}^*)^{-1} = (j_1^*)^{-1} + (j_2^*)^{-1} \quad (12)$$

where

$$j_1^* = I_1 (r_1^*)^{-2} \quad j_2^* = I_2 (r_2^*)^{-2}. \quad (13)$$

The introduction of the quantities j_1^* , j_2^* , and j_{12}^* instead of the usually defined quantities K_1 , K_2 , and K_{12} , which in this treatment can be defined as

$$K_1^* = \frac{j_1^*}{m_1} \quad K_2^* = \frac{j_2^*}{m_2} \quad K_{12}^* = \frac{j_{12}^*}{m_{12}}, \quad (14)$$

makes Eqs (5)–(8) more readable. In these equations, as well as in relaxation equations presented in this paper, j_1^* and j_2^* play a similar role with respect to rotation as m_1 and m_2 do for translation.

From Eqs (1) and (2) it can be seen that in Eq. (2) only a part of the collisional impulse \mathbf{J} usually discussed in the Bryan-Pidduck model effects the change of angular velocity, because r_α^* is smaller than r_α and thus $r_\alpha^* \mathbf{k} \wedge \mathbf{J}$ is smaller than $r_\alpha \mathbf{k} \wedge \mathbf{J}$. This idea has been clearly introduced in the previous paper [14]. However, according to Eq. (2), in Eq. (5) of Reference [14] S_1 and S_2 should be replaced by the square roots of these quantities. The previous form of these equations followed from the idea of some effective moments of inertia which need not be introduced in this treatment because the introduction of r_α^* is sufficient to overcome all the difficulties discussed. In the above, we have not discussed the possibility of the influence of quantum effects on the possible values of j_α^* or K_α^* because we do not anticipate that these effects could change the ranges of r_α^* presented in Eqs (3) and (4).

3. Collisions of spherical top molecules with structureless atoms

The collision between the spherical top molecules α and structureless atom γ could not be described by the Bryan-Pidduck model even after the introduction of the roughness factor, because this quantity, connected with both colliding molecules, could not be ap-

plied to the encounter of a partially rough sphere with a smooth sphere. That is why Sather and Dahler [9] first tried to introduce $K_\gamma = 0$, basing their arguments on a discussion of collision equations for rough spheres [3, 4], according to which in the collisions of two rough spheres characterized by $K_1 = K_2 = 0$ their linear and angular velocities become uncoupled. In the next paper [10] they applied the idea introduced by Widom [15], according to which the collision of the molecule α and atom γ is treated by replacing the radius r_α for the molecule α by the sum of the radii $r_\alpha + r_\gamma$, and by considering the atom γ to be a point.

Because of the quantum restrictions [16] we assume that in this case the atoms γ cannot rotate. From Eq. (2) it can be seen that it is equivalent to either

$$r_\gamma^* = 0 \quad (15)$$

or

$$I_\gamma = \infty \quad (16)$$

because then the angular velocity of the atom γ cannot change. The results (15) and (16) are trivial because the atom γ cannot change its angular velocity either if the acting force in a collision between the atom γ and the atom B of the molecule AB_n is central, or if the rotational inertia of the atom γ is infinitely large. Condition (16), which could be connected with an introduction of an effective moment of inertia, looks very cumbersome and we think that the introduction of an average effective radius $r_\gamma^* = 0$ is reasonable. The inequality (4) is still satisfied because for the atoms γ the distance between nuclei does not exist and $r_\gamma' = 0$.

From Eqs (15), (7), (13), and (10) we see that

$$\omega_\gamma' = \omega_\gamma \quad (17)$$

and

$$V_\perp = (\underline{U} - \underline{k}\underline{k}) \cdot (\underline{c}_\gamma - \underline{c}_\alpha) + r_\alpha^* \underline{k} \wedge \omega_\alpha. \quad (18)$$

As a consequence, the angular velocity ω_γ for the α - γ collisions does not appear in the collision equations (5)–(8).

From Eqs (13) and (14) it can be readily seen that conditions (15) or (16) are equivalent to

$$(J_\gamma^*)^{-1} = 0 \quad (19)$$

and

$$(K_\gamma^*)^{-1} = 0. \quad (20)$$

The introduction of the last condition enabled us to obtain the relaxation equations in a form which gave the calculated results in the experimental range [14]. These equations will be analyzed more extensively in the next section.

