

Fig. 1 Geometry of the plate

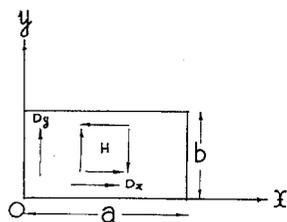
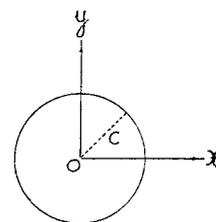


Fig. 2 Geometry of the plate



Now Eq. (4) takes the form

$$\iint (\nabla_0^4 f - \lambda^2 f) f(x,y) dx dy = 0 \tag{8}$$

In polar coordinates, Eq. (8) can be put as

$$\iint (\nabla_1^4 \psi - \lambda^2 \psi) \psi(r,\theta) r dr d\theta = 0 \tag{9}$$

where ∇_1^4 can be obtained from ∇_0^4 by means of the relations $x = r \cos\theta$, $y = r \sin\theta$, and $\psi(r,\theta)$ is a function satisfying the boundary conditions. For a circular plate, ψ is independent of θ , and so Eq. (9) becomes

$$\int_0^c (\nabla_{11}^4 \psi - \lambda^2 \psi) \psi(r) r dr = 0 \tag{10}$$

where λ^2 can be determined from Eq. (8) or (10), as the case may be, by choosing $f(x,y)$ or $\psi(r)$ suitably.

Rectangular Plates

Case 1

For a plate (Fig. 1) simply supported on all its sides, $f(x,y)$ for the fundamental mode is given by

$$f(x,y) = A_1 \sin(\pi x/a) \sin(\pi y/b) \tag{11}$$

On substituting in Eq. (8),

$$\lambda^2 = \pi^4 [(D_x/a^4) + (2H/a^2b^2) + (D_y/b^4)] \tag{12}$$

a well-known result.^{2, 3}

Case 2

For a plate simply supported along $y = 0$, $y = b$ and clamped along $x = 0$, $x = a$,

$$f(x,y) = A_2 [\sin(\pi y/b)] x^2(x - a)^2 \tag{13}$$

and

$$\lambda^2 = 504(D_x/a^4) + (24\pi^2 H/a^2b^2) + (\pi^4 D_y/b^4) \tag{14}$$

as against almost the same value given in Ref. 2.

Case 3

For a plate clamped along its sides,

$$f(x,y) = A_3 x^2(x - a)^2 y^2(y - b)^2 \tag{15}$$

$$\lambda^2 = 504(D_x/a^4) + 288(H/a^2b^2) + 504(D_y/b^4) \tag{16}$$

and this same value was obtained in Ref. 2. by another method.

Circular Plates

Case 1

For a plate clamped along its boundary (Fig. 2),

$$\psi(r) = A_4 [1 - 2(r^2/c^2) + (r^4/c^4)] \tag{17}$$

$$\lambda^2 = (40/c^4) [D_x + (2H/3) + D_y] \tag{18}$$

For isotropy in this case, $\lambda^2 = 106.7D/c^4$, comparing well with the exact value $\lambda^2 = 104.2 D/c^4$ of Ref. 4.

Case 2

For a plate simply supported along its boundary,

$$\psi(r) = A_5 \left[1 - \left(\frac{6 + 2\nu}{5 + \nu} \right) \frac{r^2}{c^2} + \left(\frac{1 + \nu}{5 + \nu} \right) \frac{r^4}{c^4} \right] \tag{19}$$

Taking $\nu = 0.3$, Eq. (10) gives

$$\lambda^2 = (1/c^4) [9.24D_x + 5.62H + 9.24D_y] \tag{20}$$

which in the case of isotropy becomes $\lambda^2 = 24.1 D/c^4$, almost coinciding with the exact value $\lambda^2 = 23.60 D/c^4$ reported in Ref. 4.

