

PROBLEMS IN EFFUSION

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## ABSTRACT

The flow of rarefied gases from a vessel through an orifice into vacuum is studied here. Special conditions of this study are that the mean free path of the molecules is of the same order of magnitude as the hole diameter; furthermore the thickness of the wall is neglected. Knudsen [1,2] investigated this effusion problem for constant conditions throughout the gas, assuming Maxwellian velocity distribution and very large mean free paths. In the present study the influence of a one-dimensional temperature gradient extending from the wall upstream into the gas is investigated. Formulae for the massflux and the spatial intensity distribution of the outflowing molecules are calculated for steady flow conditions. Finally the behavior corresponding to a nonstationary temperature gradient ( according to a suddenly heated or cooled wall) is studied.

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LIST OF SYMBOLS.

c	velocity of a molecule
$c_p$	specific heat at constant pressure
d	thermal diffusivity $\left[ \frac{\text{cm}^2}{\text{sec}} \right] = \frac{\beta}{c_p \cdot \rho}$
f	name of a function
k	Boltzmann constant
$k_1, k_2$	constants
n	number of molecules flowing out per unit area and time
p	pressure
r	radius in polar coordinate systems
t	time
u	component of the velocity of a molecule in x-dir.
v	" " " " " " " " y- "
w	" " " " " " " " z- "
x	coordinate normal to the wall
y, z	cartesian coordinates in the plane of the wall
A	area
D	diameter of a rigid spherical molecule
N	number density, number of molecules per unit vol.
P	probability distribution
R	gas constant
T	absolute temperature K
V	volume

- $\alpha$  coefficient in the exponential temp. distrib.  
 $\beta$  heat conduction coefficient  
 $\beta_x, \beta_y$  terms in the Maxwellian velocity distribution function  
 $\gamma$  dimensionless coefficient  
 $\delta$  thickness of a gas layer  
 $\epsilon$  dimensionless coefficient  
 $\lambda$  mean free path  
 $\mu$  coordinate  
 $r$  coordinate  $r = \mu \cos \theta$   
 $\rho$  density  
 $\tau$  collision time  
 $\psi$  probability function  
 $\gamma$  angle in the wall plane (see Fig. 2, p. 8)  
 $\omega$  solid angle  
  
 $\theta$  angle between  $r$  and the normal to the wall  
 $\Omega$  expectation of collisions

Subscripts:

- $c$  "cone"  
 $o$  original state at infinity  
 $t$  "total"  
 $w$  state at the wall  
  
 $\theta$  "in direction of  $\theta$ "

## I. INTRODUCTION

Knudsen [2] derived a formula for the outflux of molecules from a vessel through an orifice into vacuum for a very rarefied gas. (mean free path of the molecules is large compared to the hole diameter). The thickness of the wall of the vessel and its influence on the outflux were neglected. The state of the gas was assumed to be constant throughout the container and Maxwellian velocity distribution of the particles was used. For these simplified conditions one obtains the so-called cosine-law (Knudsen [2], Clausius [3]) for the spatial intensity distribution of the outflowing molecules.

In the present study the condition of a homogeneous gas state throughout the vessel is omitted. The influence of a one-dimensional temperature gradient extending from the wall into the gas on the outflux of molecules is investigated. A correction formula for the massflux for steady flow is obtained. The spatial intensity distribution of the outflowing particles under this condition is studied and compared with Knudsen's cosine-law distribution. The nonstationary case is discussed later on ( according to a sudden change of the wall temperature).

A list of important books and papers on this subject is given at the end of this study.



## II. IMPORTANT ASSUMPTIONS AND RELATIONS

In the following study a few basic assumptions are made:

1. The wall between gas and vacuum extends to infinity on both sides and is infinitely thin. Therefore the effect of the thickness of the wall on the rate of outflux is neglected.
2. The temperature gradient is normal to the wall. This yields an essentially one-dimensional problem. The temperature is a function of  $x$  only, where  $x$  is the coordinate normal to the wall.
3. The variables of state of the gas are constant along layers parallel to the wall corresponding to the temperature in the layer. The perfect gas law

$$p = \rho RT \quad (1)$$

applies.

4. Basic relations of kinetic theory derived by means of the Maxwellian velocity distribution law apply locally, such that each point in space has its own Maxwellian distribution corresponding to its temperature. The following relations are used:

mean velocity corresponding to Maxwellian distr.:

$$\bar{c} = \sqrt{\frac{8RT}{\pi}} \quad (2)$$

mean free path corresponding to Maxwellian distr.:

$$\lambda = \frac{1}{\sqrt{2} N \pi D^2} = \frac{kT}{\sqrt{2} p \pi D^2} \quad (3)$$

5. For the stationary case constant pressure is assumed throughout the gas. The reason for this assumption is that equilibrium and thus stationary state can only occur if the momentum exchange between layers of the gas is balanced.
6. The accommodation coefficient  $\alpha_T = 1$ . This means that molecules hitting the wall attain the same energy level as the wall. But this restriction is not important in our case. If an accommodation coefficient smaller than 1 has to be considered, only the wall temperature  $T_w$  in the formulae to be given has to be replaced by  $\alpha_T \cdot T_w$ .
7. The molecules are treated as elastic spheres.

### III. CORRECTION FORMULAE FOR THE STATIONARY CASE.

#### 3.1. Mean Free Path as Function of Temperature.

##### Averaging Process over Space. Modified Poisson-Distribution.

The assumption that each point in space has its own Maxwellian distribution according to its temperature implies the existence of a different mean free path  $\lambda$  at each point.  $\lambda$  is a function of temperature.

It will be necessary for the derivation later on to calculate the probability for a molecule to travel a certain distance without collision. For homogeneous conditions in space ( temperature, density, pressure are constants) this probability is simply given by the Poisson-distribution

$$e^{-\frac{x}{\lambda}} \quad (4)$$

But in our case temperature and density have gradients throughout the space. A molecule starting at a certain point  $P_1$  in space has an average expectation of traveling a certain distance without collision corresponding to the temperature  $T_1$  at  $P_1$  ( $\lambda(T)$  represents this expectation). But this expectation changes during the motion of the molecule because the density and temperature of the surrounding of the molecule change. It is therefore necessary to replace the Poisson-distribution by another expression, which takes care of this change in expectation or mean free path during the motion.

We derive this formula as follows:

A molecule starts at a point  $P_1$  in space (see Fig. 1)

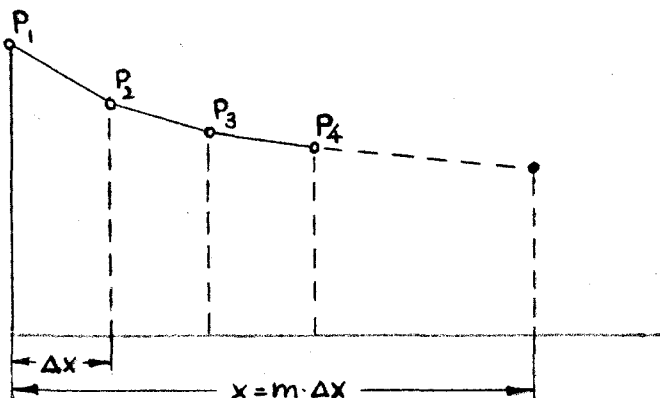


Fig. 1

with mean free path expectation  $\lambda_1$  and travels a short distance  $\Delta x$ . During this motion the conditions are thought to be unchanged. Therefore the probability of moving over this distance without collision is  $e^{-\frac{\Delta x}{\lambda_1}}$ . Suddenly the conditions change and the mean free path expectation changes correspondingly from  $\lambda_1$  to  $\lambda_2$ . The probability of moving from  $P_2$  to  $P_3$  without collision is therefore  $e^{-\frac{\Delta x}{\lambda_2}}$ . The total probability for the motion from  $P_1$  to  $P_3$  becomes then  $e^{-\frac{\Delta x}{\lambda_1}} \cdot e^{-\frac{\Delta x}{\lambda_2}}$ . This process has to be repeated until the molecule collides after  $m$  steps at  $x$ . Therefore we write for the total probability:

$$\begin{aligned} P(m\Delta x) &= e^{-\frac{\Delta x}{\lambda_1}} \cdot e^{-\frac{\Delta x}{\lambda_2}} \dots \dots e^{-\frac{\Delta x}{\lambda_m}} = e^{-\sum_{i=1}^m \frac{\Delta x}{\lambda_i}} \\ &= e^{-\frac{m\Delta x}{m} \sum_i \left(\frac{1}{\lambda_i}\right)} \end{aligned}$$

We define now as an "average value of mean values":

$$\frac{1}{\lambda} = \frac{1}{m} \sum_{i=1}^m \left(\frac{1}{\lambda_i}\right) = \frac{1}{m\Delta x} \sum_{i=1}^m \frac{\Delta x}{\lambda_i}$$

and going to the limit  $\Delta x \rightarrow dx$ :

$$\frac{1}{\lambda} = \frac{1}{x} \int_0^x \frac{dx}{\lambda(x)}$$

thus:

$$\sum_{i=1}^m \frac{1}{m} \left(\frac{1}{\lambda_i}\right) \rightarrow \frac{1}{x} \int_0^x \frac{dx}{\lambda(x)}$$

Introducing this in our above relation and approaching

the limit  $\Delta x \rightarrow dx$  we find:  $P(m\Delta x) \rightarrow P(x)$

$$P(x) = e^{-\int_0^x \frac{dx}{\lambda(x)}}$$

(5)

This is the modified Poisson-distribution.

### 3.2. Derivation of the Basic Integral.

We use the above result (5) now in order to obtain an expression for the rate of massflux through the orifice under our conditions. We deal with a small volume element  $dV$  of gas in our semi-space (see Fig.2).

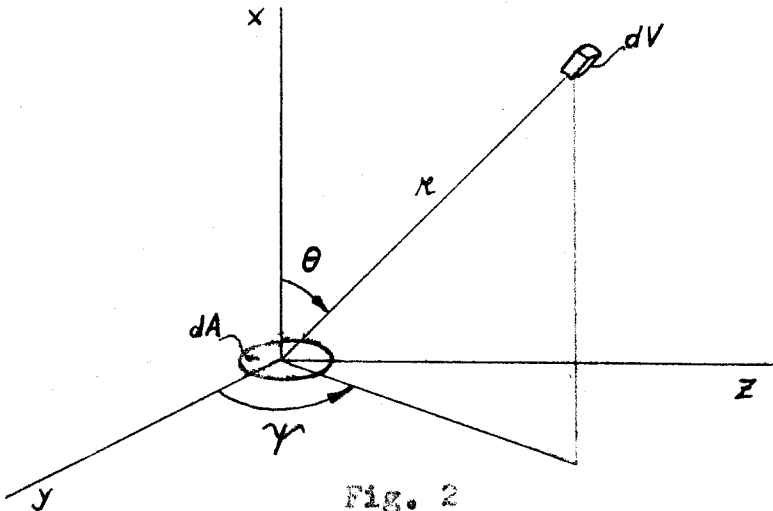


Fig. 2

The average number of molecules colliding in  $dV$  per unit time is equal to the average number of molecules in  $dV$  multiplied by the probability of collision of a molecule per unit time:

$$n_c = \frac{\bar{c}(x)}{\lambda(x)} dV \cdot N(x)$$

The molecules colliding in  $dV$  are scattered in random. The number of molecules per unit time which collide in  $dV$ , leave  $dV$  in direction of  $dA$  and reach  $dA$  without further collision is then (using (5)):

$$\frac{\bar{c}(x)}{\lambda(x)} N(x) dV \frac{dA / \cos \theta}{4\pi r^2} e^{-\int_0^r \frac{dx}{\lambda(x)}} \quad (6)$$

We get the total number of molecules hitting the area  $dA$

of the wall by integrating over the whole semi-space. This number is equal to the number of molecules flowing through a hole of area  $dA$  in a wall of zero thickness. We choose spherical polar coordinates. Hence we obtain for unit area:

$$dV = r^2 \sin \theta \, d\theta \, d\psi \, dr$$

$$n = \frac{1}{4\pi} \int_{\psi=0}^{2\pi} d\psi \int_{\theta=0}^{\frac{\pi}{2}} \int_{r=0}^{\infty} \frac{\bar{c}(x) N(x)}{\lambda(x)} \sin \theta \cos \theta e^{-\int_0^r \frac{dr}{\lambda(x)}} dr \, d\theta$$

$$n = 2 \int_0^{\frac{\pi}{2}} \sin \theta \cos \theta \, d\theta \int_{r=0}^{\infty} \frac{\bar{c}(x) N(x)}{4} \cdot \frac{1}{\lambda(x)} e^{-\int_0^r \frac{dr}{\lambda(x)}} dr$$

We call:

$$\frac{\bar{c}(x) N(x)}{4} = F(x)$$

Using relation (1) and (2):

$$F(x) \sim \frac{\sqrt{T}}{T} = \frac{1}{\sqrt{T}}$$

Comparison with Knudsen's formula:

$$n_w = \frac{\bar{c}_w \cdot N_w}{4} \sim \frac{1}{\sqrt{T_w}}$$

yields finally:

$$F(x) = n_w \sqrt{\frac{T_w}{T}} \quad (7)$$

Replacing  $dr$  by  $dx/\cos \theta$  and introducing (7) leads to:

$$n = 2n_w \int_0^{\frac{\pi}{2}} \sin \theta \cos \theta \, d\theta \int_{r=0}^{\infty} \sqrt{\frac{T_w}{T}} \cdot \frac{1}{\lambda(x)} e^{-\int_0^x \frac{dx}{\lambda(x) \cos \theta}} \frac{dx}{\cos \theta} \quad (8)$$

In this derivation collisions between molecules are already taken in account. Corresponding to equation (6)

all molecules reaching the orifice are counted after having had their last impact with other particles. Hence the problem that some molecules approaching the hole might be "knocked" out of their way by other particles is eliminated.