To complete the discussion of collision equations we should explain that according to this treatment two colliding atoms γ cannot be discussed as rough spheres but as smooth spheres because they cannot contain non-central atoms which are the source of roughness.

4. Relaxation equations

As we showed previously our modified model can be used in a simple way in the Sather-Dahler theory of rotational relaxation in dilute gases if the functions A and B introduced on page 2032 of reference [9] are applied to our modified model. These functions were introduced for the α - α collisions through the formula

$$\mathbf{J} = m_1[AV_{\parallel} - B(V_{\parallel} + V_{\perp}) + C\mathbf{k} \wedge (V_{\parallel} + V_{\perp})]. \quad (21)$$

From the collision equations (1), (5), (9), (10), (13) and (14) it can be seen that

$$A = \frac{-1}{1+K_1^*} \quad B = \frac{K_1^*}{1+K_1^*} \quad C = 0. \quad (22)$$

From Eq. (22) it follows that the condition discussed by Sather and Dahler

$$A = B - 1 \quad (23)$$

is satisfied for our modified model and that the function B from Eq. (22) can be introduced to Eq. (24) from reference [9]. For self-relaxation we then get

$$\frac{dT_{\text{rot},\alpha}}{dt} = -\frac{1}{\tau_{\alpha}}(T_{\text{rot},\alpha} - T_{\text{tr},\alpha}) \quad (24)$$

where t is time, τ_{α} — the relaxation time for equilibration of rotational temperature $T_{\text{rot},\alpha}$ and translational temperature $T_{\text{tr},\alpha}$ of the molecules α , and

$$\tau_{\alpha} = \frac{3}{4} \frac{(m_{\alpha} + j_{\alpha}^*)^2}{m_{\alpha} j_{\alpha}^*} \frac{1}{N_{\alpha\alpha}}. \quad (25)$$

Here the collision frequency $N_{\alpha\alpha}$ is given by

$$N_{\alpha\alpha} = 16r_{\alpha}^2 n_{\alpha} \left(\frac{\pi k T_{\text{tr},\alpha}}{m_{\alpha}} \right)^{\frac{1}{2}} \quad (26)$$

where n_{α} is the number density of the molecules α . From Eqs (26) and (14) it can be easily seen that for $r_{\alpha}^* = r_{\alpha}$, Eq. (25) simplifies to the Wang Chang-Uhlenbeck formula [17]. The formula for the rotational relaxation collision number $Z_{\text{rot},\alpha\alpha}$ which describes the number of collisions during one relaxation time is

$$Z_{\text{rot},\alpha\alpha} = \frac{3}{4} \frac{(m_{\alpha} + j_{\alpha}^*)^2}{m_{\alpha} j_{\alpha}^*}. \quad (27)$$

In the case of a mixture of gases of spherical top molecules α and β the Sather-Dahler relaxation equations for the rate of change of the translational temperature can be modified as follows, after an introduction of the effective radii r_{α}^* and r_{β}^* :

$$\frac{dT_{\text{tr},\alpha}}{dt} = - \sum_{\beta} \frac{T_{\text{tr},\alpha} - T_{\text{tr},\beta}}{\tau_{\alpha\beta 1}} - \sum_{\beta} \frac{T_{\text{tr},\alpha} - T_{\text{rot},\alpha}}{\tau_{\alpha\beta 2}} - \sum_{\beta} \frac{T_{\text{tr},\alpha} - T_{\text{rot},\beta}}{\tau_{\alpha\beta 3}} \quad (28)$$

where the relaxation coefficients $\tau_{\alpha\beta i}$ ($i = 1, 2, 3$) are

$$\tau_{\alpha\beta 1} = \frac{3}{8} m_{\alpha} m_{\beta} (m_{\alpha}^{-1} + m_{\beta}^{-1})^2 \left(1 + \frac{j_{\alpha\beta}^*}{m_{\alpha\beta} + j_{\alpha\beta}^*} \right)^{-1} N_{\alpha\beta}^{-1} \quad (29)$$

$$\tau_{\alpha\beta 2} = \frac{3}{8} m_{\alpha} j_{\alpha}^* [m_{\alpha\beta}^{-1} + (j_{\alpha\beta}^*)^{-1}]^2 N_{\alpha\beta}^{-1} \quad (30)$$

$$\tau_{\alpha\beta 3} = \frac{3}{8} m_{\alpha} j_{\beta}^* [m_{\alpha\beta}^{-1} + (j_{\alpha\beta}^*)^{-1}]^2 N_{\alpha\beta}^{-1} \quad (31)$$

and the α - β collision frequency $N_{\alpha\beta}$ is

$$N_{\alpha\beta} = 2(r_{\alpha} + r_{\beta})^2 n_{\beta} \left(\frac{2\pi k T_{tr,\alpha\beta}}{m_{\alpha\beta}} \right)^{\frac{1}{2}} \quad (32)$$

where

$$m_{\alpha\beta}^{-1} T_{tr,\alpha\beta} = m_{\alpha}^{-1} T_{tr,\alpha} + m_{\beta}^{-1} T_{tr,\beta}. \quad (33)$$

