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Discrepancies between Theoretical and Experimental Values of Temperature behind a Shock Wave

by

J. Wilson

DISCREPANCIES BETWEEN THEORETICAL AND EXPERIMENTAL
VALUES OF TEMPERATURE BEHIND A SHOCK WAVE

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SUMMARY

In using the sodium-line reversal technique for measuring temperature,
a discrepancy between calculated and measured temperatures behind shock waves
has been observed. Possible reasons for this discrepancy are discussed.
These include (i) boundary layer effects, (ii) reduction of the shock speed
caused by dissociation of Na I, (iii) collision-limiting and non-equilibrium
effects on the radiation from the Na.

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1 INTRODUCTION

The sodium-line reversal technique as developed by Clouston, Gaydon and Glass[1] has proved to be a powerful tool for measuring temperature in a shock tube. The technique is effectively a comparison of the radiation from small amounts of sodium added to the test gas with the radiation from a source of known temperature. Early results[1,2] showed that the measured temperatures were in rough agreement with values calculated from the shock speed. However recent experiments at R.A.E. have shown that the measured temperatures are between about $60^\circ K$ and $100^\circ K$ lower than the calculated values. A similar discrepancy has been observed by Bauer[3] using chromium carbonyl instead of sodium. If the method is to be used to determine temperatures accurately, the reason for this discrepancy must be understood.

Possible causes of the discrepancy are (i) collision limiting of the radiation from the sodium (ii) change of gas properties by the addition of sodium (iii) large reflectivity of the sodium (iv) boundary-layer effects. These causes are examined below, and the conclusions used to interpret experimental work performed to determine which plays the greatest role.

2 DESCRIPTION OF THE SODIUM LINE REVERSAL TECHNIQUE

The apparatus for the single-beam line reversal technique is drawn schematically in Fig.1. Light from a tungsten lamp is focussed by lens 1 at the centre of the shock tube, and by lens 2 at the photomultiplier. Stops are provided to ensure that the effective area and solid angle as seen by the photomultiplier are the same for radiation from the gas and from the tungsten lamp, and an interference filter is used to isolate the sodium D lines. The temperature of the tungsten lamp is measured with an optical pyrometer.

The test gas is passed over heated sodium iodide before being admitted to the shock tube, and so contains a small amount of sodium iodide. The passage of a shock wave through the gas dissociates the sodium iodide, giving free sodium atoms. Before the shock arrives the photomultiplier receives radiation from the tungsten lamp only; after the shock has passed it receives radiation from the tungsten lamp, but partially absorbed by the sodium in the test gas, and also the emission from the sodium. If no change in signal is seen (a so-called "match" or "reversal") then the emission from the sodium must equal the amount of radiation from the tungsten lamp absorbed by the sodium, i.e.

$$\underbrace{R_\omega(T_B)}_{\substack{\text{Radiation from}\\ \text{lamp alone}}} = \underbrace{(1 - \alpha_\omega)R_\omega(T_B)}_{\substack{\text{Transmitted radia-}\\ \text{tion from lamp}}} + \underbrace{\varepsilon_\omega R_\omega(T_{Na})}_{\substack{\text{Emitted radiation}\\ \text{from sodium}}} \qquad (1)$$

where $R_\omega(T)$ = spectral radiancy at temperature T and wave number ω

α_ω = spectral absorptivity of the sodium

ε_ω = spectral emissivity of the sodium

T_B = black body temperature of the tungsten lamp

T_{Na} = temperature of the sodium.

The spectral radiancy is given by the well known formula of Planck

$$R_\omega(T) = \frac{2\pi h c^2 \omega^3}{\left[\exp\left(\frac{hc\omega}{kT}\right) - 1\right]} \tag{2}$$

where h = Planck's constant

c = speed of light

k = Boltzmann's constant.

By Kirchhoff's Law, $\alpha_\omega = \varepsilon_\omega$ and consequently, at a match

$$R_\omega(T_B) = R_\omega(T_{Na}) \tag{3}$$

which can only be satisfied if the temperature of the sodium is the same as the black body temperature of the tungsten lamp.   Since the above is true at all wave numbers, the result is unaffected by the fact that the photomultiplier receives radiation over a range of wave numbers (as determined by the interference filter).

The assumption is now made that the temperature of the gas is the same as that of the sodium.   Thus if the tungsten lamp can be set at an appropriate temperature, and if the strength of the shock can be controlled accurately enough to achieve a match behind the shock, the gas temperature can be measured. In practice this is difficult to do, and it is preferable to use a double beam technique instead.

The double beam technique employs two beams of the type just described. However, instead of attempting to set the temperatures of the lamps at the gas temperature, one is set higher, and the other lower than the expected temperature behind the shock.   Then if one lamp is at a black body temperature T_1, and its photomultiplier gives a signal y_1 behind the shock (relative to the signal before the shock passage, i.e. y_1 is the A.C. signal only), and T_2 and y_2 are the lamp temperature and photomultiplier signal for the other beam

$$y_1 = k_1 \int_{\Delta\omega} \varepsilon_\omega [R_\omega(T_{Na}) - R_\omega(T_1)] \, d\omega \tag{4}$$

$$y_2 = k_2 \int_{\Delta\omega} \varepsilon_\omega [R_\omega(T_{Na}) - R_\omega(T_2)] \, d\omega \tag{5}$$

where the integration is to be performed over all wave numbers for which ε_ω differs from zero (i.e. over the whole "width" of the D lines). Here k is a constant of proportionality depending on the geometry of the beams, the transmission of the interference filter and the photomultiplier response, and must be made equal for the two beams by prior calibration. Since the lines are narrow it is possible to approximate the above expressions by

