

Modelling of confined flow cooling nozzles for vibrational cooling

C. J. H. Thiart,* G. P. van Zyl,** E. Ronander* and E. H. Mathews***
(First received November 1992, Final version March 1993)

Abstract

The success of the molecular laser isotope separation process is mainly dependent on the design of the correct profile for a confined flow cooling nozzle. The performance of the nozzle determines the size and efficiency of the plant. This article examines and develops a simulation method for the determination of the vibrational temperatures inside of such nozzles which are necessary to achieve design requirements. No complete method could be found in the literature for such analysis. All relevant aspects of flow cooling, except condensation, are taken into account by the proposed simulation. This includes gas dynamic properties, collision parameters, vibrational relaxation and adiabatic energy transfer in the heterogeneous gas mixtures. This model has been successfully verified. Further work includes the modification of the model to generate various nozzle geometries and to investigate certain design requirements. This method will then eliminate expensive hit and miss optimization of these types of nozzles.

Introduction

Uranium enrichment is entering a new era, as many of the present enrichment plants across the world will reach the end of their lifetimes by the middle of this decade. New enrichment plants will thus be needed. Conventional methods for uranium enrichment such as gas diffusion, gas centrifuge and separation nozzles operate on the principle of the difference in mass of the two most abundant isotopes of uranium, namely, ^{235}U and ^{238}U . The difference in the mass of these two isotopes is small and therefore results in a small kinematic difference during enrichment. This results in large numbers of enrichment steps to achieve the required degree of enrichment suitable for nuclear reactors. It leads to colossal cascades and thus to high unit costs for enrichment. An ideal concept will be one that achieves the necessary degree of enrichment with one step. This can be done by laser processes.

Laser processes can be divided into two categories, namely, the atomic vapor laser isotope separation process (AVLIS) and the molecular laser isotope separation process (MLIS). The MLIS process suits South African conditions the best, because of the relative low scale of future production and the availability of existing UF_6 production plants used in current enrichment plants. Germany and Japan are also developing the MLIS process.

Selective absorption of laser photons in the MLIS process can be done more efficiently when the UF_6 molecule is in the vibrational ground state. At room temperature only 45% of the UF_6 molecules are in the ground state while this value increases to 5% at 200K and to 75% at 70K. Free jets [1, 2, 3] were often used to achieve cooling to this low temperature. The very low downstream gas densities in these free jets prevent economic operation of

large scale plants. Confined nozzles give higher downstream densities, but condensation becomes a major problem due to the higher densities. The density and condensation conditions downstream in the flow cooling nozzle will dominate the size and thus the cost of the gas and the laser cycle of the MLIS process. We therefore strive to achieve a flow cooling nozzle with the highest possible downstream density without condensation. Vibrational flow cooling of UF_6 gas molecules is therefore one of the critical areas of the MLIS process. A pure experimental analysis of flow cooling phenomena is time consuming and fails due to the many uncertainties involved in the design and operating parameters. A successful simulation of this is therefore highly advantageous.

This article describes the modelling of vibrational cooling of polyatomic SF_6 or UF_6 in heterogeneous gas mixtures in a confined flow cooling nozzle. The polyatomic molecules are normally dissolved in a monatomic carrier gas such as Ar together with a scavenger gas such as XeF_2 . In this paper we will concentrate on the flow cooling of SF_6 and Ar mixtures due to the commercial sensitivity of the data on UF_6 and its relevant gasses. This paper only deals with flow cooling phenomena. However, once the flow simulation is completed, the possibility of condensation can be calculated with standard techniques. This provides one with a tool to investigate different nozzle geometries.

Although a microscopic approach to the modelling of vibrational cooling has not been reported in the literature, it can be used, but a lack of data on microscopic relaxation processes hampers this path. The analysis method described here has also not been reported in the literature. It provides a handy tool for theoretical design and evaluation purposes.

* Atomic Energy Corporation of South Africa Ltd.

** Compuflow Consultants

*** Professor, Department of Mechanical Engineering, University of Pretoria, 0002 Pretoria, South Africa

Formulation

There are many uncertainties to account for when modelling vibrational cooling in confined nozzles. The relative very low temperature increases the number of uncertainties, since the modelling of intermolecular behaviour at very low temperatures still has various deficiencies. These uncertainties adversely effect the determination of molecular properties for simulation purposes. Experimental determination of molecular properties at temperatures down to 50K and even lower is difficult and time consuming. The flow modelling in the nozzle is further complicated by effects such as velocity slip, adiabatic effects (the release of molecular rotational and vibrational energy while no heat cross the flow boundary to the surface of the nozzle) and condensation.