In order to integrate expression (8) we introduce a new function:

$$\mu = \int_0^x \frac{dx}{\lambda(x) \cos \theta} \quad (9)$$

$$\frac{d\mu}{dx} = \frac{1}{\lambda(x) \cos \theta} \quad \longrightarrow \quad d\mu = \frac{dx}{\lambda(x) \cos \theta}$$

with the following properties:

$$x=0 \quad \longrightarrow \quad \mu = \int_0^0 \frac{dx}{\lambda(x) \cos \theta} = 0$$

$$x \rightarrow \infty \quad \longrightarrow \quad \mu = \int_0^{\infty} \frac{dx}{\lambda(x) \cos \theta} \rightarrow \infty$$

(because  $\lambda(x) \cos \theta$  is bounded,  $\lambda(x) = \lambda(x(T))$  and  $T$  never goes to  $\infty$  for  $x \rightarrow \infty$ ).

Furthermore:

$$\mu \cos \theta = \int_0^x \frac{dx}{\lambda(x)} = \phi(x) \quad (10)$$

(only function of  $x$ !)

Therefore:

$$\sqrt{\frac{T_w}{T}} = f(x) = f(\phi(x)) = f(\mu \cos \theta) = f(v) \quad (11)$$

Inserting all these expressions in our previous equation (8) leads to the following form:

$$n = 2n_w \int_0^{\frac{\pi}{2}} \sin \theta \cos \theta d\theta \int_0^{\infty} f(\mu \cos \theta) e^{-\mu} d\mu \quad (12)$$

This is our basic integral in the form which we shall use later on.

### 3.3. Solution for Very Small Temperature Gradients.

#### Expansion in Taylor Series.

The function (11)  $f(\mu \cos \theta)$  describes essentially the form of the temperature gradient. In order to solve equation (10) for small temperature gradients it is convenient to expand  $f(\mu \cos \theta)$  in a Taylor series around a point at the wall (subscript w):

$$f(\mu \cos \theta) = \sum_0^m \frac{(\mu \cos \theta)^m}{m!} \left( \frac{d^m f}{d(\mu \cos \theta)} \right)_{\mu \cos \theta = 0}$$

or in short notation:

$$f(\mu \cos \theta) = \sum_0^m \frac{(\mu \cos \theta)^m}{m!} f^{(m)}(0)$$

Thus:

$$n = 2 n_w \sum_0^m \int_0^{\frac{\pi}{2}} \sin \theta \cos^{m+1} \theta d\theta \int_0^{\infty} \frac{\mu^m}{m!} f^{(m)}(0) e^{-\mu} d\mu$$

$$n = 2 n_w \sum_0^m \frac{1}{m+2} f^{(m)}(0)$$

$$\boxed{n = n_w \left[ 1 + 2 \sum_1^m \frac{f^{(m)}(0)}{(m+2)} \right]} \quad (13)$$

Equation (13) is the solution for very small temperature gradients. The quantity  $n_w$  is the massflux given by the Knudsen formula calculated for the gas conditions at the wall:

$$n_w = \frac{\bar{c}_w \cdot N_w}{4}$$

The derivatives  $f^{(m)}(0)$  in (13) can be computed by means



of the following procedure:

$$f(\mu \cos \theta) = f(r) \quad ; \quad r = \mu \cos \theta$$

$$\mu \cos \theta = r = 0: \quad f(0) = f(x)_{x=0} = \sqrt{\frac{T_0}{T_0}} = 1 \quad (14)$$

$$f'(\mu \cos \theta) = f'(r) = f'(x) \frac{dx}{dr}$$

$$f'(r)_{r=0} = f'(x)_{x=0} \cdot \frac{dx}{dr}(0)$$

$$f^{(2)}(r)_{r=0} = f^{(2)}(x)_{x=0} \cdot \frac{d^2x}{dr^2}(0) + f^{(2)}(x)_{x=0} \cdot \left(\frac{dx}{dr}(0)\right)^2$$

where  $f(x)$  is given by the expression for the temperature gradient and  $r = \mu \cos \theta = \phi(x)$  is given by (10) and (3).

#### 3.4. Solution for a Exponential Temperature Gradient.

We assume a temperature gradient of the form:

$$T = T_w e^{-\infty x} \quad (15)$$

We shall solve our basic integral (12) after introduction of equation (15). The choice of this exponential temperature gradient is more or less arbitrary. It was selected as an example because of the simple mathematical expressions obtained. Nevertheless this exponential gradient is a good approximation for many similarly shaped temperature distributions. This approximation will be used later on for the discussion of very small instationary temperature gradients.

The temperature function in the form of

equation (15) implies  $T=0$  at  $x \rightarrow \infty$ . But this is no real difficulty because of the exponential factor in equation (8) which suppresses everything far apart from the wall.

With use of equation (3) formula (15) yields:

$$\lambda = \lambda_w \cdot e^{-\alpha x} \quad (16)$$

Relation (9) takes now the form:

$$\mu = \int_0^x \frac{dx}{\lambda(x) \cos \theta} = \int_0^x \frac{dx \cdot e^{\alpha x}}{\lambda_w \cdot \cos \theta}$$

$$\mu = \frac{1}{\lambda_w \cos \theta} \left( \frac{1}{\alpha} e^{\alpha x} - \frac{1}{\alpha} \right) = \frac{1}{\alpha \lambda_w \cos \theta} (e^{\alpha x} - 1)$$

$$\alpha \lambda_w \cos \theta \mu + 1 = e^{\alpha x}$$

$$\sqrt{\frac{T_w}{T}} = e^{\frac{\alpha x}{2}} = \sqrt{1 + \alpha \lambda_w \cos \theta \mu} = f(\mu \cos \theta) \quad (17)$$

We introduce (17) in (12) and find:

$$n = 2n_w \int_0^{\frac{\pi}{2}} \sin \theta \cos \theta d\theta \int_0^{\infty} \sqrt{1 + \alpha \lambda_w \cos \theta \mu} \cdot e^{-\mu} d\mu \quad (18)$$

In order to get a first approximation solution of this integral one can expand the root term in a power series and neglect higher order terms:

$$\sqrt{1 + \alpha \lambda_w \cos \theta \mu} \doteq 1 + 0.5 \alpha \lambda_w \cos \theta \mu$$

The accuracy of this approximation is difficult to estimate. A better approximation of the integrand can be

found if we restrict ourselves to temperature gradients within the following limits:

$$\text{for } x = \lambda_w: \quad \frac{T_w}{T(\lambda_w)} = e^{\alpha \lambda_w} \leq 2 \quad (19)$$

For usual gases ranges  $\lambda$  at 15°C and 1  $\mu$  pressure between 4 and 10 cm (see A. Guthrie and R. Loevinger, [11]). Therefore even with the above restrictive conditions very strong temperature gradients are included (almost too strong for our initial conditions). Equation (19) yields:

$$\alpha \leq \frac{\ln 2}{\lambda_w} = \frac{0.69}{\lambda_w}$$

We choose:

$$\alpha \leq \frac{0.6}{\lambda_w}$$

By means of this restrictions it is possible to find an approximation for the integrand in formula (18) with an accuracy of about 4 percent. The calculations are carried out in Appendix I. One obtains the result:

$$\sqrt{1 + \alpha \lambda_w \cos \theta} \mu^{-1} e^{-\mu} \approx (1 + 0.42 \alpha \lambda_w \cos \theta) e^{-\mu} \quad (20)$$

$$\text{for: } 0 \leq \alpha \lambda_w \cos \theta \leq 0.6$$

Introducing this in equation (18) we finally get:

$$n = 2n_w \int_0^{\frac{\pi}{2}} \sin \theta \cos \theta d\theta \int_0^{\infty} [1 + 0.42 (\alpha \lambda_w \cos \theta) \mu] e^{-\mu} d\mu$$

$$n = 2n_w \left[ \frac{1}{2} + 0.42 \alpha \lambda_w \int_0^{\frac{\pi}{2}} \sin \theta \cos^2 \theta d\theta \int_0^{\infty} \mu e^{-\mu} d\mu \right]$$

$$n = n_w [1 + 0.28 \alpha \lambda_w] \quad (21)$$

$$\text{where } \alpha \lambda_w \leq 0.6$$

This is the solution for a steady exponential temperature gradient.

### 3.5. Derivation of an Approximate Outflux Formula for a Stationary Temperature Gradient.

We have seen in the previous sections that only a relatively small region near the wall is important for the flow correction corresponding to a temperature gradient. Let us therefore assume an average mean free path  $\bar{\lambda}$  within this small region (which is not specified otherwise) in order to avoid the averaging process used to modify the Poisson-distribution in section 3.1..

Then we can derive a formula analogously to section 3.2. for the number of molecules passing through an orifice of unit area:

$$n = n_w \int_0^{\frac{\pi}{2}} \int_0^{\infty} \frac{2}{\pi} \sqrt{\frac{T_w}{T}} \sin \theta e^{-\frac{x}{\bar{\lambda} \cos \theta}} dx d\theta \quad (22)$$

Function (22) is explicitly integrable for a temperature gradient of the following form:

$$T = \frac{T_w}{(1 + k_1 x + k_2 x^2)^2} \quad (23)$$

Proper choice of the constants  $k_1$  and  $k_2$  gives a good approximation for many temperature gradients. Transforming to a new variable  $t$  we get from (22):

$$\frac{x}{\bar{\lambda} \cos \theta} = t \quad dx = dt \bar{\lambda} \cos \theta$$

$$n = n_w 2 \int_0^{\frac{\pi}{2}} \sin \theta \cos \theta d\theta \int_0^{\infty} (1 + k_1 \bar{\lambda} \cos \theta t + k_2 \bar{\lambda}^2 \cos^2 \theta t^2) e^{-t} dt$$

$$n = n_0 \left[ 1 + \bar{\lambda} \frac{2}{3} k_1 + \bar{\lambda}^2 k_2 \right] \quad (24)$$

Remark:  $\bar{\lambda}$  has not been calculated yet. For a rough estimate we shall replace  $\bar{\lambda}$  by  $\lambda_w$  later on, because only a region near the wall is important.

### 3.6. Comparison of the Formulae (21) and (24) for a Special Numerical Case.

As an example we choose temperature gradients such that for  $x = \lambda_w \Rightarrow T = 0.8 \cdot T_w$ . We compare the results obtained when equations (21) and (24) are applied to this case.

a) Exponential gradient.

$$T = T_w e^{-\alpha x} \quad \alpha \lambda_w = \ln 0.8 = 0.223$$

$$n = n_w [1 + 0.28 \cdot 0.223]$$

$$n = n_w \cdot 1.067$$

b) We choose  $k_1 = 0$  in our two-parametric expression.