$$y_1 = k \left[R_{\omega_0}(T_{Na}) - R_{\omega_0}(T_1) \right] \int_{\Delta\omega} \varepsilon_\omega \, d\omega \qquad (6)$$

$$y_2 = k \left[R_{\omega_0}(T_{Na}) - R_{\omega_0}(T_2) \right] \int_{\Delta\omega} \varepsilon_\omega \, d\omega \qquad (7)$$

where ω_0 is the wave number at the centre of the lines. Equations (6) and (7) can be solved to give

$$R_{\omega_0}(T_{Na}) = R_{\omega_0}(T_1) + \frac{y_1}{(y_1 - y_2)} \left[R_{\omega_0}(T_2) - R_{\omega_0}(T_1) \right] \qquad (8)$$

which determines the temperature of the sodium atoms, and

$$\int_{\Delta\omega} \varepsilon_\omega \, d\omega = \frac{(y_1 - y_2)}{k \left[R_{\omega_0}(T_2) - R_{\omega_0}(T_1) \right]} . \qquad (9)$$

For an optically thin gas $\int_{\Delta\omega} \varepsilon \, d\omega$ is proportional to the concentration of the sodium atoms, and so a relative measure of this quantity could be obtained from the photomultiplier signal. For an optically thick gas $\int_{\Delta\omega} \varepsilon_\omega \, d\omega$ is a more complicated function of the sodium concentration, as will be seen later.

Thus the double beam technique gives the temperature even when no match has been achieved, and provides a measure of the sodium concentration in addition.

3   SOURCES OF DISCREPANCY

In the above description of the sodium-line reversal technique, several assumptions have been made (either explicitly or implicitly). These must now be examined to see if they do in fact hold, and if their failure to hold could

give rise to the observed disagreement between measured and calculated temperatures.

3.1 Collision limiting

Previously the assumption was made that the temperature of the sodium is the same as the temperature of the gas. Gaydon[4] has suggested that the sodium will tend to equilibrate with the vibrational temperature of the gas, which may differ from the translational temperature. However the present tests were done in oxygen at Mach numbers such that the vibrational relaxation time was short, and hence no difference exists between the vibrational and translational temperatures of the oxygen. The question as to whether the sodium atoms in fact achieve equilibrium with the gas still exists. For the radiation from the sodium to be at the equilibrium value for the gas temperature it is necessary that the population of excited sodium atoms (i.e. the radiating species) be at the equilibrium value. The population of the excited level of the sodium is brought about by collisions, and depopulation occurs either by collision or by emission of radiation. If the emission of radiation is capable of depopulating the level faster than it can be populated by collisions, the population of the level will be below the equilibrium value, and the radiation is then said to be "collision limited".

It has been suggested that this phenomenon is the reason for measured values of flame temperatures being lower than theoretical values[5]. For the population of the excited sodium to be at the equilibrium level, the rate of depopulation by collisions must be greater than that by radiation[6]. Thus if binary collisions are responsible for deactivation, a necessary condition for equilibrium radiation is[6]

$$\frac{[\text{Na}\cdot]}{\tau_R} \ll \sigma \, v \, [\text{Na}\cdot][X] \qquad (10)$$

where [Na·] is the concentration of excited sodium

τ_R is the radiative lifetime of excited sodium

σ is the cross-section for deactivation of sodium by gas X

v is the mean velocity of collisions between sodium and X

[X] is the concentration of the test gas.

For sodium $\tau_R = 1.6 \times 10^{-8}$ sec (Ref.7). Unfortunately σ, the deactivation cross-section of sodium is not known for oxygen, the parent gas in the present experiments. However, for hydrogen as parent gas, $\sigma = 0.74 \times 10^{-15}$ cm^2, and for nitrogen, $\sigma = 1.45 \times 10^{-15}$ cm^2 (Ref.8), so it does not seem unreasonable to assume a value of $\sigma = 10^{-15}$ cm^2 for oxygen. Using this value, and numerical values of v and $[O_2]$ appropriate to a shock at $M = 6.5$ propagating into 10 mm Hg of oxygen, the condition above becomes

$$\frac{1}{1.6 \times 10^{-3}} \ll 1.56 \times 10^9 \qquad (11)$$

and is thus reasonably well satisfied. Consequently collision limiting is not likely to cause the observed discrepancy, particularly since the above calculation is effectively for an optically thin gas, whereas in fact the gas will be fairly thick optically, and will re-absorb most of the emitted radiation. However, if collision limiting is occurring, its effect will be reduced if the oxygen density (and hence number of collisions/sec) is increased, and will be increased if the oxygen density is reduced, but it will be independent of changes in the sodium concentration.

3.2 Effect of sodium addition

The temperature of the gas behind the shock is usually calculated from the shock speed by assuming that no sodium is present, the actual sodium concentration present being considered too small to affect the temperature of the gas. The amount of sodium introduced into the gas is in fact difficult to control. In the present experiment sodium is introduced by passing the test gas over heated sodium iodide immediately before entering the shock tube. Behind the shock wave the sodium iodide becomes dissociated, and hence the gas must supply the heat of dissociation. If appreciable amounts of sodium iodide are present, this will lower the temperature behind the shock (i.e. compared with a shock of the same speed into a test gas containing no sodium). In this section calculations of the temperature behind shocks in oxygen containing small amounts of sodium iodide will be made, in order to estimate the magnitude of the effect.