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Computation of Kinetic Constants from Single-Pulse Shock Tube Data

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Nomenclature

A	= concentration of reactant, moles per unit volume
c	= concentration of reactant, moles per unit mass of total gas
ρ	= total gas density, mass per unit volume
M	= total gas concentration, moles per unit volume
k	= kinetic rate constant
Q	= Arrhenius pre-exponential factor in k
E	= Arrhenius activation energy
R	= molar gas constant
T	= absolute temperature
F ₅	= fraction of reactant decomposed or reacted in region 5
F _c	= fraction of reactant decomposed or reacted in region 5 plus rarefaction
Region 5	= region between arrival of reflected shock and arrival of rarefaction
Region r	= region between arrival of rarefaction and achievement of effective cutoff of reaction
c _p	= constant-pressure specific heat of total gas mixture
Q	= heat release per mole of reactant decomposed

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- γ = specific heat ratio of total gas mixture
 t_s = duration of reflected shock heating
 t_r = time between arrival of rarefaction and reaction cutoff
 ϵ_s = E/RT_{05}
 ϵ_r = E/RT_{f5}
 θ_s = $(T_{f5} - T_{05})/T_{05}$
 θ_r = $(T_{f5} - T_{cr})/T_{f5}$
 T_{f5}^* = $T_{05}(p_{f5}/p_{05})^{(\gamma-1)/\gamma}$ = adiabatic heating in region 5
 T_{c5}^* = $T_{f5}(p_{cr}/p_{f5})^{(\gamma-1)/\gamma}$ = adiabatic cooling in region 5
 ΔT_{s5} = $F_5 c_{05} Q/c_p$ = self-heating in region 5
 ΔT_{sr} = $(F_c - F_s) c_{05} Q/c_p$ = self-heating in region r
05 = subscript denoting conditions immediately after reflection
f5 = subscript denoting conditions at onset of rarefaction
cr = subscript denoting conditions at reaction cutoff
 \bar{M}_5 = $(\bar{M}_5)^m (t_s/\epsilon_s \theta_s) [\exp(\epsilon_s \theta_s) - 1]$
 X_r = $(\bar{M}_r)^m (t_r/\epsilon_r \theta_r) [1 - \exp(-\epsilon_r \theta_r)]$
 Y_5 = $(\frac{1}{2}) [A_{05} (\rho_{f5}/\rho_{05})^{1/2}]^{1/2} (t_s/\epsilon_s \theta_s) \exp(\epsilon_s \theta_s) - 1]$
 Z_r = $(\frac{1}{2}) [A_{05} (\rho_{f5}/\rho_{05}) (\rho_{cr}/\rho_{f5})^{1/2}]^{1/2} (t_r/\epsilon_r \theta_r) [1 - \exp(-\epsilon_r \theta_r)]$

SINGLE-PULSE ("chemical") shock tube experiments, as normally performed,^{1, 2} yield information on the incident shock velocity, the pressure-time profile of the gas near the end of the tube, and the composition of the product mixture. The results are most reliable when the attenuation of the incident shock is measured, in order to compute the velocity at the moment of shock reflection, and when sampling of products is restricted to gas that was close to the end plate during the reflected shock. One then can compute confidently the conditions within this sample at the moment when it entered the reflected shock. If species A undergoes decomposition or other reaction in the shock, the parameters of interest are T_{05} , p_{05} , ρ_{05} , A_{05} , and \bar{M}_{05} (see Nomenclature).

The tailored-interface method^{1, 3} is commonly used to extend the available reaction time. Recent work⁴ implies that tailoring is approached best by selecting the initial tube conditions for slight over-tailoring, i.e., so that if the diaphragm burst ideally, a weak reflected shock would be produced by the interaction of the once-reflected shock and the oncoming contact surface. The pressure profile indicates to the experimenter whether he has achieved tailoring or not. It also gives the reaction time in region 5 and the expansion rate created by the arrival of the rarefaction wave.

Pressure profiles almost invariably show that p_5 increases with time. This is attributed to an increase in the thickness of the boundary layer encountered by the reflected shock as it moves further away from the end plate. The main significance of this with respect to gas near the end plate is that it will undergo essentially isentropic compression as p_5 rises. The most important kinetic effect of this is that the temperature increases.