Then we get, using  $\bar{\lambda} = \lambda_w$ :

$$T = T_w [1 + k_2 x^2]^{-2} ; \quad \frac{1}{(1 + k_2 \lambda_w^2)^2} = 0.8 \rightarrow k_2 = \frac{0.12}{\lambda_w^2}$$

$$n = n_w \cdot 1.12$$

The result for these two different gradients shows that the deviation from the Knudsen massflux based on conditions at the wall is only of the order of 10%.

### 3.7. Discussion of Results.

For the case of constant temperature throughout the semi-space ( $T_{\text{gas}} = T_w$ ) Knudsen's formula yields:

$$n = \frac{N_w \cdot \bar{c}_w}{4} = n_w$$

But:

$$n_w \sim \frac{1}{\sqrt{T_w}}$$

and hence:

$$\frac{n_{w1}}{n_{w2}} = \sqrt{\frac{T_{w2}}{T_{w1}}} \quad (25)$$

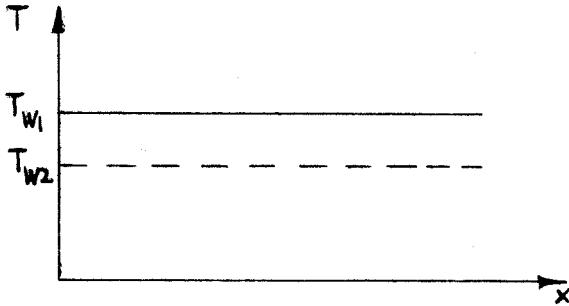


Fig. 3.

This means that the massflow is inversely proportional to the temperature of the gas (see Fig.3 ).

The above simple relation holds for constant temperature throughout the space. In the case of a negative temperature gradient one has therefore to expect that the massflow will be larger than the flow corresponding to the highest temperature  $T_w$ , because great parts of the halfspace are at a lower temperature (see Fig. 4).

In this study it was always assumed that the wall was hotter than the gas. This is no necessary

restriction. For the case of a cooler wall formulae (21)

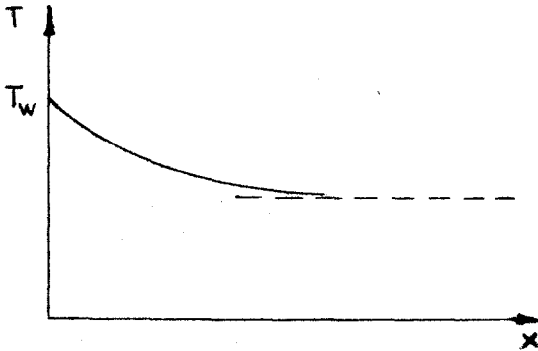


Fig. 4.

and (24) can be used, but the positive sign has to be replaced by a negative sign in formula (21).

Therefore the results (21) and (24) are qualitatively correct, because they give values of massflow larger than the massflow corresponding to the highest temperature (for the case of a hot wall). But furthermore these formulae (21), (24) and the special values of section 3.6. show that the influence of the wall temperature is dominant and that a lower ( or higher ) temperature in the semi-space does affect the massflow only by a correction of about 5+20%.

IV. SPATIAL DISTRIBUTION OF THE OUTFLOWING MOLECULES  
FOR THE CASE OF A STEADY TEMPERATURE GRADIENT.

Clausing [3] has plotted the angular distribution pattern of molecules emerging from the orifice for the simple cosine-law of Knudsen. We want to obtain an expression for the spatial distribution of particles which passed the orifice according to our special conditions (temperature-gradient). We shall compare our result with Clausing's diagram.

We can specialize our formula (21) to Knudsen's relation by putting  $\alpha = 0$ :

$$n = 2n_w \int_0^{\frac{\pi}{2}} \sin \theta \cos \theta d\theta \int_0^{\infty} 1 \cdot e^{-\mu} d\mu$$

$$n = n_w$$

q.e.d.

Knudsen's cosine-law for diffuse reflection states, that the number of molecules reflected at an angle  $\theta$  to the normal of the wall within a solid angle  $d\omega$  is given by:

$$n_{\theta} = \frac{n_w \cos \theta}{\pi} d\omega$$

where  $n_w$  is the total number of oncoming or reflected molecules per unit area. From the conservation of the equilibrium in the conditions of the upper semi-sphere it follows that this law of angular distribution also holds for the arriving molecules. But  $n_w$  is in our case



the number of molecules passing through a hole of unit area. Therefore the molecules spread out according to the same molecular distribution after having passed the orifice.

We use spherical polar coordinates in order to derive the relation. With Fig.5 it follows:

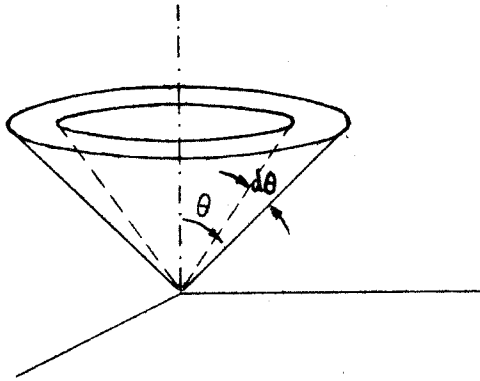


Fig. 5

Corresponding to Knudsen's cosine-law the number of molecules spread within two cones with half-angles  $\theta$  and  $(\theta + d\theta)$  becomes:

$$n_{c\theta} = \frac{n_w \cos \theta}{\pi} \sin \theta d\theta \int_0^{2\pi} d\psi$$

$$n_{c\theta} = 2 n_o \sin \theta d\theta \cdot \cos \theta \quad (26)$$

This holds for Knudsen's relation. By comparison with our formula (18) and dealing only with a cone between  $\theta$  and  $(\theta + d\theta)$  we obtain:

$$n_{c\theta} = 2 n_w \sin \theta d\theta \cdot \underbrace{\cos \theta \int_0^{\infty} [1 + 0.42(\alpha \lambda_w \cos \theta) \mu] e^{-\mu} d\mu}_A \quad (27)$$

The term A in (27) corresponds to Knudsen's cosine-term

and is our "direction factor";

$$A = \cos\theta \int_0^{\infty} [1 + 0.42 (\alpha \lambda_w \cos\theta) \mu] e^{-\mu} d\mu$$

$$A = \cos\theta [-e^{-\mu} + 0.42 \alpha \lambda_w \cos\theta (-e^{-\mu}) (\mu+1)]_0^{\infty}$$

$$A = \cos\theta [1 + 0.42 \alpha \lambda_w \cos\theta] \quad (28)$$

Thus the temperature gradient brings essentially a  $\cos^2\theta$ -change to the Knudsen-law.

For the case of a cooler wall equation (28) reads analogously:

$$A = \cos\theta [1 - 0.42 \alpha \lambda_w \cos\theta] \quad (28a)$$

We compare now the simple Knudsen-factor  $A_k = \cos\theta$  and our factor  $A$ . In polar coordinates the curve for  $\cos\theta$  is a circle. (See Diagram 1). The shape of our  $A$ -curve can be determined in the following way:

$$A_{\theta=0} = 1 + 0.42 \alpha \lambda_w$$

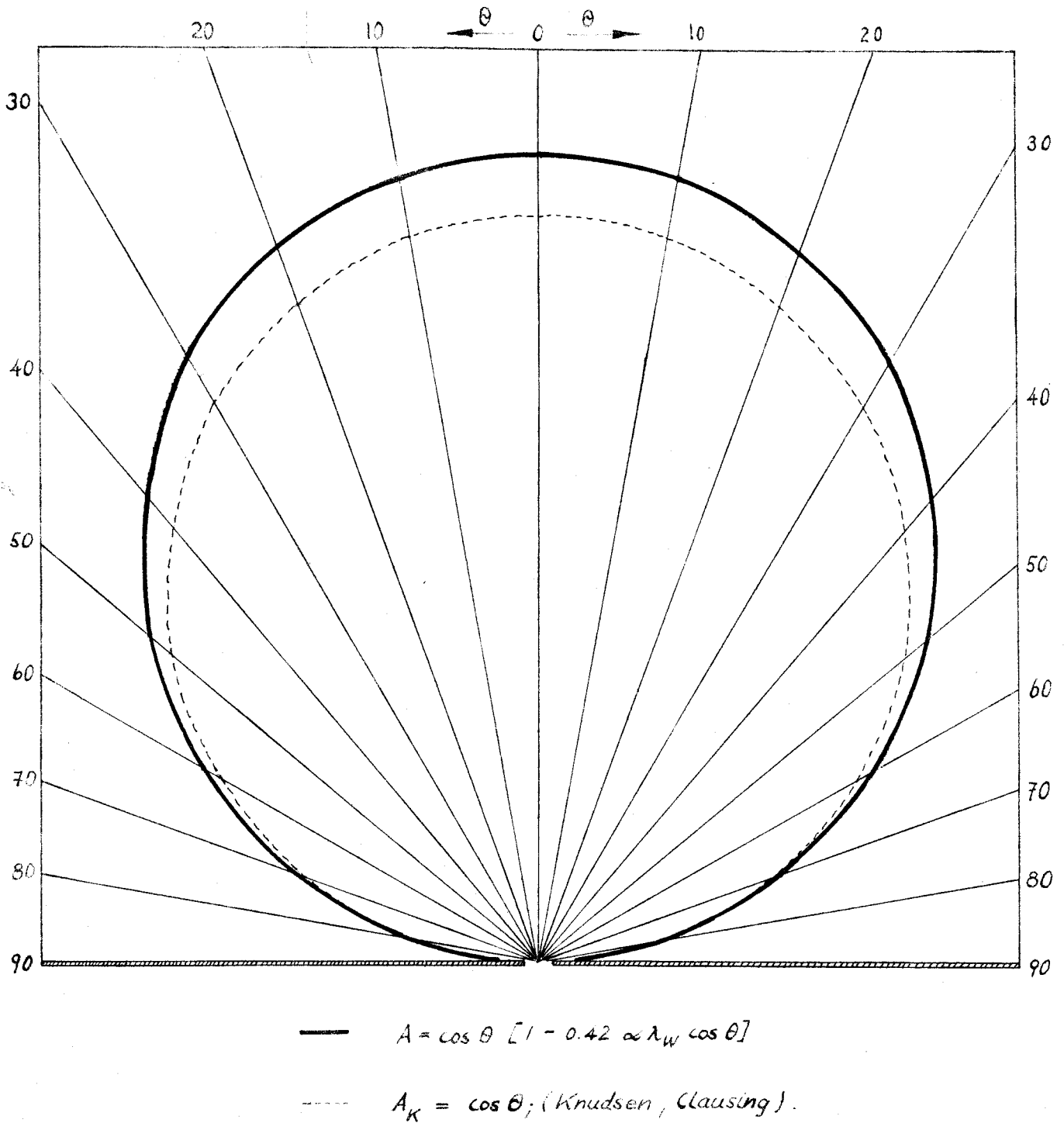
$$\frac{A}{A_{\theta=0}} = \frac{1 + 0.42 \alpha \lambda_w \cos\theta}{\underbrace{1 + 0.42 \alpha \lambda_w}_{< 1}} \cos\theta < \left( \frac{A_k}{A_{k(\theta=0)}} \right)_{\text{Knudsen}} = \cos\theta, \quad (29)$$

Therefore our curve is an ovoid with its largest diameter in the direction of the x-axis. (See Diagram 1, page 22).

Furthermore:

$$\frac{dA}{d\theta} = -\sin\theta [1 + 0.42 \alpha \lambda_w \cos\theta] - \cos\theta \cdot 0.42 \alpha \lambda_w \sin\theta$$

$$\left( \frac{dA}{d\theta} \right)_{\theta=0} = 0$$



Diag. 1

Comparison of the spatial distributions of outflowing molecules for the cases of a temperature gradient at the wall and for uniform gas temperature (Knudsen).

This means that our curve has no sharp tip. In Diagram 1 the curve is drawn for the same numerical values which we used in section 3.6.:

$$\frac{T}{T_w} = 0.8 \quad \text{for} \quad x = \lambda_w$$

$$\propto \lambda_w = 0.228$$

$$\rightarrow A = \cos \theta [1 + 0.0937 \cos \theta]$$

#### Conclusion:

A negative temperature gradient has a "directing" effect on the massflux. The molecules do not spread out in all directions in the same way as for homogeneous gas conditions. The total massflux increases. However both effects (spatial distribution and total outflux corrections) are relatively small.