The vibrational condition of the process gas during flow cooling can be expressed by means of the vibrational population or the vibrational temperature, provided spectroscopic data exists. In this study the evaluation was done by comparing measured and simulated vibrational temperatures.

The modelling of vibrational characteristics of the process gas can be divided into three main categories which will be discussed in more detail under separate headings in the rest of this section. These categories are:

- the determination of the *gas dynamic conditions* through the nozzle to establish pressures, densities etc.,
- the determination of the *collision frequency* (rate of molecular interactions based on kinetic theory) of the process gas with all other gasses in the gas mixture as it influences the nozzle design and
- the determination of the *vibrational relaxation* (the process where the vibrational energy is deposited among other molecules in order to attain a thermodynamic equilibrium state among the internal modes of motion of the molecule) through the nozzle as it influences the number of molecules for laser separation and condensation.

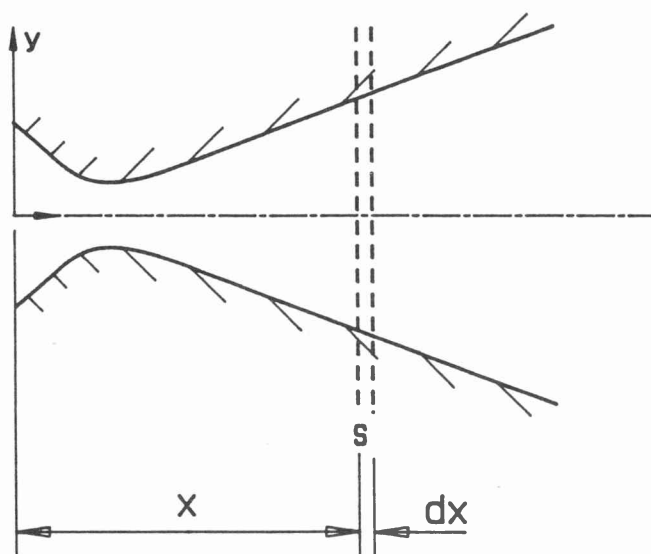


FIG. 1. Schematic representation of a control volume s , at distance x and thickness dx , for the modelling of molecular relaxation through a De Laval nozzle.

When modelling the vibrational cooling, the nozzle is numerically divided into small volume increments, as shown in figure 1. For the derivation of the equations consider a volume element s at a distance x with length dx .

(a) Gas dynamic conditions

The starting point of the simulation is to simulate the gas dynamic conditions in the flow cooling nozzle. It serves as a basis for further analysis of the collision parameters and the vibrational relaxation parameters. The gas dynamic parameters can be calculated by applying standard gas dynamic mathematics provided that the *effect of velocity slip can be quantified*.

The effects of velocity slip, where the lighter molecules migrate to the lowest pressure outer region, are very prominent in free jets due to the great degree of expansion (3 dimensional) and the high difference in the molecular mass of SF_6 or UF_6 compared to the carrier gas (Ar/He). In confined nozzles the situation is not necessarily the same. When a carrier gas with a high molecular mass such as Ar is used, the situation can be quite different especially if the expansion is well controlled. This was proved by recent experiments at the AEC in South Africa (unpublished work). It was shown that a well designed nozzle, suitable for MLIS conditions, will give only a relatively small degree of velocity slip. For the gas mixture in this paper the velocity slip was less than 2% of the maximum velocity. Therefore, adequate accuracy can be attained by assuming no slip. This leads to the following assumptions:

- the gas mixture at any position in the nozzle is well mixed and bulk conditions can be used,
- the ratio of the amount of process gas to any other gas in the mixture at any position during expansion is the same as at any position in the pre-expansion region,
- no velocity slip occurs and
- a one dimensional model of the system is suitable.

By applying these assumptions together with the geometry of the nozzle, the gas dynamic properties such as temperature, pressure, density, etc. at each increment can easily be calculated. This serves as a basis for further modelling.

(b) Collision frequency

The nozzle shape directly influences the collision frequency which is needed to establish vibrational relaxation times. When simulating collision frequency it was assumed that:

- molecules are spherical,
- molecules only contain kinetic energy of the translation mode,
- no external forces are applied on the molecules and
- the internal energy distribution of molecules of every gas is independent of position and is at any position governed by the Boltzmann equation.