The temperature changes further because species A decomposes. When the decomposition is exothermic, the temperature rises. If the decomposition rate is modest, and dilution of A by an inert gas (usually argon) is of the order of a hundredfold or larger, the heat release will not produce a wave but only will tend to expand the gas. In principle, this expansion affects the apparent reaction time in region 5 (t_s), but the effect is small.

Cooling rates due to the quenching rarefaction are finite, and so the total reaction time is larger than t_s . Some additional decomposition occurs in the environment of changing temperature and density within the rarefaction. The problem is to determine the decomposition rate constant corresponding to temperature T_{05} . First approximations to the kinetic order of reaction and the activation energy may be obtained by ignoring the changing temperature in region 5 and the extra reaction in the rarefaction.

Suppose that the reaction is established to be essentially of n th order in A and of m th order in M (M is the total gas concentration). The rate of change of concentration of A

is given by

$$-dA/dt = -(dA/dt)_{\text{chem}} - (dA/dt)_{\text{compression}} \quad (1)$$

Now

$$-(dA/dt)_{\text{chem}} = k M^m A^n \quad (2)$$

and

$$-(dA/dt)_{\text{compression}} = -cd\rho/dt = -(A/\rho)d\rho/dt \quad (3)$$

So

$$-d \ln A/dt = k M^m A^{n-1} - d \ln \rho/dt \quad (4)$$

or

$$-dc/c^n = k M^m \rho^{n-1} dt \quad (5)$$

This equation is integrated, and the resulting Arrhenius plot of experimental rate constants is used to judge the correctness of the assumed order. Because the rate is not very sensitive to density changes (which generally will not exceed 10%), mean values of M and ρ can be used. These are defined adequately by

$$\bar{M} = M_0(\rho_f/\rho_0)^{1/2} \quad (6a)$$

and

$$\bar{\rho} = \rho_0(\rho_f/\rho_0)^{1/2} \quad (6b)$$

where the subscripts refer to initial and final conditions.

The integration can be written in a general form. However, as an illustration that is kinetically significant, consider the case for a reaction that is first-order in A . Then

$$-d \ln c/dt = k M^m \quad (7)$$

It is convenient to consider region 5 and the rarefaction separately. For region 5, integration gives

$$-\ln\left(\frac{c_{f5}}{c_{05}}\right) = (\bar{M}_5)^m \int_0^{t_s} k dt \quad (8)$$

where k is a function of T . For an exothermic reaction,

$$T_{f5} = T_{f5}^* + \Delta T_{s5} \quad (9)$$

where

$$T_{f5}^* = T_{05}(p_{f5}/p_{05})^{(\gamma-1)/\gamma} \quad (10)$$

and

$$\Delta T_{s5} = F_5 c_{05} Q/c_p \quad (11)$$

\bar{M}_5 is given by

$$\bar{M}_5 = M_{05}(\rho_{f5}/\rho_{05})^{1/2} \quad (12)$$

where ρ_{f5}/ρ_{05} is determined by the combination of adiabatic compression and self-heating due to reaction:

$$\rho_{f5}/\rho_{05} = (p_{f5}/p_{05})^{1/\gamma} (T_{f5}^*/T_{05}) \quad (13)$$

To simplify the integration of Eq. (8), it is helpful to adopt the (good) approximation that the temperature changes linearly with time:

$$T \doteq T_{05}(1 + \theta_s t/t_s) \quad (14)$$

Then

$$-\ln\left(\frac{c_{f5}}{c_{05}}\right) = -\ln(1 - F_5) = \alpha(\bar{M}_5)^m \int_0^{t_s} \exp\left(-\frac{E}{RT}\right) dt \quad (15a)$$

$$= \alpha(\bar{M}_5)^m \int_0^{t_s} \exp\left[-\frac{E}{RT_{05}} \left(1 + \frac{\theta_s t}{t_s}\right)\right] dt \quad (15b)$$

or, since $\theta_5 \ll 1$,

$$-\ln\left(\frac{c_{f5}}{c_{05}}\right) \doteq \bar{Q}(\bar{M}_5)^m \int_0^{t_5} \exp\left[\frac{-E(1 - \theta_5 t/t_5)}{RT_{05}}\right] dt \quad (15c)$$

$$\doteq k_{05}(\bar{M}_5)^m \int_0^{t_5} \exp\left(\frac{E\theta_5 t}{RT_{05}t_5}\right) dt \quad (15d)$$

$$= k_{05}(\bar{M}_5)^m \left(\frac{t_5}{\epsilon_5\theta_5}\right) [\exp(\epsilon_5\theta_5) - 1] \quad (15e)$$

or

$$1 - F_5 = \exp(-k_{05} W_5) \quad (16)$$

It is this equation that ultimately will be used for computation of k_{05} .