For a positive temperature gradient (wall cooler than the gas) the above statements hold analogously. Thus the total outflux in this case is smaller than for a constant gas state throughout the semi-space. In this case the molecules spread more to the sides than normal to the wall.

V. DISCUSSION OF THE CASE OF AN UNSTEADY TEMPERATURE GRADIENT AT THE WALL.

5.1. The Heat Transfer Equation for Very Small Temperature Gradients.

We deal with the same physical arrangement as in the previous sections with the only difference that the wall is now suddenly heated or cooled. Therefore the temperature gradient changed with time corresponding to the heat flux into the halfspace.

$$T = T(x, t) \quad (30)$$

The coefficient of heat conductivity and the density change with temperature. Hence the differential equation for the heat transfer must be written as follows:

$$\frac{\partial T}{\partial t} = d \frac{\partial^2 T}{\partial x^2} + \frac{\partial d}{\partial x} \cdot \frac{\partial T}{\partial x} \quad (31)$$

$$d = \frac{\beta(T)}{c_p \cdot \rho(T)} = \text{function of } T$$

Equation (31) is a partial differential equation, and the solution would be relatively complicated. But for small gradients we can simplify the relation in the following manner:

In the previous section we have already seen that only the state of a thin layer next to the wall is really important for the calculation. But

this thin layer will be heated or cooled very soon after the instant in which the temperature of the wall is suddenly raised or lowered. Therefore the terms  $\frac{\partial d}{\partial x}$  and  $\frac{\partial T}{\partial x}$  can be assumed as relatively small in this layer. Their product can be neglected in a first order approximation (this certainly does not hold for the very first moment after increase or decrease of the wall temperature). Thus we get:

$$\frac{\partial T}{\partial t} = \frac{\beta(T)}{\rho(T) \cdot c_p} \cdot \frac{\partial^2 T}{\partial x^2} = \frac{\beta(x, T)}{\rho(x, t) \cdot c_p} \cdot \frac{\partial^2 T}{\partial x^2} \quad (32)$$

Furthermore we assume by the same reasoning as above (small layer near the wall) that

$$\frac{\beta(T)}{\rho(T) \cdot c_p} = d(T) \doteq d(T_{wall}) = \text{const.} \quad (33)$$

$d$  is the so-called thermal diffusivity.

In that way we have finally reduced equation (31) to the usual heat transfer equation for solid bodies:

$$\frac{\partial T}{\partial t} = d_w \cdot \frac{\partial^2 T}{\partial x^2} \quad (34)$$

The solution of this relation is well known. The boundary conditions for our special problem are:

$$T(0, t) = T_w ; \quad T(x, 0) = T_0 ; \quad \begin{matrix} x > 0 \\ t > 0 \end{matrix} \quad (35)$$

The solution takes the form:

$$\frac{T - T_0}{T_w - T_0} = 1 - \operatorname{erf} \frac{x}{\sqrt{4d_w t}} \quad (36)$$

$$\text{where: } \operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\xi^2} d\xi$$

Equation (36) is the transient one-dimensional heat

flow solution for conduction from a surface at constant temperature  $T_w$  into a semiinfinite medium initially at  $T_0$ . Actually this approximation turns out to be very good as shown experimentally by W.C.Griffith [5].

### 5.2. A Solution for Very Small Unsteady Temperature Gradients.

We want to obtain a formula for the mass-flux as a function of time according to the temperature change with time. If we introduce relation (36) in (12) and integrate by graphical or numerical methods our problem is principally solved. But the error-function cannot be used explicitly for analytic integrational operations which we want to make with function (36) in order to show the general behaviour. Using another function as an approximation for (36) enables us to integrate explicitly. We take

$$\frac{T - T_0}{T_w - T_0} = e^{-1.8 \frac{x}{\sqrt{4d_w t}}} \quad (37)$$

as the approximate function. Curves of functions (36) and (37) are plotted in Diagram 2 (p. 27).

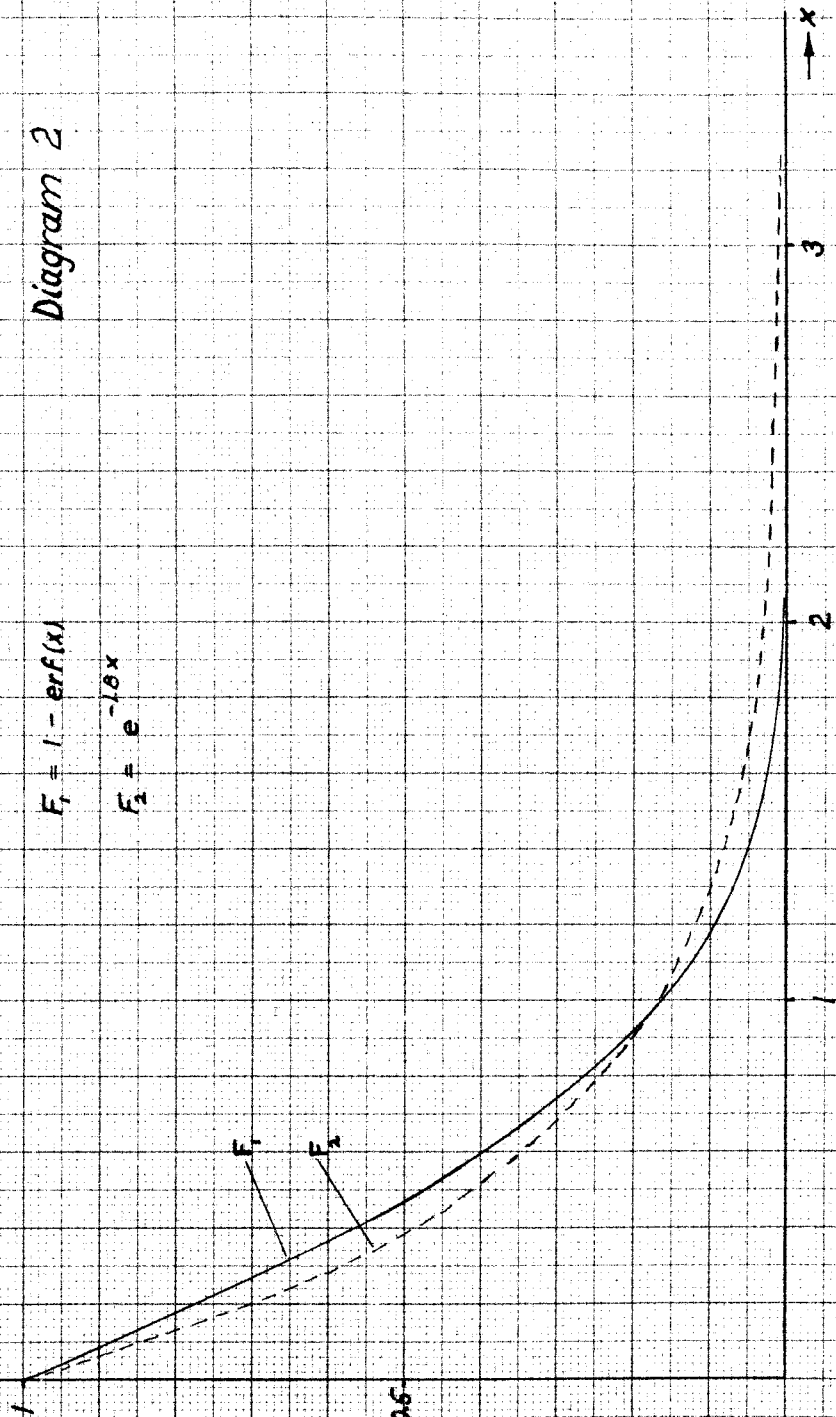
For our special example we assume furthermore that the initial temperature is very low

$$T_0 \approx 0$$

Diagram 2

$$F_1 = 1 - \text{erf}(x)$$

$$F_2 = e^{-10x}$$





Then repeating the process of section 3.4.:

$$\frac{T}{T_w} = e^{\frac{-1.8x}{\sqrt{4d_w t}}} \longrightarrow \frac{\lambda}{\lambda_w} = e^{\frac{-1.8x}{\sqrt{4d_w t}}}$$

$$\mu = \int_0^x \frac{dx}{\lambda(x) \cos \theta} = \int_0^x \frac{e^{\frac{1.8x}{\sqrt{4d_w t}}}}{\lambda_w \cos \theta} dx$$

$$\frac{1.8}{\sqrt{4d_w t}} \lambda_w \cos \theta \mu + 1 = e^{\frac{1.8x}{\sqrt{4d_w t}}}$$

and

$$n = 2 \int_0^{\frac{\pi}{2}} \sin \theta \cos \theta d\theta \int_0^{\infty} n_w \sqrt{1 + c \lambda_w \cos \theta \mu} e^{-\mu} d\mu$$

where:

$$c = \frac{1.8}{\sqrt{4d_w t}}$$

In order to be able to make the same approximation as in section 3.4. we have to restrict ourselves to certain values of  $c$ :

$$c \leq \frac{0.6}{\lambda_w}$$

For example:

$\lambda_w = 5 + 10$  cm at  $1 \mu$  pressure and  $15^\circ \text{C}$  for common gases:

$$\frac{1.8}{\sqrt{4d_w t}} \left[ \frac{1}{\text{cm}} \right] \leq 0.1 \div 0.5 \left[ \frac{1}{\text{cm}} \right]$$

Therefore the resultant formula after integration does not hold for very small  $t$ , that means it does not hold for the first moment after the temperature increase at the wall. But this is essentially the same restriction as for the validity of equation (32) as stated there.

Applying relation (21) properly yields then:

$$n = n_w \left[ 1 + 0.28 \frac{1.8}{\sqrt{4d_w t}} \lambda_w \right]$$

$$n = n_w \left[ 1 + 0.252 \frac{\lambda_w}{\sqrt{d_w t}} \right] \quad (38)$$

The properties of the massflow described by this formula are essentially the same as in section 3.4.. Equation (38) shows that for increasing time the massflux approaches the Knudsen value, as it was to be expected.

### 5.3. Another Solution for Very Small Unsteady Temperature Gradients.

Relation (34) yields after integration:

$$\frac{\partial T}{\partial x} = \text{const} \frac{1}{\sqrt{d_w t}} e^{-\frac{x^2}{4d_w t}} \quad (39)$$

Then we make a definition (see Liepmann and Roshko, [12], p.315):

$$\xi(0, t) \cdot \delta = \int_0^{\infty} \xi \, dx \quad ; \quad \xi = \frac{\partial T}{\partial x} \quad (40)$$

$$\longrightarrow \delta = \sqrt{\pi d_w t} \quad (41)$$

Thus we replaced the actual temperature distribution by a discontinuous one.  $\delta$  is a layer, in which the gradient  $\frac{\partial T}{\partial x}$  is constant and has the same value as at the wall. The thickness of the layer increases with time. The remaining part of the gas is at constant temperature. (See Fig. 6). Using this as an approxi-

mation leads to the following:

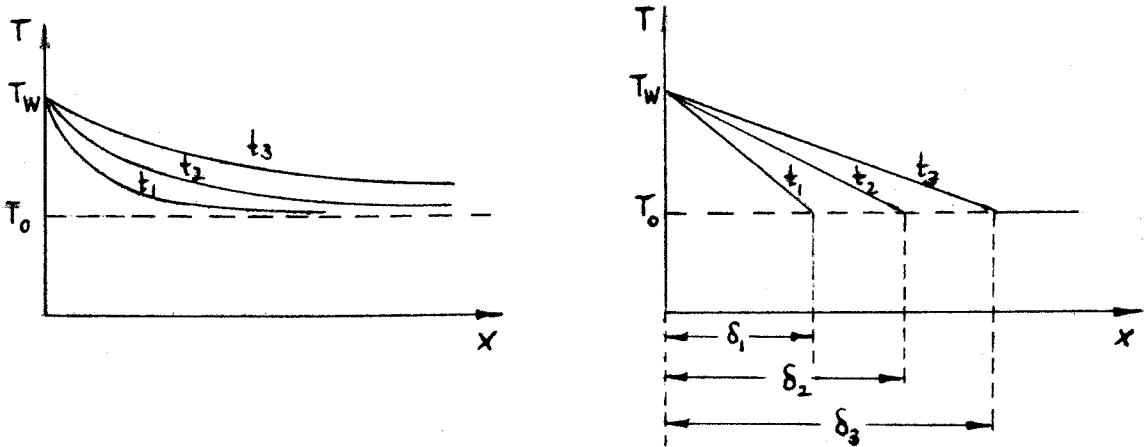


Fig. 6.