For binary collisions the collision frequency between any two gasses can be given by [4]:

$$Z_{ij} = n_j \bar{\sigma}_{0ij} \cdot \Omega_{ij}^{(2,2)*}(T_{ij}^*) \cdot \bar{c}_{ij} \quad (1)$$

where $\bar{c}_{ij} = \{ \frac{1}{2}(\bar{c}_i)^2 + (\bar{c}_j)^2 \}^{\frac{1}{2}}$

The subscript *i* represents the process gas and the subscript *j* represents any other gas in the gas mixture. *n_j* is the number density of gas *j*. The effective collision cross section [5, 6] $\bar{\sigma}_{0ij}$ between molecules *i* and *j* and can be given by:

$$(\bar{\sigma}_{0ij})_s = \sqrt{2} \pi (d_{0ij}^2)_s \quad (2)$$

where *d_{0ij}* is the effective collision diameter between gasses *i* and *j*. The standard collision integral for temperature correction [7] of the collision cross section is given by $\Omega_{ij}^{(2,2)*}(T_{ij}^*)$ where $T_{ij}^* = kT/\epsilon_{ij}$ and $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$. The potential parameters ϵ_i and ϵ_j are for molecules *i* and *j* respectively with *T* the temperature and *k* the Boltzmann constant.

As our previous assumptions lead to Maxwell conditions, the molecular velocity of gas *i* is the standard Maxwell velocity, namely:

$$(\bar{c}_i)_s = \left(\frac{8 k T}{\pi m_i} \right)_s^{\frac{1}{2}} \quad (3)$$

with *m_i* the mass of molecules of gas *i*. This enables us to calculate vibrational relaxation times.

(c) Vibrational relaxation

Vibrational relaxation takes place during the temperature decrease in the nozzle and leads to an increased vibrational ground state population. The higher the ground state population the greater the risk of condensation but also the number of molecules for laser separation. Vibrational relaxation of a donor molecule takes place only when an acceptor molecule is available. This accepted photon will be stored as vibrational and/or rotational and/or translational energy.

Modelling of vibrational relaxation in the nozzle can be divided into three main categories which will be discussed in more detail under separate headings in the rest of this section. These categories are:

- the determination of the *vibrational temperature* through the nozzle,
- the determination of the *effective relaxation time* of the process gas and
- the determination of the *adiabatic effects* through the nozzle.

(i) *Vibrational temperature*

The work in this section will enable us to calculate the vibrational temperature through the nozzle. The relaxation of vibrational energy in a single polyatomic gas [8] can be given by:

$$- \frac{dE_v}{dt} = \frac{1}{\tau} (E_v - E_v(T_{tr})) \quad (4)$$

where τ is the isothermal relaxation time. *E_v* is the average

vibrational energy at the vibrational temperature *T_v* and *E_v(T_{tr})* is the average vibrational energy at the translational temperature *T_{tr}*. As it was assumed that the specific heat, *C_{v0}*, is independent of temperature and that the temperature would never deviate far from the equilibrium temperature, *T₀*, the previous equation will lead to the following relationship [8]:

$$- \frac{dT_v}{dt} = \frac{1}{\tau} (T_v - T_v(T_0)) \quad (5)$$

Vibrational relaxation in a volume increment under the conditions of flow cooling is an adiabatic constant volume process. The adiabatic conditions can easily be expressed in terms of the isothermal conditions. Isothermal conditions would result in a constant translational temperature during expansion in a small volume increment. Adiabatic conditions state that after translational cooling is done, the stored vibrational energy is deposited into the gas mixture resulting in an increase of the translational temperature while no heat cross the flow boundary to the surface of the nozzle. The nozzle geometry forces the gas mixture to cool translationally. Schematic representations of both these processes are given by figures 2 and 3. By means of an energy balance the equilibrium temperature, [8] *T₂*, can be expressed by the following relation:

$$T_2 = \frac{\tilde{C}}{C_{v0}} T_1 + \frac{C_{vv}}{C_{v0}} T_0 \quad (6)$$

with \tilde{C} the specific heat for translation, *C_{vv}* the specific heat for vibration and *C_{v0}* the specific heat at constant volume. *T₀* And *T₁* are the translational temperatures before and after the step decrease in temperature respectively. By means of a further energy balance the following energy balance can be deducted:

$$T_v - T_{tr} = \frac{C_{v0}}{\tilde{C}} (T_v - T_2) \quad (7)$$

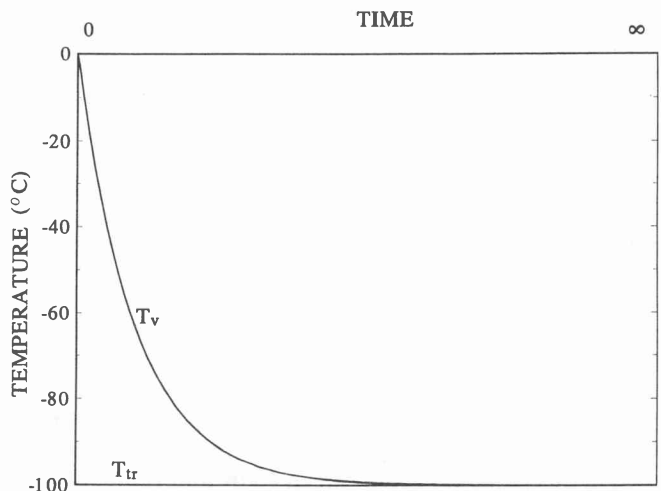


FIG. 2. Schematic representation of isothermal relaxation in a gas. *T_{tr}* and *T_v* is the translational and vibrational temperature respectively.

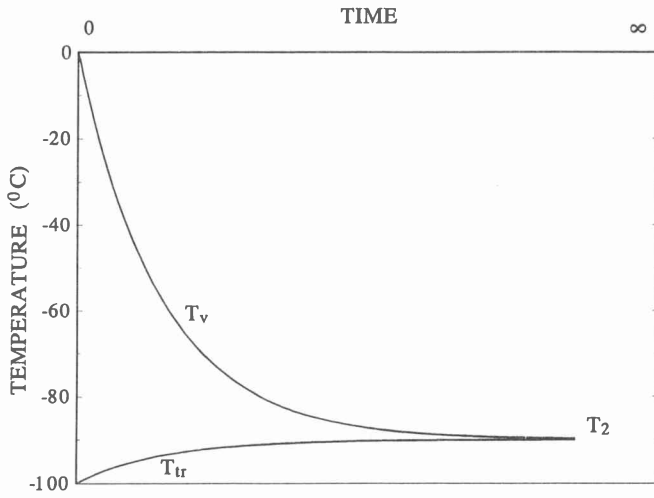


FIG. 3. Schematic representation of adiabatic relaxation in a gas. T_{tr} and T_v is the translational and vibrational temperature respectively.

By substituting the previous expression into equation (5) the differential equation for a single relaxing gas follows [8] namely:

$$-\frac{dT_v}{dt} = \frac{C_{v0}}{\tilde{C}} \frac{1}{\tau} (T_v - T_2) \quad (8)$$

This equation can be solved and it follows that [8]:

$$T_v = T_2 + (T_0 - T_2)e^{-t/\tau_1} \quad (9)$$

where $\tau_1 = (\tilde{C}/C_{v0})\tau$ is the adiabatic relaxation time.

In a mixture of polyatomic gasses all the gasses relax together resulting in a effective value for T_2 namely T_2' :

$$T_2' = T_1 + \frac{\sum_i C_i [T_{2i} - T_1]}{\sum_i C_i} \quad (10)$$

The corresponding relaxation equation is as follows:

$$T_v = T_2' + (T_0 - T_2')e^{-t/\tau_1} \quad (11)$$

Equation (11) enables us to calculate the vibrational temperature, T_v , at any point in the nozzle.

(ii) Effective relaxation time

The modelling accuracy of vibrational characteristics through the nozzle is mainly dependent on the correct determination of vibrational relaxation times for every type of collision. Each interaction of the process gas with each other gas species present lead to a separate relaxation time. At temperatures below 300K vibrational relaxation times for SF_6 and UF_6 and four other gas combinations were determined by means of an analytical approach. This aspect is not the purpose of this paper and will not be discussed here. The values for relaxation times used in this paper ranged between 400K and 150K for the purpose of this study. Above 300K measured values were used. The relevant relaxation properties for SF_6 and Ar

Temperature [K]	Z_{10}^{aa} (SF_6)	Z_{10}^{ab} (SF_6/Ar)
150	4 612	11 584
200	3 631	8 233
250	2 600	4 902
300	1 862	3 162
350	1 288	2 065
400	962	1 478

Table I Vibrational relaxation properties for SF_6 and Ar. Z_{10}^{aa} is the number of collisions for the vibrational relaxation of pure SF_6 and Z_{10}^{ab} for SF_6 dissolved in 100% Ar.

mixtures, used for verification in this paper, are given in Table I.