The rate of change of the rotational temperature is

$$\frac{dT_{rot,\alpha}}{dt} = - \sum_{\beta} \frac{T_{rot,\alpha} - T_{rot,\beta}}{\tau_{\alpha\beta 1'}} - \sum_{\beta} \frac{T_{rot,\alpha} - T_{tr,\alpha}}{\tau_{\alpha\beta 2'}} - \sum_{\beta} \frac{T_{rot,\alpha} - T_{tr,\beta}}{\tau_{\alpha\beta 3'}} \quad (34)$$

where

$$\tau_{\alpha\beta 1'} = \frac{3}{8} j_{\alpha}^* j_{\beta}^* [m_{\alpha\beta}^{-1} + (j_{\alpha\beta}^*)^{-1}]^2 N_{\alpha\beta}^{-1} \quad (35)$$

$$\tau_{\alpha\beta 2'} = \frac{3}{8} j_{\alpha}^* m_{\alpha} [m_{\alpha\beta}^{-1} + (j_{\alpha\beta}^*)^{-1}]^2 N_{\alpha\beta}^{-1} \quad (36)$$

$$\tau_{\alpha\beta 3'} = \frac{3}{8} j_{\alpha}^* m_{\beta} [m_{\alpha\beta}^{-1} + (j_{\alpha\beta}^*)^{-1}]^2 N_{\alpha\beta}^{-1} \quad (37)$$

For a mixture, in which the concentration of molecules α is very small in comparison to that of atoms γ , the rotational relaxation collision number $Z_{rot,\alpha\gamma}$ denotes the number of collisions suffered by each rotating molecule during one relaxation time in the process of equilibration of rotational temperature of molecules α and translational temperature of atoms γ . This number can be obtained as a product of $\tau_{\alpha\gamma 3}$, $N_{\alpha\gamma}$ in the following form:

$$Z_{rot,\alpha\gamma} = \frac{3}{8} \frac{m_{\alpha} + m_{\gamma}}{m_{\alpha}} \frac{(m_{\alpha\gamma} + j_{\alpha\gamma}^*)^2}{m_{\alpha\gamma} j_{\alpha\gamma}^*} \quad (38)$$

where because of Eqs (12) and (19)

$$j_{\alpha\gamma}^* = j_{\alpha}^*. \quad (39)$$

If we take into consideration that $2m_{\alpha\alpha} = m_{\alpha}$ and $2j_{\alpha\alpha}^* = j_{\alpha}^*$ (cf. Eqs (11) and (12)) we see that Eqs (38) and (27) have the same form.

From Eqs (39), (13) and (14) we have

$$K_{\alpha\gamma}^* = \frac{I_{\alpha}}{m_{\alpha\gamma} (r_{\alpha}^*)^2}. \quad (40)$$

In accordance with the suggestion of Widom [15] mentioned above, the sum $r_\alpha + r_\gamma$ appeared (in place of r_α^*) in the Sather-Dahler formula for $Z_{\text{rot}, \alpha\gamma}$ making the values of $K_{\alpha\gamma}$ much smaller, and the values of $Z_{\text{rot}, \alpha\gamma}$ much larger.

We should also take into account that

$$\frac{(m_\alpha + j_\alpha^*)^2}{m_\alpha j_\alpha^*} = \frac{\left(1 + \frac{j_\alpha^*}{m_\alpha}\right)^2}{\frac{j_\alpha^*}{m_\alpha}} = \frac{\left(1 + \frac{m_\alpha}{j_\alpha^*}\right)^2}{\frac{m_\alpha}{j_\alpha^*}} \quad (41)$$

From these trivial identities we see that after taking into consideration Eq. (14), K_α^* or $\frac{1}{K_\alpha^*}$ can be introduced into Eq. (27), because in these equations the only measure of the rate of equilibration is the mutual ratio of the quantities m_α and j_α^* . The same role can be played by $K_{\alpha\gamma}^*$ or $\frac{1}{K_{\alpha\gamma}^*}$ in Eq. (38). We can write Eqs (27) and (38) in the same form as Eqs (11) and (12) from reference [14].