$$\lambda = \lambda_w - \gamma x \quad \text{for} \quad 0 \leq x \leq \delta$$

$$\lambda = \lambda_0 \quad \text{for} \quad x \geq \delta$$

Using our relation (12) properly yields:

$$v_w = \frac{1}{\gamma} [\ln \lambda_w - \ln (\lambda_w - \gamma x)] = \frac{1}{\gamma} \ln \left( \frac{\lambda_w}{\lambda_w - \gamma x} \right) \quad (42)$$

for  $0 \leq x \leq \delta$

$$v_0 = \frac{1}{\gamma} \ln \left( \frac{\lambda_w}{\lambda_w - \gamma \delta} \right) + \frac{x - \delta}{\lambda_0} \quad \text{for} \quad \delta \leq x \quad (43)$$

Furthermore:

$$\frac{T_w}{T} = \frac{T_w}{T_w - \epsilon x} \quad 0 \leq x \leq \delta \quad (44)$$

$$\frac{T_w}{T} = \frac{T_w}{T_0} \quad \delta \leq x \quad (45)$$

$$0 \leq x \leq \delta: \quad (43) \rightarrow x = \frac{\lambda_w e^{\gamma v} - \lambda_w}{\gamma e^{\gamma v}} \quad (46)$$

$$\text{thus:} \quad \frac{T_w}{T} = \frac{1}{1 + \frac{\epsilon}{T_w} \lambda_w \frac{(e^{\gamma v} - 1)}{e^{\gamma v}}} = f(v) = f(\mu \cos \theta)$$

Observing that the integrand dies out rapidly for in-

creasing  $x$  ( $x \geq \delta$ ) and using the Taylor-expansion procedure given in section 3.3. leads to:

$$n = n_0 \left[ 1 + \frac{2}{3} \frac{(T_w - T_0)}{T_0} \cdot \frac{\lambda_w}{\delta} + \frac{1}{2} \left[ \frac{(T_w - T_0)}{T_0} \cdot \frac{\lambda_w}{\delta} \right]^2 \dots \right] \quad (47)$$

$$\delta = \delta(t)$$

Remark: Relation (47) is not valid for very short times after the temperature increase at the wall (Very steep temperature gradients occur then!)

#### 5.4 Simple Model for the Gas Behavior Near the Wall

##### Immediately after a Temperature Change at the Wall.

Up to this point, very short times after a sudden temperature change at the wall had to be excluded in our calculations. Before we consider the effects which occur immediately after the temperature increase (or decrease) at the wall, a very simple and instructive model for the gas behavior at this moments shall be described.

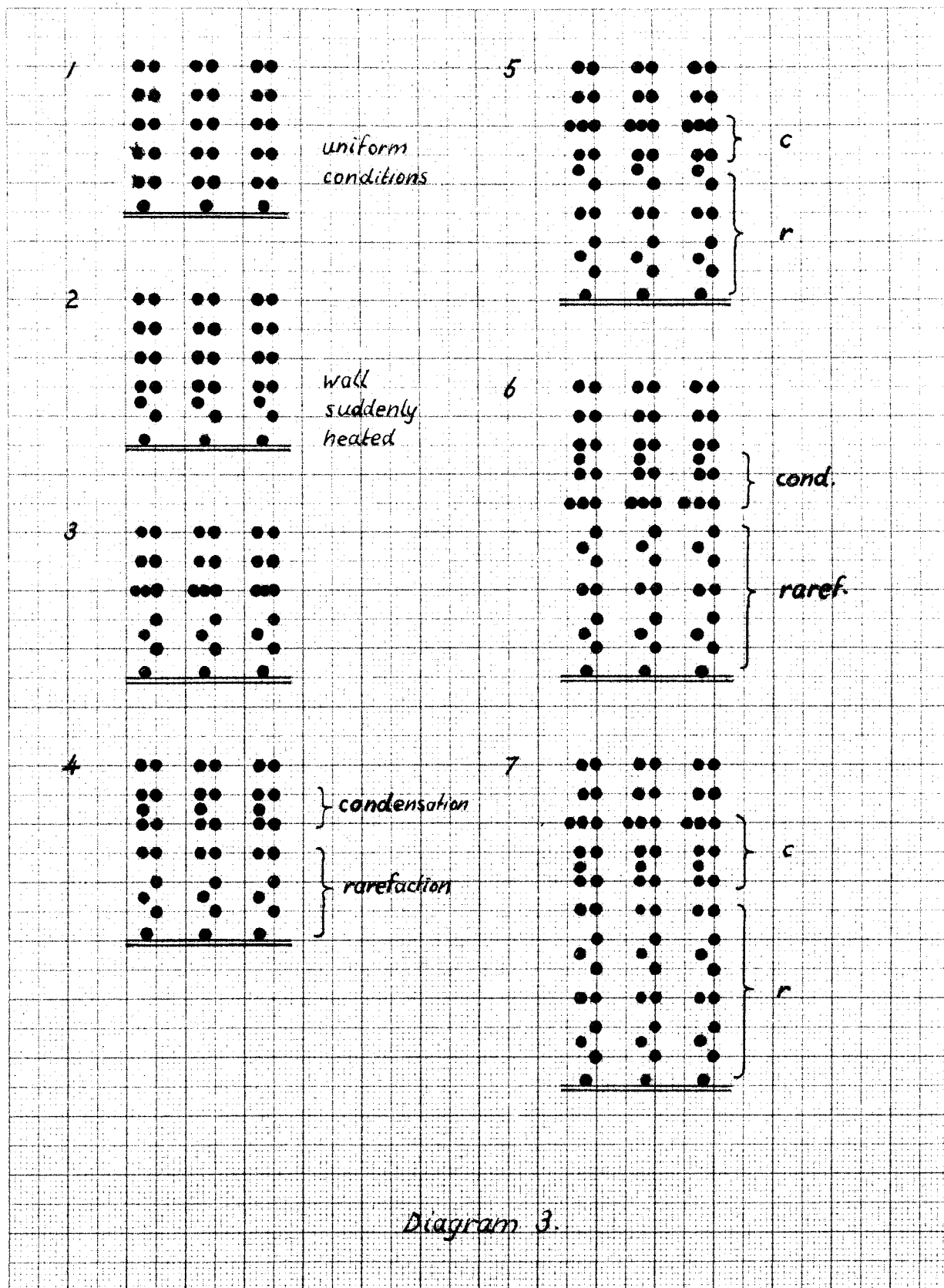
In a real gas the molecules collide frequently with each other and exchange their momentum, energy and direction of motion. The sudden energy input at the wall when the temperature is raised is carried away by reflected molecules. These particles collide and exchange their higher energy to other molecules

very soon. Therefore this energy spreads away from the wall in a very complicated manner (in "zig-zag" curves). To illustrate the overall effect of a suddenly raised wall temperature we assume the following:

- a) The space above the wall is filled with rigid spherical molecules moving only in a direction normal to the wall.
- b) All particles have the same velocity.
- c) The particles are reflected normal to the wall and obtain a speed in the opposite direction.
- d) The speed of the reflected molecules corresponds to to the temperature of the wall.
- e) The particles do not collide with each other.

Under these assumptions we can draw a simple model for the gas motion near the wall. Diagram 3 on page 33 illustrates the change of the particle motion when the wall temperature is suddenly raised.

From these figures it is easy to see that after the increase of temperature a layer of low density occurs next to the wall. The thickness of this layer increases with time. Moving away from the wall is another layer of high density (similar to a shock front). The thickness of this layer also increases with time.



One can write (see Diagram 3, p. 33):

$$\begin{array}{ll}
 c_1 m \tau - c_0 (m+1) \tau & \text{condensation} \\
 & \text{layer thickness} \\
 c_1 (m+1) \tau & \text{rarefaction} \\
 & \text{layer thickness}
 \end{array}
 \left. \vphantom{\begin{array}{l} c_1 m \tau - c_0 (m+1) \tau \\ c_1 (m+1) \tau \end{array}} \right\} \text{for a sud-} \\
 \hspace{15em} \text{denly heated} \quad (48) \\
 \hspace{15em} \text{wall}$$

is the time between 2 impacts of molecules at the wall.

m. index  $1, 2, 3, \dots, m$

Going to the limit  $\tau \rightarrow 0$ :

$$\begin{array}{ll}
 (c_1 - c_0) t & \text{condensation layer} \\
 & \text{thickness} \\
 c_0 t & \text{rarefaction layer}
 \end{array}
 \quad (48a)$$

This model shows the behavior of a real gas for very short times after the temperature raise. The higher momentum of the reflected particles "pushes" the oncoming molecules away and the condensation and rarefaction layers are created. But because of the complicated interactions of the molecules is this effect not as sharp as in our model and the distinction between this layers gets weaker and weaker with increasing time (the energy exchange between "slow" and "fast" molecules smoothens the effect with increasing time).

An analogous model can be set up for the case of a sudden temperature drop at the wall. Then a condensation layer occurs next to the wall and a rarefaction wave spreads into the space.

5.5. Behavior of a Maxwellian Gas Near a Wall in the First Moments after a Sudden Temperature Rise at the Wall. Approximate Calculation of the Outflux of Molecules for the first two Collision Times after the Temperature Rise.

In order to study the unsteady behavior of a gas near a wall corresponding to the boundary conditions the velocity distribution function has to be known. This distribution function (a function of the macroscopic variables of state, of space and of time) has to satisfy the Maxwell-Boltzmann equation. This problem was recently treated by Kichiro Takao [7] who split the distribution function in two parts (arriving and reflected particles) and was thus able to match the boundary conditions at a wall and to satisfy the Maxwell-Boltzmann equation. He obtains a system of partial differential equations for the macroscopic variables of state and the velocity components in analogy to the equations of motion in continuum theory. These equations have to be solved in order to study the complete behavior of a gas with space and time.

We are interested in the gas behavior for very short time after the wall temperature has been increased or decreased. For the time when the first high energy molecules collide for the first time after their



impact with the suddenly heated wall (this means for one collision time after the temperature rise of the wall) the density distribution of the gas in the semi-space can be computed in a much simpler way than the one mentioned above. Once the density distribution is known we can easily calculate the approximate outflux for very short time by using the fact that only a thin layer of the thickness of a mean free path is of importance for the outflux.

We proceed now in calculating the density distribution for one collision time after the temperature change of the wall. Assuming that in this very first moment the reflected molecules have also a Maxwellian velocity distribution but an energy level according to the temperature of the wall we can write for this distribution:

$$f_1 = A_1 e^{-\beta_1 (u^2 + v^2 + w^2)} du dv dw \quad (49)$$

The reflected molecules have only positive u-components of velocity. Therefore in order to normalize the distribution function we have to integrate between the following limits:

$$\int_{u=0}^{+\infty} \int_{v,w=-\infty}^{+\infty} A_1 e^{-\beta_1 (u^2 + v^2 + w^2)} du dv dw = 1$$

$$A_1 = 2 \left( \frac{\beta_1}{\pi} \right)^{\frac{3}{2}} \quad (50)$$

We determine  $\beta_1$  in the usual way:

$$\bar{u}^2 = A_1 \int_{u=0}^{\infty} \iint_{v,w=-\infty}^{+\infty} u^2 e^{-\beta_1(u^2+v^2+w^2)} du dv dw$$

$$\bar{u}^2 = \frac{1}{2\beta_1}$$

$$\bar{v}^2 = A_1 \int_{u=0}^{\infty} \iint_{v,w=-\infty}^{+\infty} v^2 e^{-\beta_1(u^2+v^2+w^2)} du dv dw$$

$$\bar{v}^2 = \frac{1}{2\beta_1} \quad \text{analogously:} \quad \bar{w}^2 = \frac{1}{2\beta_1}$$

$$\bar{c}^2 = \bar{u}^2 + \bar{v}^2 + \bar{w}^2 \quad \Rightarrow \quad \bar{c}^2 = \frac{3}{2\beta_1} \quad (51)$$

But a basic relation of kinetic theory states that

$$\bar{c}^2 = 3RT_1 \quad \Rightarrow \quad \beta_1 = \frac{1}{2RT_1} \quad (52)$$