The differential equation for SF_6 and UF_6 in a heterogeneous gas mixture can be expressed as follows:

$$\left(\frac{dE_v}{dt}\right)_{UF_6/SF_6} = \sum_{A_i} \left(\frac{dE_v}{dt}\right)_{UF_6/SF_6-A_i} \quad (12)$$

where A_i is all the possible collision partners in the gas mixture. For each collision there is a characteristic relaxation time resulting in:

$$\left(\frac{dE_v}{dt}\right)_{UF_6/SF_6} = \frac{1}{\sum_i \tau_i} (E_v - E_v(T_{tr})) \quad (13)$$

Considering the up and down scattering of vibrational quanta the relaxation times [9] for every collision process can be expressed by:

$$\tau = \frac{Z_{10}}{Z_{ij} (1 - \exp(-h\nu_m/kT))} \quad (14)$$

where Z_{10} is the number of collision for relaxation and ν_m is the lowest vibrational frequency. The term in brackets represents the fraction of molecules that experience up scattering ($\nu = 0 \rightarrow 1$). The effective value for τ can be expressed by:

$$\frac{1}{\tau_c} = \sum_i \frac{1}{\tau_i} \quad (15)$$

where i is all the gasses in the mixture. Thus the effective relaxation time, τ_c , for SF_6 or UF_6 and all relevant gasses can be calculated.

(iii) Adiabatic effects

A gas mixture suitable for MLIS conditions will most probably consist of at least three gasses of which two will be polyatomic. Thus the vibrational energy of the two relaxing gasses will be divided between the translational modes of all the present gasses. By means of an energy balance it can be proven for a single relaxing gas that:

$$T_{tr} = T_1 + \frac{C_{vv}}{\bar{C}} (T_v - T_0) \quad (16)$$

Analogous to the previous equation the resulting translational temperature for a gas mixture with i gasses can be written as:

$$T_{tr} = T_1 + \frac{\sum_i C_{vvi} [T_{0i} - T_{vi}]}{\sum_i \bar{C}_i} \quad (17)$$

The flow of energy during the flow cooling process is determined by the nozzle geometry which results in a certain flow velocity. Because deposited rotational and vibrational energy from the molecules cannot influence the flow velocity of the system, what happens to vibrational energy that is deposited into the flow system?

The temperature of a collection of gas particle will be determined by the distribution of the random translational velocities of all the particles around the most probable velocity, in other words, the Maxwell distribution. During expansion in a nozzle the flow is directed in one direction due to pressure energy that is converted into kinetic energy. Directing one random component of the translational motion results in a decrease of the random distribution around the most probable velocity. The Maxwell distribution moves to the left (figure 4) and results in a decrease in temperature. Vibrational energy that has been deposited into the system doesn't influence the directed velocity but will be accumulated by the random motion of the other translational modes. The increased random motion around the fixed flow velocity results in an increased translational temperature.

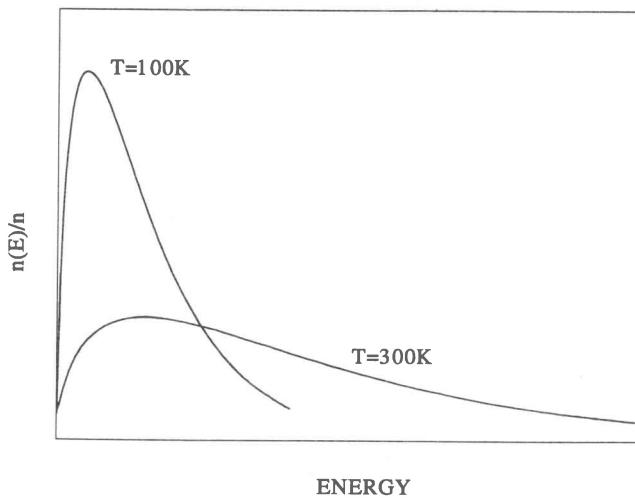


FIG 4. Schematic representation of temperature increase or decrease in a supersonic nozzle. $n(E)/n$ is the fraction of molecules at energy E to the total number of molecules.