A similar approach is used in region r , the rarefaction. The main difference is that one must define a point at which the reaction may be said to have stopped. The approximation is adopted that the reaction is quenched when the rate has dropped to 5% of its value at the start of the rarefaction. Essentially, this defines a cutoff temperature, ignoring the minor effect of changing density. The value of T_{cr} therefore is given by

$$5 \times 10^{-2} \exp(-E/RT_{f5}) = \exp(-E/RT_{cr})$$

or

$$3 + E/RT_{f5} = E/RT_{cr} \quad (17)$$

The pressure profile in the rarefaction is related to the temperature profile by the adiabatic gas law. Hence the cutoff pressure and cutoff time can be picked from the experimental record. A mean value of M is adopted, and linearity of temperature change with time is again assumed. An equation similar to Eq. (15) results:

$$-\ln(c_{cr}/c_{f5}) = k_{f5}(\bar{M}_r)^m (t_r/\epsilon_r\theta_r) [1 - \exp(-\epsilon_r\theta_r)] \quad (18)$$

But k_{f5} is related to k_{05} by

$$k_{f5} = k_{05} \exp(\epsilon_r\theta_5) \quad (19)$$

and so

$$-\ln(c_{cr}/c_{f5}) = k_{05}(\bar{M}_r)^m (t_r/\epsilon_r\theta_r) \times [1 - \exp(-\epsilon_r\theta_r)] \exp(\epsilon_r\theta_5) \quad (20)$$

Now the final fraction of A which is undecomposed is given by

$$1 - F_c = c_{cr}/c_{05} = (c_{cr}/c_{f5})(c_{f5}/c_{05}) = (c_{cr}/c_{f5})(1 - F_5) \quad (21)$$

$$= (1 - F_5) \exp[-k_{05} X_r \exp(\epsilon_r\theta_5)] \quad (22)$$

Making use of Eq. (16), one obtains

$$\ln(1 - F_c) = [1 + (X_r/W_5) \exp(\epsilon_r\theta_5)] \ln(1 - F_5) \quad (23)$$

Because X_r , W_5 , ϵ_r , and θ_5 all depend upon F_5 in complicated ways, Eq. (23) is solved by trial and error. Once F_5 is determined, k_{05} is computed using Eq. (16). When a series of k values have been computed in this way, a least squares analysis may give a value of E substantially different from the one assumed. The new value then may be used to give an improved set of k values.

In an experimental study of hydrazine decomposition using a conventional single-pulse shock tube,⁵ the procedure outlined here was programmed for an IBM 7074 computer. The activation energy in this example is low enough (approximately 35 kcal) and the cooling is slow enough that a substantial fraction (as much as 25%) of the total decomposition occurs in the rarefaction. Thus the use of the corrections in such a case is essential. To illustrate the point, Fig. 1 shows a comparison between the set of uncorrected k values and the

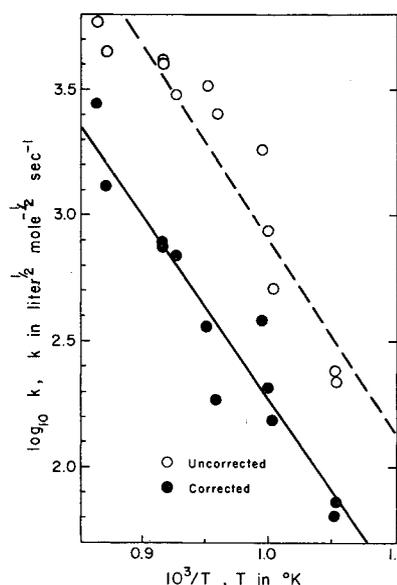


Fig. 1. Arrhenius plot illustrating the effect of the correction procedure upon kinetic data for hydrazine decomposition for the case $m = \frac{1}{2}$, $n = 1$

corrected set for the assumed case, $m = \frac{1}{2}$, $n = 1$. The uncorrected values are computed on the assumption that no reaction occurs in the rarefaction, and that conditions throughout the heating time in the reflected shock are those computed for the initial conditions at the moment of reflection.