The probability of finding a molecule with an absolute velocity between  $c$  and  $dc$  regardless of its direction of motion is found now; using (49), (50), (52):

$$f_1 = 2 (2\pi RT_1)^{-\frac{3}{2}} e^{-\frac{1}{2RT_1}(u^2+v^2+w^2)} du dv dw$$

The "volume element"  $du dv dw$  in the "velocity space" can be replaced by  $c^2 d\psi d\theta \sin\theta dc$ . This is just a transcription from Cartesian to spherical polar coordinates. Thus:

$$f_1 = \frac{2}{(2\pi RT_1)^{\frac{3}{2}}} c^2 e^{-\frac{c^2}{2RT_1}} \sin\theta d\theta d\psi dc$$

hence:

$$\psi(c) = \int_0^{2\pi} d\psi \int_0^{\frac{\pi}{2}} \sin\theta d\theta \cdot \frac{2c^2 e^{-\frac{c^2}{2RT_1}}}{(2\pi RT_1)^{\frac{3}{2}}} dc$$

$$\psi(c) = \frac{4\pi}{(2\pi RT_1)^{\frac{3}{2}}} c^2 e^{-\frac{c^2}{2RT_1}} dc \quad (53)$$

Using (53) we obtain for the mean velocity:

$$\bar{c} = \int_0^{\infty} c \varphi(c) dc = \sqrt{\frac{8RT_1}{\pi}}$$

After these preliminary remarks about the distribution function of the reflected molecules immediately after the change in wall temperature we shall make the following considerations:

We know the number of particles hitting unit surface before the wall temperature was changed:

$$n_0 = \frac{N_0 \bar{c}_0}{4}$$

Therefore immediately after the instant in which the temperature has been raised (analogous arguments hold for a cooled wall)  $n_0$  molecules per unit surface are moving upwards with higher energy. This means that two Maxwellian gases of different energy levels are mixing. This statement is only true until the reflected molecules have collided once after their impact with the wall because then they exchange energy and the velocity distribution is no longer Maxwellian. Thus the following calculations hold only for one collision time after the temperature change of the wall, but they give a simple method of computing the number density distribution of the gas for this moment.

Now we shall make use of formulae and relations given in the book of Kennard [8]. In order

to save space we do not copy the derivation but give only the final results stated there:

Total expectation of collisions per second between a ray molecule with velocity  $c_1$  and Maxwellian distributed gas molecules (Kennard [8], p. 108, eqn.103a);

$$\bar{\Omega}_{c_1 t} = \frac{N_0 \pi D^2}{\sqrt{\pi} \beta_0} \left[ e^{-x^2} + \left(2x + \frac{1}{x}\right) \int_0^{\frac{x}{\sqrt{\beta_0}}} e^{-y^2} dy \right] \quad (54)$$

where:

$$x = \sqrt{\beta_0} c_1$$

$$y = \sqrt{\beta_0} c_0 \quad \beta_0 = \frac{1}{2RT_0}$$

Combining (53) and (54) we can compute a mean expectation of collisions for our reflected molecules:

$$\bar{\bar{\Omega}}_{c_1 t} = \frac{N_0 \pi D^2}{\sqrt{\pi} \beta_0} \frac{4\pi}{2\pi RT_1 \sqrt{2\pi RT_1}} \int_{c_1=0}^{\infty} \left[ e^{-\beta_0 c_1^2} + \left(2\beta_0 c_1 + \frac{1}{c_1}\right) \int_0^{c_1/\sqrt{\beta_0}} e^{-\beta_0 c_0^2} dc_0 \right] c_1^2 e^{-\frac{c_1^2}{2RT_1}} dc_1$$

$$\bar{\bar{\Omega}}_{c_1 t} = \frac{2N_0 D^2}{RT_1 \sqrt{T_1/T_0}} \int_{c_1=0}^{\infty} \left[ e^{-\beta_0 c_1^2} + \left(2\beta_0 c_1 + \frac{1}{c_1}\right) \int_0^{c_1/\sqrt{\beta_0}} e^{-\beta_0 c_0^2} dc_0 \right] c_1^2 e^{-\frac{c_1^2}{2RT_1}} dc_1 \quad (55)$$

The integration procedure of this equation (55) is given in Kennard, p. 111. It is briefly outlined in Appendix II.

The final result is:

$$\bar{\bar{\Omega}}_{c_1 t} = \frac{2N_0 \pi D^2}{\sqrt{\pi} \beta_0 \beta_1} \sqrt{\beta_0 + \beta_1} = \pi N_0 D^2 \sqrt{\bar{c}_0^2 + \bar{c}_1^2} \quad (56)$$

For the time before the wall temperature has changed is  $c_1 = c_0$ :

$$\bar{\bar{\Omega}}_{c_0 t} = \pi N_0 D^2 \sqrt{2} \bar{c}_0 \quad (56a)$$

This is the well known result for one gas of Maxwellian distribution.

The collision time (time between two subsequent collisions) is then simply:

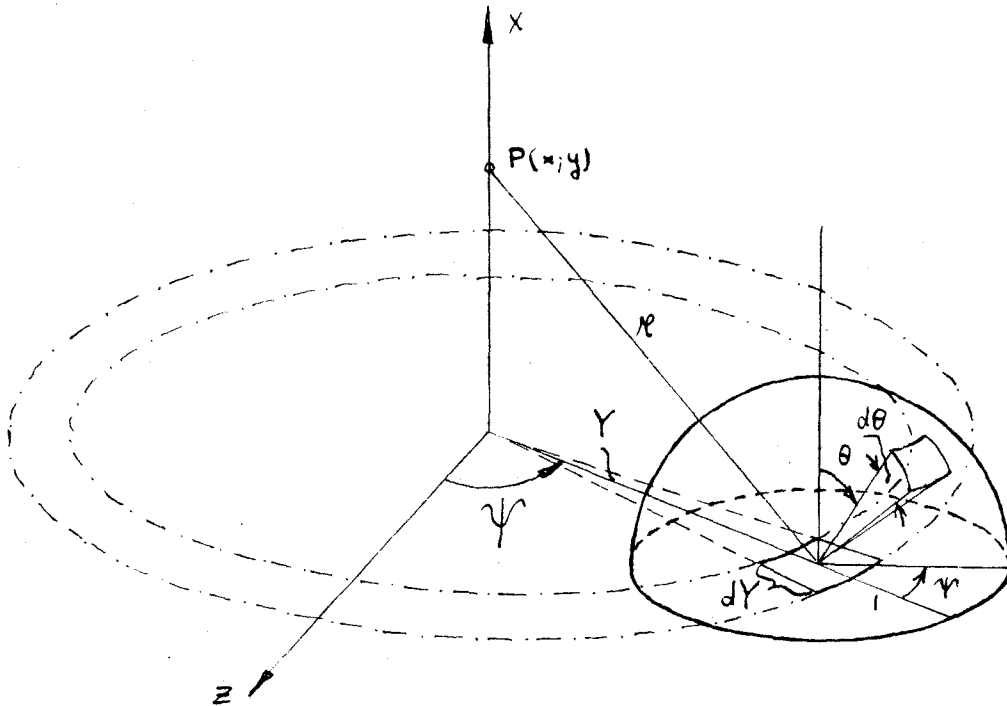
$$\bar{\tau} = \frac{1}{\bar{\Omega}_{ct}} \left[ \frac{N_0}{\text{collision}} \right] \quad (57)$$

Therefore we obtain for the mean free path:

$$\bar{\lambda} = \bar{c} \cdot \bar{\tau} \quad ; \quad \bar{\lambda} = \frac{\bar{c}}{\bar{\Omega}_{ct}} \quad (58)$$

So far we arrived at an expression for the mean free path of the reflected "wall molecules", which holds only for very short time after the temperature change. In this calculation only encounters between "fast" wall particles and particles in the undisturbed semi-space have been counted. Collisions between two "fast" molecules have been neglected as rare compared to the first kind. We shall now proceed to calculate the number of first collisions of the reflected molecules after they left the wall as a function of space. These "first" collisions occur one collision time  $\bar{\tau}$  after the wall has been suddenly heated. Therefore the collision distribution to be calculated will hold for this time instant:

$\frac{N_0 \bar{c}_0}{4}$  particles hit the wall per unit time and surface before the change in wall temperature. Therefore  $\frac{N_0 \bar{c}_0}{4}$  particles leave unit surface of the wall with a higher energy at the moment when the wall temperature is raised. According to Fig.7 and using Knudsen's cosine-law we can therefore say:



Fig;7

Number of "fast" molecules leaving unit surface per unit solid angle:

$$\frac{n_0}{\pi} \cos \theta Y dY d\psi \sin \theta d\theta d\psi$$

From this number a part collides between  $r$  and  $dr$ :

$$n_r = \frac{n_0}{\pi} \cos \theta Y dY d\psi \sin \theta d\theta d\psi \frac{1}{r^2} e^{-\frac{r}{\lambda}} dr$$

Hence number of collisions at  $r$  and  $\theta$  per unit volume  $r^2 \sin \theta d\theta d\psi dr$ :

$$n_c = \frac{n_0}{\pi} \cos \theta Y dY d\psi \frac{1}{r^2} \frac{1}{\lambda} e^{-\frac{r}{\lambda}} \quad (59)$$

Then total number of collisions per unit volume at  $x$ :

$$n_t = \int_{\psi=0}^{2\pi} \int_{Y=0}^{\infty} \frac{n_0}{\pi} \cos \theta Y dY d\psi \frac{1}{r^2} \frac{1}{\lambda} e^{-\frac{r}{\lambda}}$$

$$n_t = 2n_0 \int_x^\infty \frac{x}{\kappa} \kappa d\kappa \frac{1}{\kappa^2} \cdot \frac{1}{\lambda} e^{-\frac{\kappa}{\lambda}} = 2n_0 \left(\frac{x}{\lambda}\right) \int_x^\infty \frac{e^{-\frac{\kappa}{\lambda}}}{\kappa^2} d\kappa$$

because:  $\cos \theta = \frac{x}{\kappa} = \frac{\sqrt{\kappa^2 - Y^2}}{\kappa}$  and  $\kappa^2 = x^2 + Y^2$

$$\rightarrow Y dY = \kappa d\kappa$$

we call:  $\frac{\kappa}{\lambda} = z$

$$n_t = 2n_0 \left(\frac{x}{\lambda}\right) \int_{\frac{x}{\lambda}}^\infty \frac{e^{-z}}{\lambda^2 z^2} \lambda dz$$

Introducing a modified Knudsen number  $K = \frac{x}{\lambda}$ :

$$n_t = 2n_0 \cdot \frac{1}{\lambda} K \int_K^\infty \frac{e^{-z}}{z^2} dz \quad (60)$$

This integral is of the general form (Gröbner-Hofreiter, Integraltafel, Wien 1949, p.108):

$$\int \frac{e^{\lambda t}}{t^n} dt = -e^{\lambda t} \sum_{\nu=1}^{n-1} \frac{\lambda^{\nu-1}}{(n-1-\nu)! \nu!} \cdot \frac{1}{t^{n-\nu}} + \frac{\lambda^{n-1}}{(n-1)!} \text{Ei}(\lambda t) \quad (61)$$

Hence for our case  $\lambda = -1$ ;  $n = 2$ :

$$\int_K^\infty \frac{e^{-z}}{z^2} dz = \left[ -e^{-z} \frac{1}{(1-1)! 1!} \cdot \frac{1}{z} + \frac{(-1)}{1} \text{Ei}(-z) \right]_K^\infty$$

because:  $(m; -d; \nu) = d^\nu \frac{\Gamma(\frac{m}{d} + 1)}{\Gamma(\frac{m}{d} - \nu + 1)} \left( = 1 \frac{\Gamma(1+1)}{\Gamma(1)} = 1 \right)$

$$\int_K^\infty \frac{e^{-z}}{z^2} dz = \left[ -e^{-z} \cdot \frac{1}{z} - \text{Ei}(-z) \right]_K^\infty = \frac{1}{K} e^{-K} + \text{Ei}(-K)$$

where:

$$\text{Ei}(-z) = \int_{-\infty}^{-z} \frac{e^t}{t} dt = \int_\infty^z \frac{e^{-t}}{t} dt$$

Thus finally:

$$n_t = 2n_0 \cdot \frac{1}{\lambda} \left[ e^{-K} + K \cdot \text{Ei}(-K) \right] \quad (62)$$

This is the number of molecules leaving unit surface at time  $t=0$  and colliding for the first time at  $t=\tau$  at a distance  $x$  from the wall. The expression

$$\phi = \left[ e^{-K} + K \text{Ei}(-K) \right] \quad (63)$$

can be tabulated or plotted. See Diagram 4, page 44.