Once the gas dynamic conditions in the nozzle have been calculated, the conditions in the remaining downstream control volumes should thus be corrected for the deposited internal energy by correcting the γ -value ($= C_{po}/C_{vo}$) of the gas mixture. Mathematically it can be expressed by:

$$(\gamma)_{s+1} = (\gamma)_s \cdot \frac{(T_{tr})_{new}}{(T_{tr})_{old}} \quad (18)$$

where $(T_{tr})_{old}$ and $(T_{tr})_{new}$ are the translational temperatures before and after depositing vibrational energy respectively. A forward correction can be done by:

$$(\bar{a})_{s+1} = [\gamma RT/\bar{M}]_{s+1}^{1/2} \quad (19)$$

Now that we can account for the effect of deposited vibrational energy on the translational temperature, vibrational and translational cooling through a confined nozzle can be accurately simulated.

Verification

The modelling technique was evaluated by comparing measured (infrared absorption spectroscopy) and predicted vibrational temperatures of fourteen confined nozzles with different profiles, using a 1% SF₆-99% Ar gas mixture. At a certain random downstream position an infrared absorption spectrum was taken. The theoretical vibrational temperature at the specific position was calculated by applying the principles described in this article. Collision diameters and potential parameters for a Lennard-Jones potential were needed for the simulation and are given in table II.

	d_{ii} [Å]	$\epsilon/K[K]$
Ar	3.418 ^a	124.0 ^a
SF ₆	5.462	159.7

^aReference 6

Table II Collision properties for SF₆ and Ar. d_{ii} is the effective collision diameter and ϵ is a potential parameter.

The resulting experimental and theoretical values for the fourteen different nozzles are given in table III. The average deviation between the experimental and theoretical analysis was 3.1%. A tolerance of $\pm 10K$ was allowed on the experimental measurements, since the determination of the vibrational temperature from infrared absorption spectra is an analytical process. Table III proves that high expansion ratios do not necessarily give high vibrational cooling. Successful flow cooling thus mainly lies in finding a correct nozzle profile. Subsequent measurements for UF₆-Ar mixtures have shown similar accuracy to that of SF₆-Ar.

Conclusions

The proposed method can be summarized and categorized into three simulation procedures. Firstly the gas dynamic conditions were calculated by applying standard gas dynamic mathematics. Once this was done the collision frequency and the vibrational relaxation phenomena could be simulated. This led to the calculation of the vibrational ground state population.

Experimental T_v [K]	T_v [K]	Theoretical T_{tr} [K]	Error [%]
220	207.5	36.6	5.7
172	167.2	57.6	2.8
214	213.9	47.9	0.05
206	198.4	51.4	3.7
225	228.3	24.0	1.5
215	219.9	25.4	2.3
215	226.1	26.1	5.2
220	226.1	27.0	2.8
190	178.1	45.9	6.3
187	191.0	47.0	2.1
200	207.9	29.8	4.0
196	200.0	32.2	2.0
195	188.0	28.2	3.6
160	157.6	86.7	1.5

Table III Measured and calculated vibrational temperatures (T_v) in fourteen confined nozzles. Every point represents a different nozzle profile and an arbitrary point downstream of the throat. The gas mixture is 1% SF₆ and 99% Ar. T_{tr} is the translational temperature.

The simulation of the vibrational temperature can now be done with relative ease by applying the proposed

method. This procedure enabled us to model and evaluate newly designed nozzle profiles before expensive experiments were carried out.

A good correlation between simulated and experimental values was found bearing in mind the difficulty inherent in measurements.

Future developments will concentrate on the simulation of condensation phenomena. A nozzle design simulation programme resulting from future work can then be used to optimize and integrate plant parameters.

References

1. H. Mikami, Nuclear Science and Engineering **67**, 235 (1978).
2. P. Raghuraman and P. Davidovits, Phys. Fluids **21**, 9 (1978).
3. P. Coda, Comitato Nazionale Energia Nucleare Report No. CNEN-RT/FI(81)32, 1982.
4. C. J. H. Thiant, PhD Thesis, University of Pretoria, Pretoria, 1992.
5. W. L. Fite, Expansion of Gases from Molecular Beam Sources, Research Note #1, Extranuclear Laboratories, 1971.
6. E. G. D. Cohen, in Lectures in Theoretical Physics, edited by W. E. Brittin, Barut and Guenin, (Gordon and Breach Publishers, London, 1967), Vol IX C, pp. 279-283.
7. J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, Molecular Theory of Gases and Liquids, (John Wiley & Sons, New York, 1954).
8. K. F. Herzfeld, T. A. Litovitz, Absorption and Dispersion of Ultrasonic Waves, (Academic Press, London, 1959), Chap. 2.
9. L. D. Lambert, Vibrational and Rotational Relaxation in Gases, (Clarendon Press, Oxford, 1977), p. 9.