Modifications of single-pulse shock tubes⁶ may increase quenching rates by factors of 5 to 10. Here, one may be able to assume that the total reaction time equals t_5 . Even in the usual single-pulse tube, reactions having large E (e.g., methane decomposition) usually may be studied without concern over reaction in the rarefaction. However, in the application of the method to combustion reactions, which typically have low activation energies, corrections almost always will be required.

The computation procedure for reaction orders other than first is entirely analogous to that just outlined. For example, a reaction that is $\frac{3}{2}$ -order in A and zero-order in M will have, instead of Eq. (5),

$$-d \ln c/dt = k c^{1/2} \rho^{1/2} \quad (24)$$

which yields

$$\left(\frac{c_{05}}{c_{f5}}\right)^{1/2} = 1 + \left(\frac{1}{2}\right) \left[A_{05} \left(\frac{\rho_{f5}}{\rho_{05}}\right)^{1/2}\right]^{1/2} \int_2^{t_5} k dt \quad (24)$$

as the analog of Eq. (8). The procedure leads to an analog of Eq. (16) given by

$$[1/(1 - F_5)]^{1/2} = 1 + k_{05} Y_5 \quad (26)$$

where Y_5 is defined in the Nomenclature. Similarly, the procedure for the rarefaction leads to an analog of Eq. (22) given by

$$[1/(1 - F_c)]^{1/2} = [1/(1 - F_5)]^{1/2} + k_{05} Z_r \exp(\epsilon_r\theta_5) \quad (27)$$

Equations (26) and (27) combine to yield an equation for F_5 which is analogous to Eq. (23):

$$[1/(1 - F_c)]^{1/2} = [1/(1 - F_5)]^{1/2} [1 + (Z_r/Y_5) \exp(\epsilon_r\theta_5)] - (Z_r/Y_5) \exp(\epsilon_r\theta_5) \quad (28)$$

As with Eq. (23), this equation must be solved by trial and error because of the complexity of its dependence upon F_5 .

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Plane Poiseuille Flow of a Rarefied Gas

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CONSIDER the problem of rarefied gas flow through a long two-dimensional channel, of length L and width d , connecting two large reservoirs at slightly different pressures P_1 and P_2 ; the channel plates and the reservoirs are being kept at the same temperature θ .

Experiments measuring the flow rate through approximately two-dimensional channels with various mean pressures were made by a number of investigators, e.g., see Rasmussen.¹ The normalized volumetric flow rate, i.e., the mass flow rate multiplied by $R\theta$ and divided by $(P_1 - P_2)$, is denoted by T . Rasmussen observed a minimum in T as a function of the mean channel pressure, which is inversely proportional to the Knudsen number.

The existence of this minimum was demonstrated theoretically in a paper by Cercignani,² who analyzed the problem for an arbitrary Knudsen number by assuming a strictly linear pressure gradient along the channel and using a simple kinetic model to describe the intermolecular collisions.

In what follows, it will be shown that the knowledge of the flow behavior in two extreme limits, i.e., the Knudsen limit and the continuum limit, will be sufficient to establish the existence of this minimum.

Choose the coordinates system such that x is in the direction of the flow, and the plates are given by $0 \leq x \leq L$ and $y = \pm d/2$.

The Knudsen limit and the continuum limit are characterized by $L/\lambda \rightarrow 0$ ($d/\lambda \rightarrow 0$ a fortiori) and $\lambda/d \rightarrow 0$, respectively, where λ is the mean free path of the gas.