Thus:

$$n_t = 2n_0 \cdot \frac{1}{\lambda} \cdot \phi \quad (64)$$

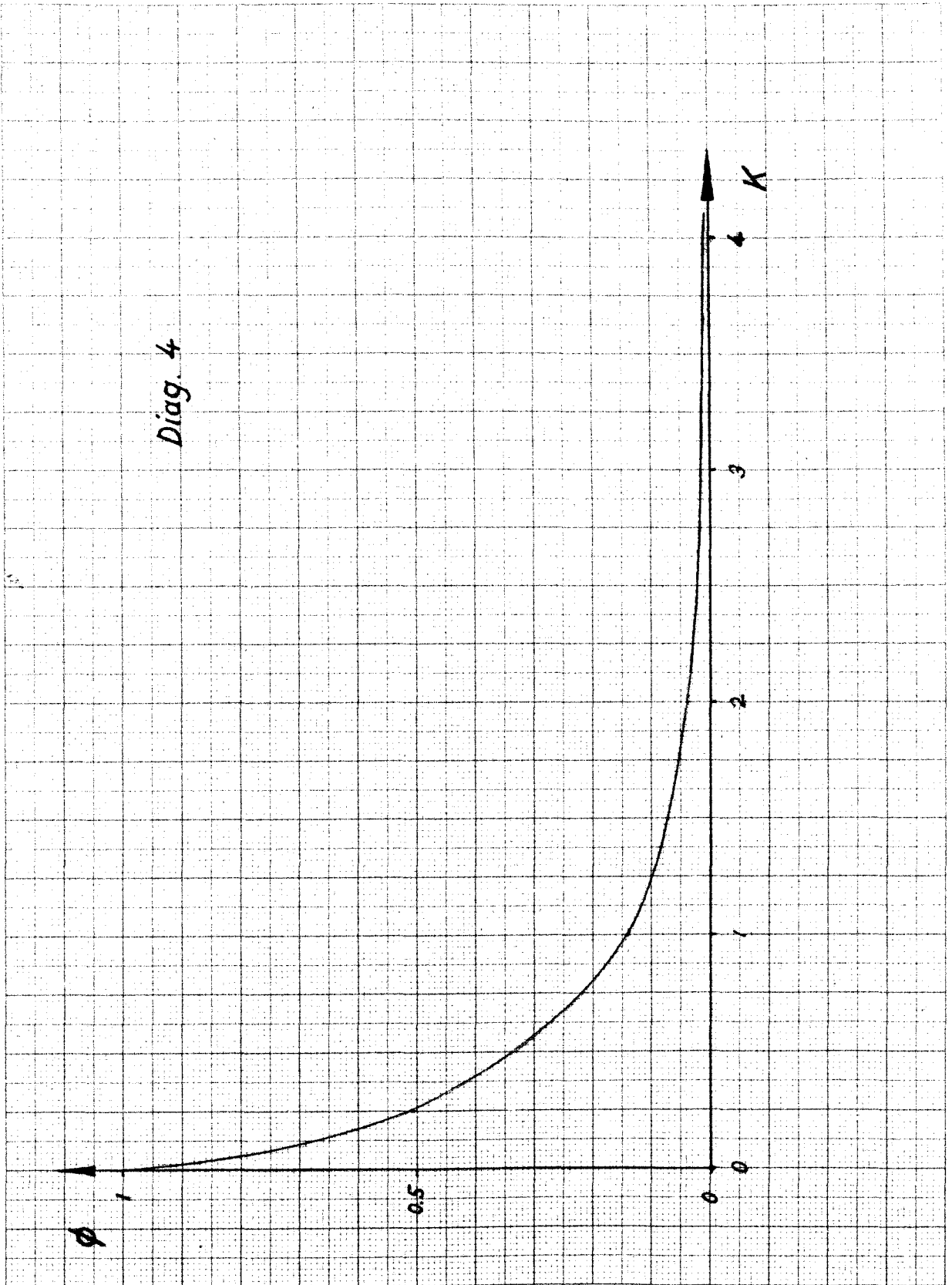
In order to obtain the change of density from the original homogeneous state for the time after the temperature increase at the wall, we argue as follows:

During the original state  $\frac{N_0 \bar{c}_0}{4}$  particles were reflected from unit surface per unit time. These molecules had their first collisions after they left the wall at a certain distance  $x$  from the wall. In order to calculate the number of colliding reflected molecules at  $x$  for the original state we use exactly the same formulae as above. We put  $\beta_1 = \beta_0$  in this case ( $\bar{c}_1 = \bar{c}_0$ ) and compute  $n_{t_0}$ .

The only change in the state of the gas in the semi-space above the wall at one collision time after the temperature rise can come from the wall,



Diag. 4



because no high energy molecules are going towards the wall yet. Therefore we can write for the change of number density at the time  $\tau$  :

$$\Delta N = n_{it} - n_{ot} \quad (65)$$

As an example the following case was calculated numerically:

$$T_0 = 300^\circ\text{K}$$

$$T_1 = 600^\circ\text{K}$$

$$R = 28.7 \cdot 10^5 \text{ [erg/gr deg]}$$

Using formulae we obtained:

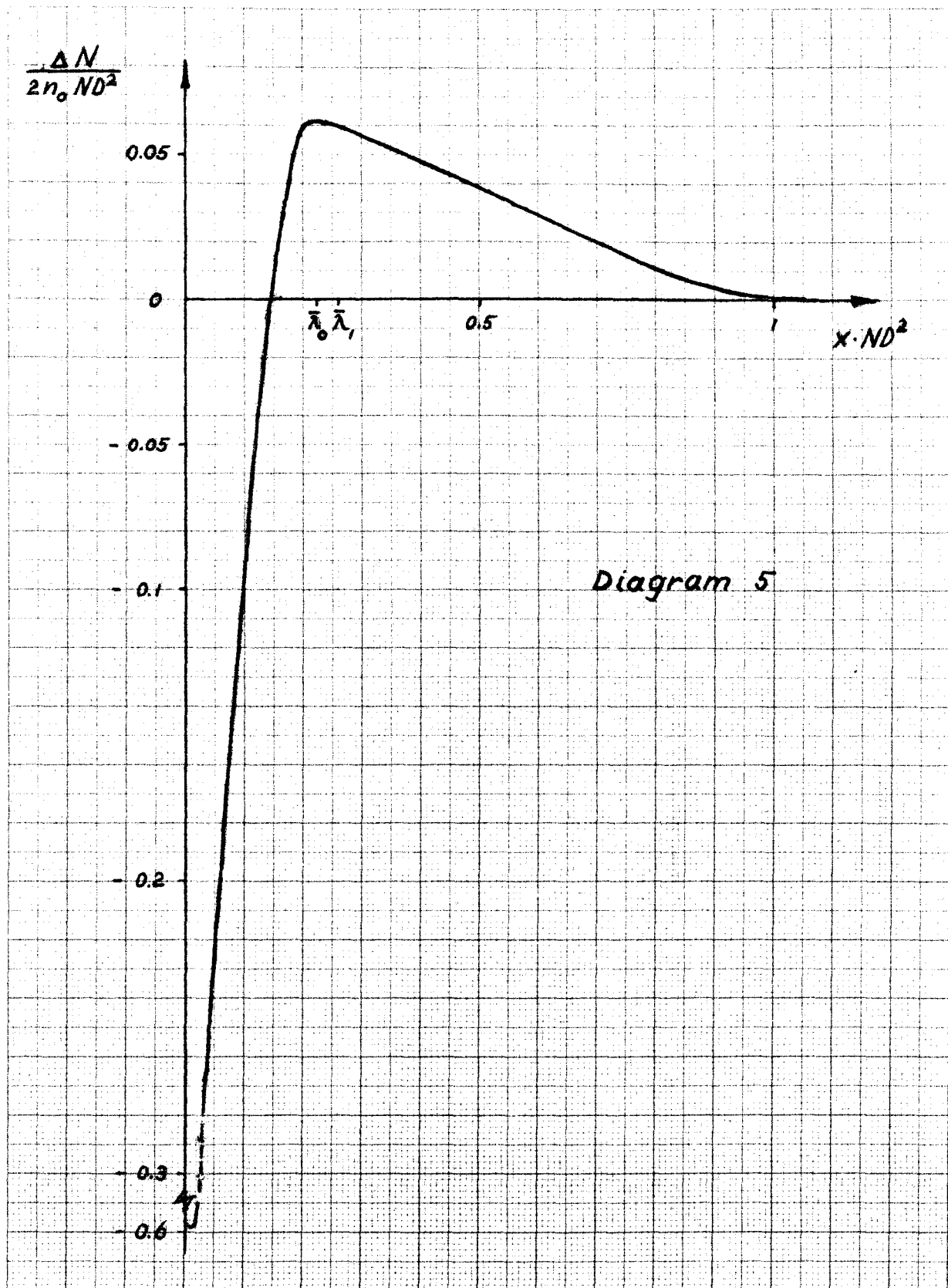
$$\tau_1 = \frac{0.392 \cdot 10^{-5}}{N_0 D^2} \quad \left[ \frac{\text{sec}}{\text{coll}} \right] \quad \left| \quad \tau_0 = \frac{0.481 \cdot 10^{-5}}{N_0 D^2} \quad \left[ \frac{\text{sec}}{\text{coll}} \right] \right.$$

$$\lambda_1 = \frac{0.26}{N_0 D^2} \quad \left[ \frac{\text{cm}}{\text{coll}} \right] \quad \left| \quad \lambda_0 = \frac{0.225}{N_0 D^2} \quad \left[ \frac{\text{cm}}{\text{coll}} \right] \right.$$

Observe:  $\left. \begin{array}{l} \tau_1 < \tau_0 \\ \lambda_1 > \lambda_0 \end{array} \right\}$  for suddenly heated wall.

Then  $n_{it}$  and  $n_{ot}$  were computed as functions of  $x$ . The difference  $\Delta N$  is plotted in Diagram 5 on page 46.

This diagram (which retains its general form also for different numerical values) shows very clear the effect of the sudden temperature raise of the wall as predicted by means of our simple model in section 5.4..A rarefaction layer occurs next to the wall and a compression layer separates this low density layer from the undisturbed part.



As a last step we can use this information about the number density at time  $\tau$  to obtain an approximate expression for the outflux of molecules through a small orifice in the wall. In the collisions which occurred at time  $\tau$  all "fast" molecules had velocity components away from the wall. Therefore the probability that "fast" molecules are going towards the wall after collision is very small. Thus we say the only change of the state of the gas which is important for the outflux at time  $2\tau$  (see remark below) is the deviation of the number density. Remembering that only the state of a layer of thickness  $\bar{\lambda}$  is important for the outflow (shown earlier!) we calculate a mean value of the number density in this layer:

$$\bar{N}_{\tau} = N_0 - \frac{\int_0^{\bar{\lambda}} \Delta N dx}{\bar{\lambda}} \quad (66)$$

Thus outflux at time  $2\tau$ :

$$n_{2\tau} \doteq \frac{\bar{N}_{\tau} \cdot \bar{c}_0}{4} \quad (67)$$

Remark:

The outflux does not change in the time interval  $0 \rightarrow \tau$  because the "fast" reflected molecules had no collision and did therefore not affect the state of the gas in the semi-space yet. The effect occurs first at time  $\tau$  when the affected molecules reach the wall.