The enthalpy for a mixture of oxygen and sodium iodide for which c is the ratio of the number of sodium iodide molecules initially present to the total number of molecules initially present is

$$H = \frac{RT}{m} \left\{ \frac{7}{2} + (1-c)\left[\frac{3}{2}\alpha + (1-\alpha)\eta\right] + \frac{3}{2}c\beta \right\} + (1-c)\alpha \frac{R}{m} T_{D_{O_2}} + c\beta \frac{R}{m} T_{D_{NaI}}$$

$$\dots (12)$$

where m = average molecular weight of the gas = $(1-c)\, m_{O_2} + c\, m_{NaI}$

α = degree of dissociation of oxygen

β = degree of dissociation of sodium iodide

η = electronic and vibrational energy of oxygen per mole divided by RT

$T_{D_{NaI}}$ = dissociation energy of sodium iodide expressed as a temperature

$T_{D_{O_2}}$ = dissociation energy of oxygen, expressed as a temperature.

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No vibrational energy has been included for sodium iodide as it will not be excited before the shock, and the sodium iodide is completely dissociated (i.e. $\beta = 1$) behind the shock for the liach numbers of interest here. Also the sodium iodide has been treated as a gas, which may not be true.

The equilibrium conditions behind the shock will be given by the solution of the conservation equations, the equation of state, and the law of mass action equations for equilibrium. In shock-fixed co-ordinates these equations are

Conservation of mass $\qquad \rho_1 \, u_1 = \rho_2 \, u_2$

Conservation of momentum $\qquad p_1 + \rho_1 \, u_1^2 = p_2 + \rho_2 \, u_2^2$

$$\left. \begin{array}{l} \\ \\ \\ \\ \end{array} \right\} \quad (13)$$

Conservation of energy $\qquad H_1 + u_1^2/2 = H_2 + u_2^2/2$

Equation of state $\qquad p = \rho \, \dfrac{RT}{m} \{1 + (1 - c) \, \alpha + c \, \beta\}$

Law of mass action for oxygen dissociation $\alpha_1 = 0$, $\qquad \dfrac{\alpha_2^2}{1 - \alpha_2} = \dfrac{K m}{4 \rho \, N_o (1 - c)}$

$$(14)$$

Law of mass action for sodium iodide dissociation $\beta_1 = 0$, $\quad \beta_2 = 1$,

where K = equilibrium constant for oxygen dissociation

N_o = Avagadro's number.

Suffix 1 refers to conditions ahead of the shock, and suffix 2 to conditions behind the shock. The calculation of K and η is described in the Appendix to Ref.9 — these calculations have been repeated and the results are given in Table 1. The conservation equations and the equation of state combine to give

$$\frac{\rho_2}{\rho_1} = \frac{2(H_2 - H_1)}{[1 + c + (1 - c) \, \alpha] \, \dfrac{RT_2}{m} - \dfrac{\rho_1}{\rho_2} \, \dfrac{RT_1}{m}} - 1 \qquad (15)$$

The term involving ρ_1/ρ_2 in the denominator on the right-hand side of this equation is small compared with the other term in the denominator. Consequently little error is made by guessing ρ_1/ρ_2 in this term (but not on the left-hand side). The equation can then be used to eliminate ρ_2 from the law

of mass action expression for oxygen. The resulting equation is solved for a_2 at a given T_2, and hence H_2 and ρ_2/ρ_1 can be calculated. This ρ_2/ρ_1 is then used as a new "guess" on the right-hand side, and the process repeated. When consistent results are obtained the velocity of the shock is given by

$$u_1^2 = \frac{2(H_2 - H_1)}{1 - (\rho_1/\rho_2)^2} \tag{16}$$

from which the Mach number follows, $M = u_1/a_1$.

Using this iteration scheme the shock equations have been solved on the R.A.E. Mercury computer for $c = 0$, 0.002, 0.004, 0.006, 0.010 and 0.020, at initial pressures of 5 mm Hg, 10 mm Hg and 20 mm Hg. In figures 2,3 and 4 the temperatures behind shocks are plotted as a function of shock Mach number. From these plots it will be seen that an addition of 1% ($c = 0.010$) of sodium iodide drops the temperature behind the shock by about $100°$ at Mach 7. The depression of temperature appears to be proportional to the fraction of sodium present, but is almost independent of initial pressure at a given Mach number. The effect is more marked at lower shock speeds, where the dissociation energy of sodium iodide is a larger fraction of the total enthalpy.

The presence of 1% of sodium iodide could therefore explain the observed discrepancy. This can be verified experimentally by measuring the fraction of sodium iodide present, and by determining whether the discrepancy is proportional to the relative fraction of sodium iodide present.

3.3 Effect of reflectivity

It was assumed previously that the sodium absorbed all the radiation from the tungsten lamp that it did not transmit. In fact the sodium may reflect some of the radiation. The transmissivity of the sodium at wave number ω becomes in this case

$$\tau_\omega = (1 - r_\omega - a_\omega) \tag{17}$$

where r_ω = the reflectivity of the sodium. Thus for the photomultiplier to receive the same amount of radiation in front of and behind the shock (i.e. at a match)

$$R_\omega(T_B) = \varepsilon_\omega R_\omega(T_{Na}) + R_\omega(T_B)(1 - r_\omega - a_\omega) \tag{18}$$

using Kirchhoff's Law again.

$$R_\omega(T_{Na}) = R_\omega(T_B)\left[1 + \frac{r_\omega}{\varepsilon_\omega}\right] \tag{19}$$

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Therefore the temperature of the sodium is higher than that of the lamp at a match, and to assume that $T_{Na} = T_B$ underestimates the temperature of the sodium. As early as 1902, Lummer and Pringsheim[10] suggested that this might be the cause of measured flame temperatures being lower than theoretical values.