If we consider that in the equations describing equilibration of translational temperatures of molecules α and β there appear expressions in the form $(m_\alpha + m_\beta)^2/m_\alpha m_\beta$, [9, 18, 19], we see that the introduction of the quantity j_α^* into rotational relaxation equations is very convenient because its role is similar to that of m_α (cf. Eqs (25), (27), (29)–(31), (35)–(37)).

From Eq. (27) we see that $Z_{\text{rot}, \alpha\alpha}$ has a minimum value which equals 3 if $m_\alpha = j_\alpha^*$. According to Eq. (38) the minimum value of $Z_{\text{rot}, \alpha\gamma}$ is $(3/2)(m_\alpha + m_\gamma)/m_\alpha$ for $m_{\alpha\gamma} = j_{\alpha\gamma}^*$. After taking into account the fact that the sizes of nuclei are much smaller than the distances between them we see from

$$I_\alpha = \frac{2}{3} m_{B_n} (r'_\alpha)^2 \quad (42)$$

that for $r_\alpha^* = r'_\alpha$ the quantities j_α^* and K_α^* can be simply expressed as

$$j_\alpha^* = \frac{2}{3} m_{B_n} \quad (43)$$

$$K_\alpha^* = \frac{2}{3} \frac{m_{B_n}}{m_{AB_n}} \quad (44)$$

In this case the value of j_α^* is still smaller than that of m_α . That is why $Z_{\text{rot}, \alpha\alpha}$ is still larger than 3. The values of $Z_{\text{rot}, \alpha\gamma}$ can be smaller than 3 because $(1/2)(m_\alpha + m_\gamma)/m_\alpha$ can be smaller than unity.

A comparison with some experimental results is presented in the next section.

5. Comparison of the theory with some experimental results

The values of the collision number $Z_{\text{rot}, \alpha\alpha}$ for rotational self-relaxation of spherical top molecules can be calculated in a simple way from Eq. (27), because j_α^* can be found from Eq. (13). Such values of the collision number $Z_{\text{rot}, \alpha\gamma}$ for rotational relaxation of spherical top molecules α in an inert gas γ can be calculated from Eqs (38) and (39).

We present the values of $Z_{\text{rot}, \alpha\alpha}$ for CH_4 , CD_4 , CF_4 , and SF_6 and the values of $Z_{\text{rot}, \alpha\gamma}$ for these molecules in the noble gases because some experimental data are available for these systems [12, 13, 20, 21]. In Tables I and II we present the results for $Z_{\text{rot}, \alpha\alpha}$ and $Z_{\text{rot}, \alpha\gamma}$, calculated for the two values of r_α^* related to inequalities (3) and (4), *i. e.* for $r_\alpha^* = r_\alpha$ and $r_\alpha^* = r'_\alpha$, respectively. The experimental values printed in parantheses are labelled with single and double asterisks for Refs [20] and [21], respectively, and the results taken from the last two references, [12] and [13], are given in parentheses without asterisks.

TABLE I

 $Z_{\text{rot}, \alpha\alpha}$ for rotational self-relaxation of spherical top molecules

CH_4	17.3 — 6.1 (12*, 9.4**, 12.3)
CD_4	11.4 — 4.5 (7*, 9.9)
CF_4	6.3 — 3.2 (3.0**)
SF_6	7.1 — 3.3 (2.8**)

TABLE II

 $Z_{\text{rot}, \alpha\gamma}$ for rotational relaxation of spherical top molecules in inert gases

	He	Ne	A	Kr	Xe
CH_4	3.0—1.9 (3.0)	11.7—4.8	22.3—8.5 (12.0)	46.0—16.8	71.6—25.9 (27.0)
CD_4	2.1—1.9 (3.3)	6.6—3.3	12.2—5.5 (7.4)	24.7—10.4	38.2—15.7 (13.5)
CF_4	2.3—3.1	1.9—2.5	2.4—2.4	3.9—3.0	5.6—3.7
SF_6	2.8—8.3	1.7—2.8	2.0—2.3	2.4—3.0	4.1—2.9

From the comparison given in Table I it can be seen that for rotational self-relaxation the experimental values of $Z_{\text{rot}, \alpha\alpha}$ are in agreement with conditions set out in the introduction to Eq. (27), the effective radius r_α^* ranging from r_α to r'_α , (*i. e.* in the range of Eqs (3) and (4)). From Table II we see that the experimental values of $Z_{\text{rot}, \alpha\gamma}$ for CH_4 and CD_4 mixed with noble gases are also in agreement with those calculated from Eq. (38) for r_α^* ranging from r_α to r'_α .