In the Knudsen limit, because of the absence of intermolecular collisions, it is possible and convenient to consider only the case in which $P_2 = 0$. This problem reduces to an integral equation for $n(x)$, the number of molecules striking a unit area of a channel plate about the point x in unit time, namely (see Ref. 3, part 1),

$$n(x) = \frac{P_1}{2m(2\pi RT)^{1/2}} \left[1 - \frac{x}{(x^2 + d^2)^{1/2}} \right] + \frac{d^2}{2} \int_0^L \frac{n(\xi) d\xi}{[(x - \xi)^2 + d^2]^{3/2}} \quad (1)$$

where R is the gas constant and m the mass of a single molecule. Equation (1) is referred to as the Clausing equation.

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The number of molecules which would escape into the vacuum end of the channel per unit cross-sectional area is given by the formula

$$Q_N = \frac{2}{Ld} \int_0^L n(x) [(x^2 + d^2)^{1/2} - x] dx \quad (2)$$

For the derivation of Eqs. (1) and (2), refer to DeMarcus (Ref. 3, parts 1 and 3).

A complete solution to Eq. (1) has not been obtained. However, using a "squeezing" method developed by DeMarcus, the following bounds for $n(x)$ and Q_N have been found:⁴

$$\frac{P_1}{m(2\pi R\theta)^{1/2}} \left[1 - \frac{x}{L} \right] \geq n(x) \geq \frac{P_1}{m(2\pi R\theta)^{1/2}} \times \left[1 + \frac{4}{3(L+d)} \left(\frac{L}{2} - x \right) \right] \quad (3)$$

for $0 \leq x \leq L/2$, and

$$\frac{P_1}{m(\pi R\theta)^{1/2}} \frac{d}{L} \log \frac{L + (L^2 + d^2)^{1/2}}{d} > Q_N > \frac{P_1}{m(\pi R\theta)^{1/2}} \times \frac{5}{6} \frac{d}{L} \log \frac{L}{d} \quad (4)$$

A sufficient requirement for Eqs. (3) and (4) to be valid is that $L/d > 100$.

Return to the original problem where $P_2 \neq 0$, and denote by T the quantity $m \cdot Q_N \cdot R\theta / (P_1 - P_2)$, i.e., the normalized volumetric flow rate per unit cross-sectional area of the channel.

By virtue of the inequalities (4), the bounds for T are

$$\left(\frac{R\theta}{2\pi} \right)^{1/2} \frac{5}{6} \frac{d}{L} \log \frac{L}{d} < T_{Kn} < \left(\frac{R\theta}{2\pi} \right)^{1/2} \frac{d}{L} \times \log \left(\frac{L + (L^2 + d^2)^{1/2}}{d} \right) \quad (5)$$

where subscript Kn indicates the value for Knudsen flow. It may be worthwhile to stress that the bounds given in (5) are exact when $L/d > 100$. For the derivation of inequalities (3–5), see Ref. 4.

On the other hand, for continuum conditions, the flow rate is known to obey the classical Poiseuille formula, namely,

$$T = \frac{d^2 P_m}{12\mu L} = \frac{d}{L} \frac{d}{\lambda} \frac{(\pi R\theta)^{1/2}}{12(2)^{1/2}} \quad (6)$$

where P_m is the mean pressure, and the viscosity μ is given by $\mu = \frac{1}{2} \rho \bar{c} \lambda$, where ρ , \bar{c} , and λ are the density, the mean thermal speed, and the mean free path of the gas, respectively. Equation (6) holds, providing that the channel is long enough that the end effects become negligible.

Formula (6) will be assumed to be valid for $d/\lambda > 100$. It can be seen by comparing Eq. (6) with the inequality (5) that

$$T(d/\lambda = 100) < T_{Kn}$$

provided $L/d > 2700$.

Therefore, with a channel having $L/d > 2700$ if one starts in the Knudsen flow regime and increases the ratio d/λ , T initially varies from T_{Kn} to a lower value $T(d/\lambda = 100)$ and then increases without bound according to formula (6). It thus becomes apparent that, for a sufficiently long channel, T must assume a minimum in the region between the Knudsen flow and the continuum flow. In other words, this implies the existence of a minimum in T as a function of the ratio d/λ .