At the temperatures and wave number in question here, the spectral radiancy can be approximated by Wien's Law

$$R_\omega = 2\pi h c^2 \omega^3 \exp\left(-\frac{hc\omega}{kT}\right) . \tag{20}$$

Inserting (20) into (19) leads to

$$T_{Na} - T_B \approx \frac{(T_{Na})^2 k}{hc\omega} \ell n \left(1 + \frac{r_\omega}{\varepsilon_\omega}\right) \tag{21}$$

For the sodium D lines $\omega = 16,970$ cm^{-1}. The shocks used in the experiments were such that $T_{Na} \approx 2500^\circ K$, and for an optically thick gas $\varepsilon_\omega \to (1 - r_\omega)$. Consequently

$$T_{Na} - T_B \approx 260 \, \ell n \left(\frac{1}{1 - r_\omega}\right) . \tag{22}$$

Thus if the reflectivity of the gas can be calculated, an estimate of temperature difference between the sodium and the tungsten lamp can be made. The spectral reflectivity is related to the index of refraction n_ω at wave number ω, by

$$r_\omega = \left(\frac{n_\omega - 1}{n_\omega + 1}\right)^2 . \tag{23}$$

The index of refraction of a spectral line is given by dispersion theory[11],[12] as

$$(n_\omega^2 - 1) = \frac{2N e^2 f \, 4\pi(\omega - \omega_0)}{m \, \omega_0 [16\pi^2 c^2 (\omega - \omega_0)^2 + \gamma^2]} \tag{24}$$

where   e = charge on an electron

m = mass of an electron

N = density of sodium atoms in atoms/cc

f = oscillator strength of sodium line

ω_0 = wave number at centre of the sodium line

γ = reciprocal of the effective radiative lifetime.

The maximum reflectivity will be at minimum index of refraction which occurs at $-4\pi\, c(\omega - \omega_0) = \gamma$ and is

$$(\hat{n}_\omega^2 - 1) = -\frac{N\, e^2\, f}{m\, c\, \omega_0\, \gamma} = -1.7 \times 10^{-16}\, N\, f. \tag{25}$$

For the sodium line at $\lambda = 5890\ \overset{o}{\text{A}}$, $f = 0.67$. It will be shown later that in the experiments $N \approx 5 \times 10^{15}$, and $\gamma \approx 3 \times 10^{9}$ sec^{-1} when the initial pressure is 10 mm Hg. For these conditions

$$(\hat{n}_\omega^2 - 1) \approx -0.6$$

and hence

$$r_\omega \approx 0.05 . \tag{26}$$

From equation (22) the temperature difference between the sodium and the tungsten lamp turns out to be 12°K.

The above calculation has only considered one wave number - that for which the reflectivity is a maximum. In fact the photomultiplier receives radiation over the whole width of the spectral lines, and the calculation should be modified accordingly. However this cannot give a greater temperature difference than that found at the maximum reflectivity, and since this is small compared with observed temperature differences, the calculation is unnecessary. A more valid criticism of the above calculation is that it has neglected Doppler broadening, although the lines are predominantly Doppler-broadened in the experiments. For Doppler-broadened lines the index of refraction will be given by

$$(n_\omega^2 - 1) = \frac{2N\, e^2\, f}{m\, \omega_0} \frac{(\ell n2)^{\frac{1}{2}}}{b_D\, \sqrt{\pi}} \int_{-\infty}^{\infty} \frac{4\pi(\omega - \omega_0 + x)\, e^{-\left(\frac{x^2\, \ell n2}{b_D^2}\right)}}{16\pi^2\, c^2(\omega - \omega_0 + x)^2 + \gamma^2}\, dx$$

$$\ldots \tag{27}$$

where b_D = Doppler half width of the spectral line = $(\ell n2)^{\frac{1}{2}}\left(\frac{2kT}{mc^2}\right)^{\frac{1}{2}} \omega_0$.

In view of the complexity of the integral, the calculation has not been performed for this case. However it does not seem likely that the result of such a calculation would differ markedly from the previous result.

The conclusion is that reflectivity is unlikely to be the cause of the observed temperature discrepancy. This can be verified experimentally by observing whether or not the temperature discrepancy depends only on absolute sodium concentration, as would be the case if it were caused by reflectivity.

3.4 Boundary-layer effects

If the sodium is not in an isothermal region, the line reversal technique will measure some form of average temperature. Strong and Bundy[13] have performed calculations for the case of two adjacent isothermal regions of different temperature, and have shown that it is not necessary that reversal be achieved at each wave number in order to obtain an overall reversal with an instrument of low resolution. That is to say that the two layers of sodium may absorb more radiation from the tungsten lamp than they emit at some wave numbers, and emit more than they absorb at other wave numbers, but when integrated over all wave numbers, the amount of radiation absorbed equals that emitted. These calculations checked well with experiments on flames.

In a shock tube, a boundary layer develops along the wall of the tube, and the sodium in the boundary layer will be at a different temperature from that in the main stream. In order to estimate the apparent reversal temperature, a knowledge of the density and temperature throughout the boundary layer is required; this can then be used in an analysis similar to that of Strong and Bundy. In view of the laboriousness of such a calculation it has not been attempted, and further remarks will be based on more general considerations.