6. Discussion

The main thesis of this paper is the assumption that in collision equations for spherical top molecules α the molecular radius r_α should be replaced by the effective radius r_α^* which is smaller than r_α (*cf.* Eqs (2) and (3)), and that for structureless atoms γ which

cannot rotate, the effective radius r_γ^* equals 0. The introduction of these assumptions into the Sather-Dahler theory made it possible to obtain formulae for the rotational relaxation collision numbers $Z_{\text{rot}, \alpha\alpha}$ (Eq. (27)) and $Z_{\text{rot}, \alpha\gamma}$ (Eq. (38)), which gave the calculated values of these numbers within the experimental range. Before this, the collisions of the structureless atoms γ with the rough spheres α could not be discussed in a consistent way. That is why Sather and Dahler, basing their arguments on the fact that the change of translational velocities for two rough spheres γ is the same as for smooth spheres if $K_\gamma = 0$ [3], first tried to introduce that condition [9]. In the next paper [10] they further introduced Widom's assumption [15] that in this case the mass and radius of molecule α should be replaced by the reduced mass and sum of the radii $r_\alpha + r_\gamma$, respectively, whereas the atom γ should be treated as a point. This led to their formula for $Z_{\text{rot}, \alpha\gamma}$ which gave much higher values than the experimental ones. These results were worse than those obtained from Widom's relaxation theory [15], in which rough spheres in such collisions were assumed to be translationally at rest. Our idea that $(j_\gamma^*)^{-1} = 0$ and $(K_\gamma^*)^{-1} = 0$ makes it possible to overcome these difficulties. These assumptions enabled us not only to derive the equations for collision numbers mentioned but also to get collision equations (cf. Eqs (5)–(8)) and rotation relaxation equations (cf. Eqs (24), (25), (28)–(31), and (34)–(37)) in a simple form.

In these equations the quantities j_α^* and $j_{\alpha\beta}^*$, defined in Eqs (12) and (13), play a similar role as the masses m_α and $m_{\alpha\beta}$. As we see from Eq. (41), K_α^* describes the mutual ratio between j_α^* and m_α only. A similarity can be seen between equations for relaxation of translational temperatures for the molecules characterized by m_α and m_β , and such equations for rotational relaxation for molecules characterized by m_α and j_α^* (cf. discussion under Eq. (41)). The reasons for the advantage of introducing the quantity j_α^* become obvious if we take into account the fact that j_α^* is a very good measure of rotational inertia because it is composed of two quantities: the moment of inertia, which describes the tendency of counteracting the change of angular momentum and the effective radius, which describes the tendency of effecting such a change through the capture of one molecule by another in a collision. We think that the idea of introducing $r_\gamma^* = 0$ for structureless atoms can be extended to the treatment of rotational relaxation of mixtures composed of structureless atoms and any kind of molecules which can rotate. This idea can also be introduced into the description of diffusion in systems composed of spherical top molecules and structureless atoms. The correction factor introduced for comparison of the diffusion coefficient of such systems with the diffusion coefficients for smooth spheres [22] would then be equal to $[m_\gamma + (m_\alpha + m_\gamma) K_\alpha^*] / [m_\gamma + 2(m_\alpha + m_\gamma) K_\alpha^*]$. For light atoms such as He in mixtures with heavy molecules such as CCl_4 , CF_4 , SF_6 or SiBr_4 characterized by large K_α^* , this factor can have values as low as 0.6 whereas for heavy atoms such as A, Kr, and Xe in mixtures with CH_4 or CD_4 the values of this factor can be near unity.

The author would like to express his gratitude to Professor W. Fiszdon for many useful discussions and critical comments and to Professor B. Baranowski from the Institute of Physical Chemistry for his stimulating interest. He would also like to thank Professor J. Kistemaker, who enabled him to begin these investigations in the FOM Institute of Atomic and Molecular Physics in Amsterdam, and Dr A. E. de Vries, Dr P. G. Kistemaker and Dr A. Tip for many helpful discussions.

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