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APPENDIX I

We want to find an approximation for the function:

$$J = \sqrt{1 + \alpha \lambda_w \cos \theta \mu} \cdot e^{-\mu}$$

We restrict ourselves to the following values of  $\alpha$ :

$$\alpha \leq \frac{0.6}{\lambda_w}$$

Considering the function  $J$  we can therefore replace the term  $\alpha \lambda_w \cos \theta$  by  $a$ , where  $a$  is bounded between 0 and 0.6.

$$\alpha \lambda_w \cos \theta = a \leq 0.6$$

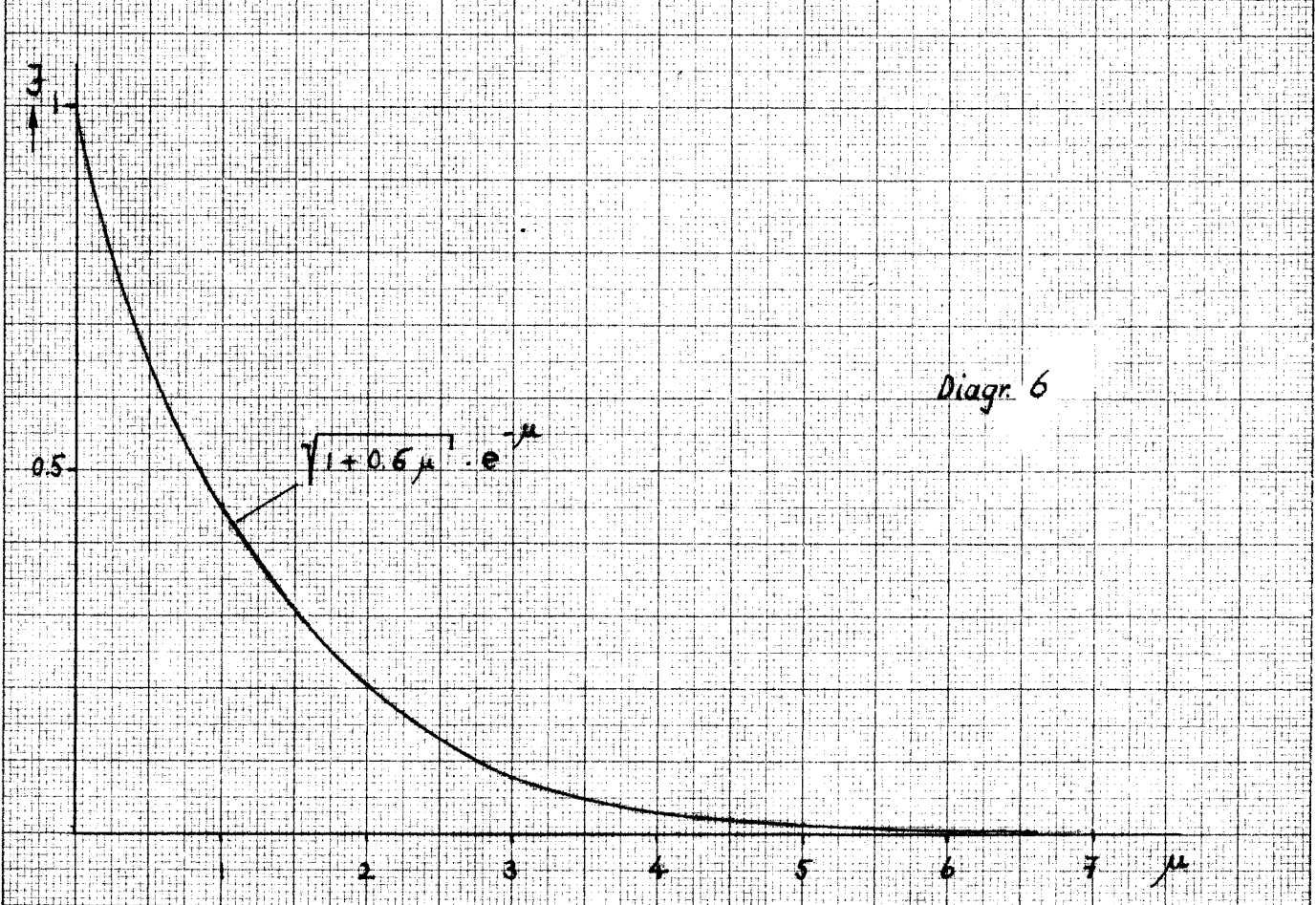
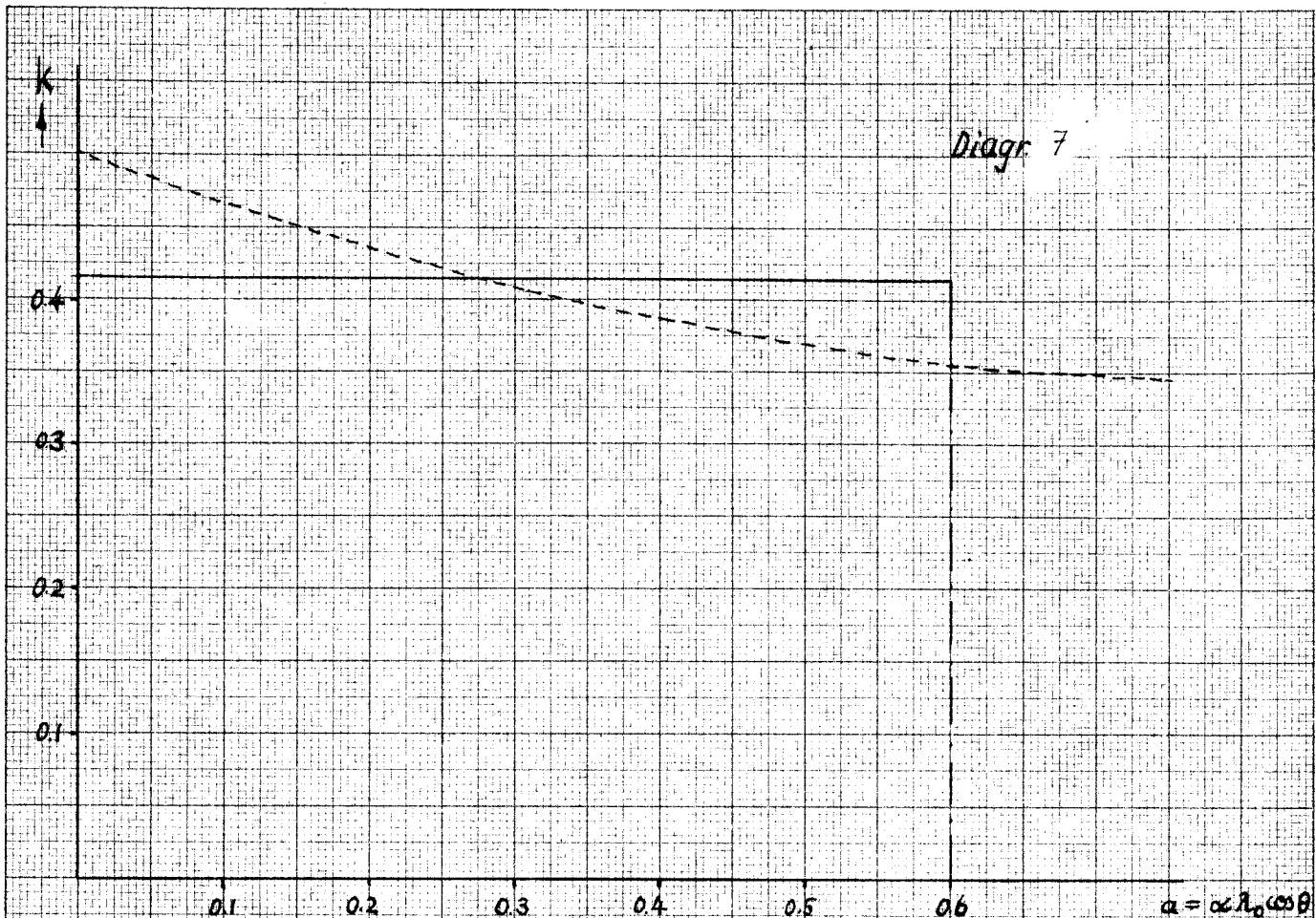
Plotting the integrand  $J = \sqrt{1 + a\mu} \cdot e^{-\mu}$  for our maximal value of  $a$  0.6 one finds, that the function approaches zero very rapidly because of the term  $e^{-\mu}$ . See Diagram 6, page 50. Diagram 6 shows that for  $\mu = 6$  the integrand  $J$  is practically zero (with an accuracy of about 0.5%). We deal therefore with the important region  $0 \leq \mu \leq 6$  and try to find an approximation of  $\sqrt{1 + a\mu}$  in terms of a linear function of  $\mu$  in order to be able to integrate our relation (18). We write:

$$\int_0^6 \sqrt{1 + a\mu} \, d\mu = \int_0^6 (1 + \frac{1}{2} a\mu) \, d\mu$$

$$\frac{2}{3a} (1 + a\mu)^{\frac{3}{2}} \Big|_0^6 = \left[ \mu + \frac{2a\mu^2}{2} \right]_0^6$$

This yields:

$$K = \frac{[(1 + 6a)]^{\frac{3}{2}} - 1}{27 a^2} - 9a$$



$$\lim_{a \rightarrow 0} k = 0.5 \quad (\text{by d'Hospital's rule})$$

The function  $k$  is plotted in Diagram 7, page 50. The slope of the  $k$ -curve is relatively smooth and we approximate this curve therefore by a function  $k_c = \text{const}$  for our region  $0 \leq a \leq 0.6$ . Evaluation of  $k_c$  yields  $k_c = 0.42$ , (the areas underneath the curves are equal). In this way we get an approximate constant  $k_c$  valid for all  $a = \alpha \lambda_w \cos \theta$  in the region  $0 \leq a \leq 0.6$ . Furthermore our integrand  $J$  takes the form:

$$\sqrt{1 + \alpha \lambda_w \cos \theta \mu} \cdot e^{-\mu} \doteq (1 + 0.42 \alpha \lambda_w \cos \theta \mu) e^{-\mu}$$

$$\text{for } 0 \leq \alpha \lambda_w \cos \theta \leq 0.6$$



APPENDIX II

We would like to integrate the following expression:

$$\bar{n}_{c,t} = \frac{2N_0 D^2}{RT_1 \sqrt{T_1/T_0}} \int_{c_1=0}^{\infty} \left[ e^{-\beta_0 c_1^2} + (2\beta_0 c_1 + \frac{1}{c_1}) \int_0^{c_1} e^{-\beta_0 c_0^2} dc_0 \right] c_1^2 e^{-\frac{c_1^2}{2RT_1}} dc_1 \quad (55)$$

Instead of integrating  $c_0$  from 0 to  $c_1$  and then  $c_1$  from 0 to  $\infty$  we invert the order of integration and integrate first  $c_1$  from  $c_0$  to  $\infty$  and then  $c_0$  from 0 to  $\infty$  :

Thus for the second part of the integral (55) we write:

$$\begin{aligned} \int_{c_1=0}^{\infty} (2\sqrt{\beta_0} c_1 + \frac{1}{c_1}) \left( \int_0^{c_1} e^{-\beta_0 c_0^2} dc_0 \right) c_1^2 e^{-\frac{c_1^2}{2RT_1}} dc_1 &= \\ &= \int_0^{\infty} dc_0 \int_0^{\infty} (2\sqrt{\beta_0} c_1^3 + \frac{c_1}{\sqrt{\beta_0}}) e^{(-\beta_0 c_0^2 - \beta_1 c_1^2)} dc_1 \\ &= \frac{\sqrt{\pi}}{\sqrt{\beta_0} \beta_1^2} \left( \frac{1}{2} \frac{\beta_0 + \frac{1}{2}\beta_1}{\sqrt{\beta_0 + \beta_1}} + \frac{1}{4} \frac{\beta_0 \beta_1}{(\beta_0^2 + \beta_1^2)^{\frac{3}{2}}} \right) \end{aligned} \quad (a)$$

The first part can be integrated without inverting the order of integrating:

$$\int_0^{\infty} \frac{1}{\sqrt{\beta_0}} c_1^2 e^{-(\beta_0 + \beta_1) c_1^2} dc_1 = \frac{\sqrt{\pi}}{4\sqrt{\beta_0}} \frac{1}{(\beta_0 + \beta_1)^{\frac{3}{2}}} \quad (b)$$

The total integral (55) is the sum of (a) and (b):

$$J = \frac{\sqrt{\pi}}{2\beta_1^2 \beta_0} \sqrt{\beta_0 + \beta_1}$$

Hence:

$$\bar{n}_{c,t} = \frac{2N_0 \hat{\pi} D^2}{\sqrt{\hat{\pi} \beta_0 \beta_1}} \sqrt{\beta_0 + \beta_1} = \hat{\pi} N_0 D^2 \sqrt{\bar{c}_0^2 + \bar{c}_1^2} \quad (56)$$