The main difference between any effect caused by the boundary layer and possible sources of discrepancy considered previously is that the boundary layer changes with time. Thus immediately behind the shock the boundary layer is of zero thickness, and hence there should be no discrepancy at this point; further behind the shock the boundary layer has developed, and a discrepancy may be observed. If the effect is large enough to be observable, transition to turbulence should be quite noticeable. Boundary-layer theory shows that the boundary layer thickness depends on the inverse square root of the Reynolds number. Thus a higher initial density means a thinner boundary layer, and hence a smaller discrepancy. Unfortunately any discrepancy caused by collision limiting is also reduced by increased density, and therefore the time dependence of the boundary layer effect will have to be used to discriminate this effect from that of collision limiting.

3.5 Summary

For convenience the possible sources of a temperature discrepancy are listed below, with the factors that affect them.

Sources of discrepancy	Discrepancy increases with
Collision limiting	decreasing density of test gas
Sodium addition	increasing ratio of sodium to test gas
Reflectivity	increasing absolute sodium concentration
Boundary layer	time; decreasing density of test gas; turbulence

4.   EXPERIMENTAL WORK

4.1 Determination of the sodium atom concentration

In order to estimate the amount by which the addition of sodium iodide can depress the temperature (due to its dissociation energy) and the amount by which the effect of reflectivity appears to depress the temperature, it is necessary to have some idea of the concentration of sodium atoms in the tube. Measuring the amount of sodium iodide added before the gas enters the tube is difficult and unreliable, since some of it settles on the wall of the shock tube. It is therefore preferable to measure the concentration actually present in the test gas at the time the shock passes. Since the oscillator strengths for the sodium D lines are known, this can be done by measuring the radiation from the D lines behind the shock.

The double-beam apparatus has been used for this measurement (though a single beam is sufficient), with the difference that the tungsten lamps were off during the run. The photomultipliers thus measured only the emission from the sodium during the run. After the run, the tungsten lamps were set at a black-body temperature equal to the temperature behind the shock as calculated from the shock speed, and the corresponding photomultiplier signal noted. The ratio of the photomultiplier signal during the run to that caused by the tungsten lamp is a comparison of the emission from the sodium at a given temperature with the radiation from a black body at the same temperature, over a known wave number range (as determined by the filter) and for the same beam geometry. The transmission of the interference filter was measured with a spectrometer (see Fig.5) and the spectral response of the photomultiplier was obtained from manufacturers' data.

Theory

The spectral radiancy of a single line at wave number ω is defined by

$$R_\omega = \varepsilon_\omega R^o_\omega \qquad (28)$$

where R^o_ω = spectral radiancy of a black body at wave number ω. The spectral emissivity ε_ω is given by

$$\varepsilon_\omega = (1 - e^{-P_\omega X}) \qquad (29)$$

where P_ω = spectral absorption coefficient

   X = optical depth = (path length)×(partial pressure of radiating species)

and hence the line radiancy becomes

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$$R_L = \int_0^\infty R_\omega \, d\omega \qquad (30)$$

$$\approx R^o_{\omega_o} \int_0^\infty (1 - e^{-P_\omega X}) \, d\omega$$

for a line centred at ω_o since the range over which ε_ω differs from zero is very small in the case of a line.

To evaluate the integral it is necessary to know how the spectral absorption coefficient depends on ω. This will be determined by whether the line is collision, naturally or Doppler broadened. The natural line half-width is defined by

$$b_N = \frac{1}{4\pi c \tau_R} \qquad (31)$$

where τ_R = lifetime of excited state = 1.6×10^{-8} sec. The collision half-width is

$$b_c = \frac{1}{2\pi c} \times 3.37 \times 10^{10} \, \sigma \sqrt{\left(\frac{1}{m_{Na}} + \frac{1}{m_{O_2}}\right)} \frac{p}{\sqrt{T}} \qquad (32)$$

where σ = optical collision cross-section in $(\overset{o}{A})^2$

m_{Na} = atomic weight of sodium (gms/mole)

m_{O_2} = molecular weight of oxygen (gms/mole)

p   = total pressure in atmospheres

and the Doppler half-width is

$$b_D = \left(\frac{2k \, T \, \ell n 2}{m \, c^2}\right)^{\frac{1}{2}} \omega_o \, . \qquad (33)$$

Another important parameter is the line-shape parameter, a, defined by,

$$a = \frac{(b_N + b_c)}{b_D} \ell n 2 \, . \qquad (34)$$

various methods of solving the integral in equation (30) are described in
Ref.11. The results are summarized in the "curves of growth" (Fig.6*) in
which $R_L(\ell n2)^{\frac{1}{2}}/2R^0_{\omega_0} b_D$ is plotted against $\log_{10}(10.6\ P'X)$ with a as a
parameter. Here P' is

$$P' = \frac{(\pi \ell n2)^{\frac{1}{2}}}{b_D} \cdot \frac{e^2}{m_e c} \cdot \frac{N}{p} \cdot f(1 - e^{-hc\omega/kT}) \qquad (35)$$

where e = electronic charge (in e.s.u.)

m_e = mass of an electron

N = density of radiating species in particles/cc

p = partial pressure of radiating species

f = oscillator strength.

P' is related to the spectral absorption coefficient at the line centre
P_{ω_0} by

$$P_{\omega_0} = P'[\exp(a^2)][\text{erf c}(a)] . \qquad (36)$$

Thus if a << 1, $P_{\omega_0} \approx P'$. Consequently if the temperature and total pressure
of a gas containing an emitting specie are known, a and b_D can be calculated;
a measurement of the line radiancy yields P'X via the curves of growth, and
hence the concentration of the emitter if the oscillator strength is known.
It is also necessary to know the optical collision cross-section, and the path
length of the emitting gas.

Experimental results

An experimental oscillogram of a run with a shock Mach number of 7.04 into
oxygen containing some sodium at 10 mm Hg pressure is given in Fig.7.
Immediately behind the shock the temperature is 2500°K (but rises further behind
the shock as a result of shock attenuation), and the signal is seen to be 0.06
volts. The photomultiplier signal y_1 is proportional to the line radiancy, the
photomultiplier response at the wave number of the line, and the peak trans-
mission of the filter (since the line is much narrower than the half-width of
the filter)

$$y_1 \propto R_L\ P_{\omega_0}\ \tau_{\omega_0}$$

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* Fig.6 is reproduced from Quantitative Molecular Spectroscopy and Gas
Emissivities by S.S. Penner by kind permission of Addison-Wesley Publishing
Co. Inc. Reading, Mass.

where p_ω = photomultiplier response at wave number ω

τ_ω = filter transmission at wave number ω.

With the tungsten lamp set at $2500^\circ K$ after the run the photomultiplier signal was 1 volt. This signal, y_2, is proportional to the integral for the filter of the radiancy of a black body times the product of transmission and spectral response of the photomultiplier

$$y_2 \propto \int_0^\infty R_\omega^0 \tau_\omega p_\omega \, d\omega \ . \qquad (37)$$

Since the constant of proportionality is determined by the area and solid angle of the source, which is the same for the tungsten lamp and the sodium, and approximating

$$\frac{R_L}{R_{\omega_0}^0} = \frac{y_1}{y_2} \cdot \frac{\int_0^\infty \tau_\omega p_\omega \, d\omega}{\tau_{\omega_0} p_{\omega_0}} \ . \qquad (38)$$

From the measured filter characteristics and the photomultiplier response data listed by the photomultiplier manufacturer,

$$\tau_{\omega_0} = 0.21 \quad \text{and} \quad \frac{1}{p_{\omega_0}} \int_0^\infty \tau_\omega p_\omega \, d\omega = 120$$

and so

$$\frac{R_L}{R_{\omega_0}^0} = 34 \ . \qquad (39)$$

For the conditions behind the shock, $b_N = 0.00016 \ \text{cm}^{-1}$, $b_c = 0.0077 \ \text{cm}^{-1}$ (assuming again that $\sigma = 10 \ \text{Å}^2$), $b_D = 0.0635 \ \text{cm}^{-1}$ and hence $a = 0.087$. Consequently

$$\frac{R_L (\ell n2)^{\frac{1}{2}}}{2R_{\omega_0}^0 b_D} = 220 \ . \qquad (40)$$

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However, the curves of growth cannot be used directly, since there are **two** sodium D lines. Since the lines are far apart $(20\ cm^{-1})$ compared with their width, their line radiancies may be added to give the effective line radiancy seen by the photomultiplier. For the line at $\omega = 16,980\ cm^{-1}$ $(\lambda = 5890\ \overset{o}{A})$ the oscillator strength $f = 0.67$ and for the line at $\omega = 16,960\ cm^{-1}(\lambda = 5896\ \overset{o}{A})$, $f = 0.33$. Hence a value of $P'X_{\omega=16,980}$ is required such that $P'X_{\omega=16,980} =$

$2P'X_{\omega=16,960}$, and $\dfrac{(\ell n2)^{\frac{1}{2}}}{2b_D\ R^o_{\omega_o}}\left(R_{L_{\omega=16,980}} + R_{L_{\omega=16,960}}\right) = 220$ for $a = 0.087$.

From the curves of growth this occurs for

$$P'X_{\omega=16,980} = 10^5 . \tag{41}$$

The diameter of the shock tube, which is the path length of the emitters, is 5 cms, from which the concentration of sodium atoms

$$N = 4.5 \times 10^{15}\ atoms/cc. \tag{42}$$

Behind the shock the concentration of oxygen molecules is 2.3×10^{18} molecules/cc and thus $c = 0.002$. From Fig.3 it is seen that the temperature behind a shock into a mixture of oxygen and sodium for which $c = 0.002$ is only $20^{\circ}K$ lower than the temperature behind a shock in pure oxygen at the same Mach number. This would suggest that there is insufficient sodium iodide present to depress the temperature by the amount found experimentally. However the concentration of sodium atoms given by the above calculation is not very accurate, as it is very sensitive to the value of σ, the optical collision cross-section, which was guessed. If the true value were about half the assumed value, the concentration of sodium atoms would be three times greater. Thus to determine the sodium concentration accurately by this means, and hence decide if it is sufficient to give the observed discrepancy, the optical collision cross-section for deactivation of sodium by oxygen must be known.

4.2 Measurement of the discrepancy

If the manner in which the discrepancy between observed and calculated temperatures behind shocks varies with density and sodium concentration can be determined experimentally, it should be possible to determine the cause of the discrepancy. Accordingly shocks were run into oxygen containing sodium at 5 mm Hg, 10 mm Hg and 20 mm Hg initial pressure, and the temperature behind the shocks measured with the double-beam technique. The relative sodium concentration was varied by altering the temperature of the oven which heated the sodium iodide. As the shock waves were attenuating, the temperature at the observation point increased with time after shock passage. Consequently measurements of the shock speed at various stations along the tube were made, and the pressure at the observation point recorded. From these measurements

it is possible to calculate the temperature rise at the observation point; the method is due to Spence[14].

A typical oscillogram showing the photomultiplier record for a shock Mach number of 6.7 (as measured at the observation point) into 10 mm Hg of oxygen is given in Fig.8. The analysis of this picture along the lines of Section 2, together with the temperature rise calculated from the shock speed measurements is given in Fig.9. From Fig.9(a) it will be seen that the temperature measured by the line-reversal method is about 50°K lower than the calculated temperature shortly after the shock passage, and that this discrepancy remains constant until about 80 microseconds after shock passage, when it increases rapidly. This behaviour is typical of all the records.

The observed discrepancies for the period in which the discrepancy is constant are plotted against the initial ratio of sodium iodide molecules to total molecules present in Fig.10. In order to determine this latter quantity, a run was performed with the oven set at the same temperature as that used in the run to determine the sodium atom concentration, and the same initial pressure was used. It was assumed that the sodium atom concentration was the same for the two runs, thereby fixing the sodium atom concentration for the arbitrary value of line radiancy measured by the double-beam technique. From the appropriate region of the curves of growth it will be seen that

$$R_L \propto N^{\frac{1}{2}} \tag{43}$$

where N is the sodium atom concentration, so that the ratio of the concentration of sodium atoms for a particular run to that for the calibration run is given by the square of the ratio of the line radiancies for the two runs. The absolute value of the result is somewhat dubious however, due to the above assumption of equal sodium concentration for the calibration run and the run to determine the sodium concentration and the assumed value of the oxygen optical cross-section.

From Fig.10 it appears that the discrepancy does not depend on the density, but does depend on the relative sodium concentration. However the amount of sodium iodide present is not sufficient to depress the temperature to the extent observed, though it would be desirable to make some alternative measure of the sodium iodide concentration to confirm this. Since the discrepancy is independent of density, collision limiting does not appear to be the cause, and it was shown previously that reflectivity is an unlikely cause of the discrepancy. This would indicate that it is the presence of the boundary layer that causes the discrepancy. This indication is strengthened by the fact that transition of the boundary layer from laminar to turbulent occurs at about the same time after shock passage as the sudden increase in discrepancy mentioned previously. Transition was detected by heat transfer gauges, though with some difficulty, as the gauges tended to short out as a result of the high electron concentration due to the low ionization potential of sodium.

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* The straight line is the bisector of the angle between the lines of regression for all the data points shown.

If the boundary layer is causing the discrepancy, it would be expected that there would be no discrepancy immediately behind the shock where the boundary layer thickness is zero. That this is not observed is primarily due to the poor time response of the apparatus. As an additional effect in this region, lack of vibrational equilibrium must be considered.

Concluding remarks

The value for sodium concentration estimated in Section 4 is sufficient to account for only 20°K out of the observed temperature discrepancy of $60^{\circ} - 100^{\circ}$K in the first 100μ sec of the run. This value however was obtained by use of a number of questionable assumptions and in particular is very sensitive to the value used for the collision cross-section σ for sodium deactivation; it would be desirable to confirm this by an independent measurement of the sodium atom concentration (in this connection a direct spectro-photometric determination using a sample of gas from the channel is to be made shortly) or by repeating the experiment with a gas for which σ is known, i.e. hydrogen or nitrogen.

The most likely cause of the temperature discrepancy at later times in the run appears to be the boundary layer. As a further stage in the research of which this forms part it is planned to make an anlysis of the boundary layer along the lines of Strong and Bundy's analysis of non-uniform flames as this might point out avenues of future experimental work to test this conjecture.

Additional evidence for these conclusions is provided by the work of Bauer. In his case, collision limiting could have played a larger role, as his test gas was argon which has a low collision cross-section for sodium deactivation. However his results have the wrong density dependence for this to be the case. Bauer was able to include the heat of dissociation of chromium carbonyl in his shock calculations as he knew the amount added, so no error arose on this score. It would appear then that the boundary layer was responsible for the observed discrepancy in Bauer's work also.

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No.	Author	Title, etc.
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TABLE 1

Values of electronic and vibrational energy, and of the dissociation equilibrium constant of oxygen

$T^{\circ}K$	η	K
2000	0.5747	1.631×10^{12}
2100	0.5964	6.711×10^{12}
2200	0.6181	2.426×10^{13}
2300	0.6391	7.830×10^{13}
2400	0.6594	2.229×10^{14}
2500	0.6792	6.141×10^{14}
2600	0.6984	1.525×10^{15}
2700	0.7171	3.536×10^{15}
2800	0.7353	7.715×10^{15}
2900	0.7531	1.594×10^{16}
3000	0.7705	3.134×10^{16}

TABLE 2

Values of physical constants used

e = electronic charge = 4.8024×10^{-10} e.s.u.

m_e = mass of an electron = 9.106×10^{-28} gm

h = Planck's constant = 6.6252×10^{-27} erg sec

R = gas constant = 8.3166×10^{7} erg/mole $^{\circ}K$

k = Boltzmann's constant = 1.38042×10^{-16} erg/$^{\circ}K$

c = speed of light = 2.9979×10^{10} cm/sec

N_o = Avogadro's number = 6.0247×10^{23} molecules/mole

$T_{D_{O_2}}$ = dissociation energy of oxygen expressed as a temperature = $59,370^{\circ}K$

$T_{D_{NaI}}$ = dissociation energy of sodium iodide expressed as a temperature = $36,300^{\circ}K$
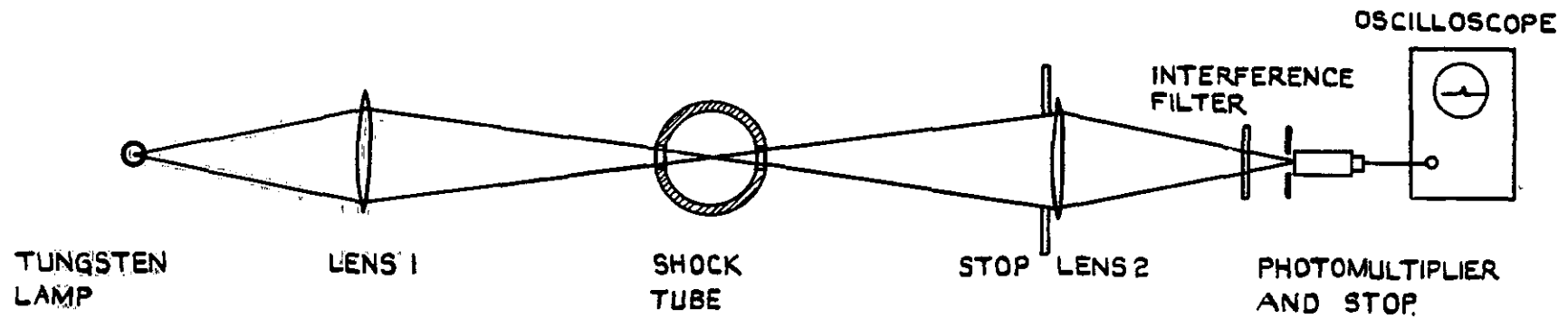
FIG. I. DIAGRAM OF APPARATUS FOR SINGLE-BEAM SODIUM-LINE REVERSAL MEASUREMENTS.
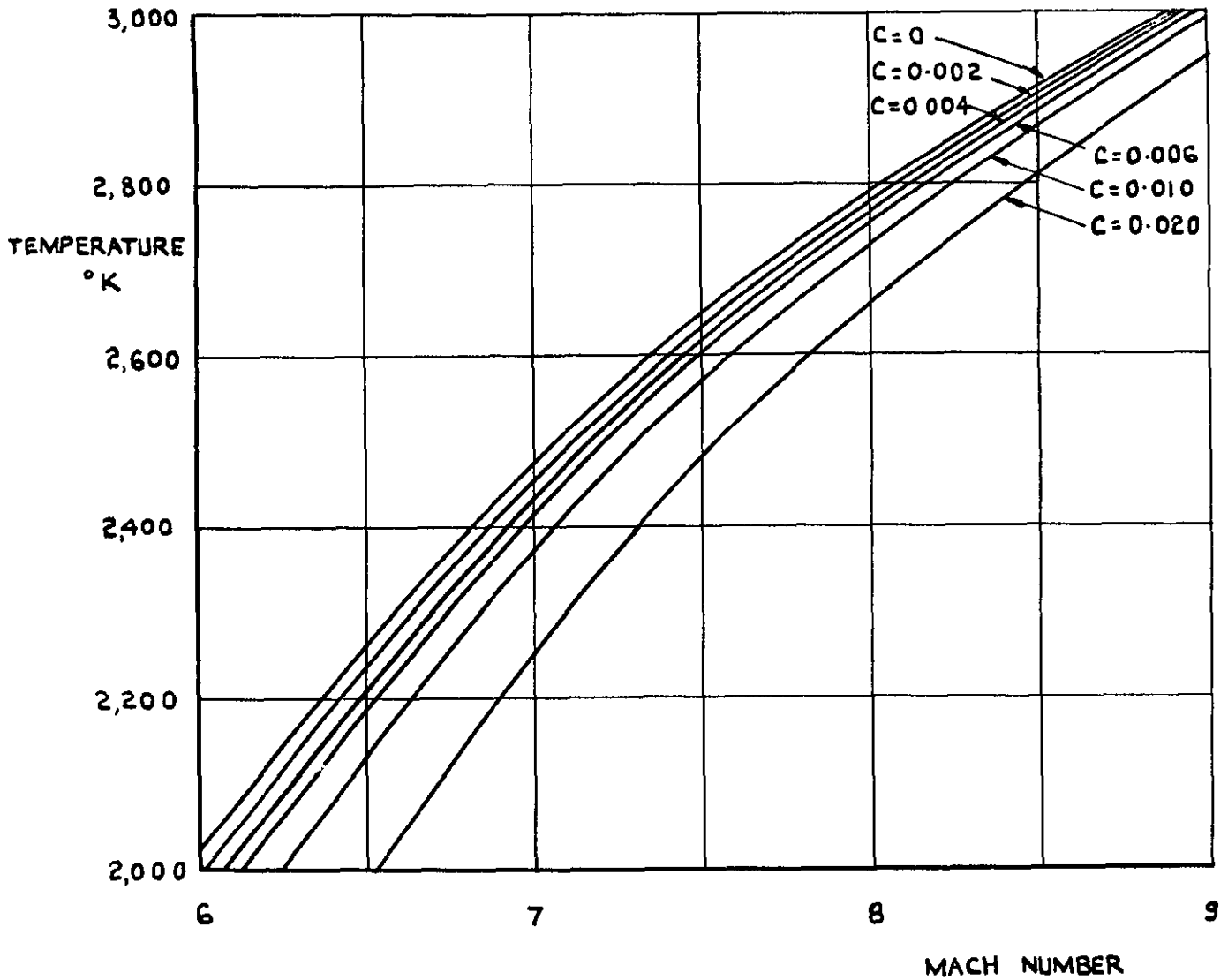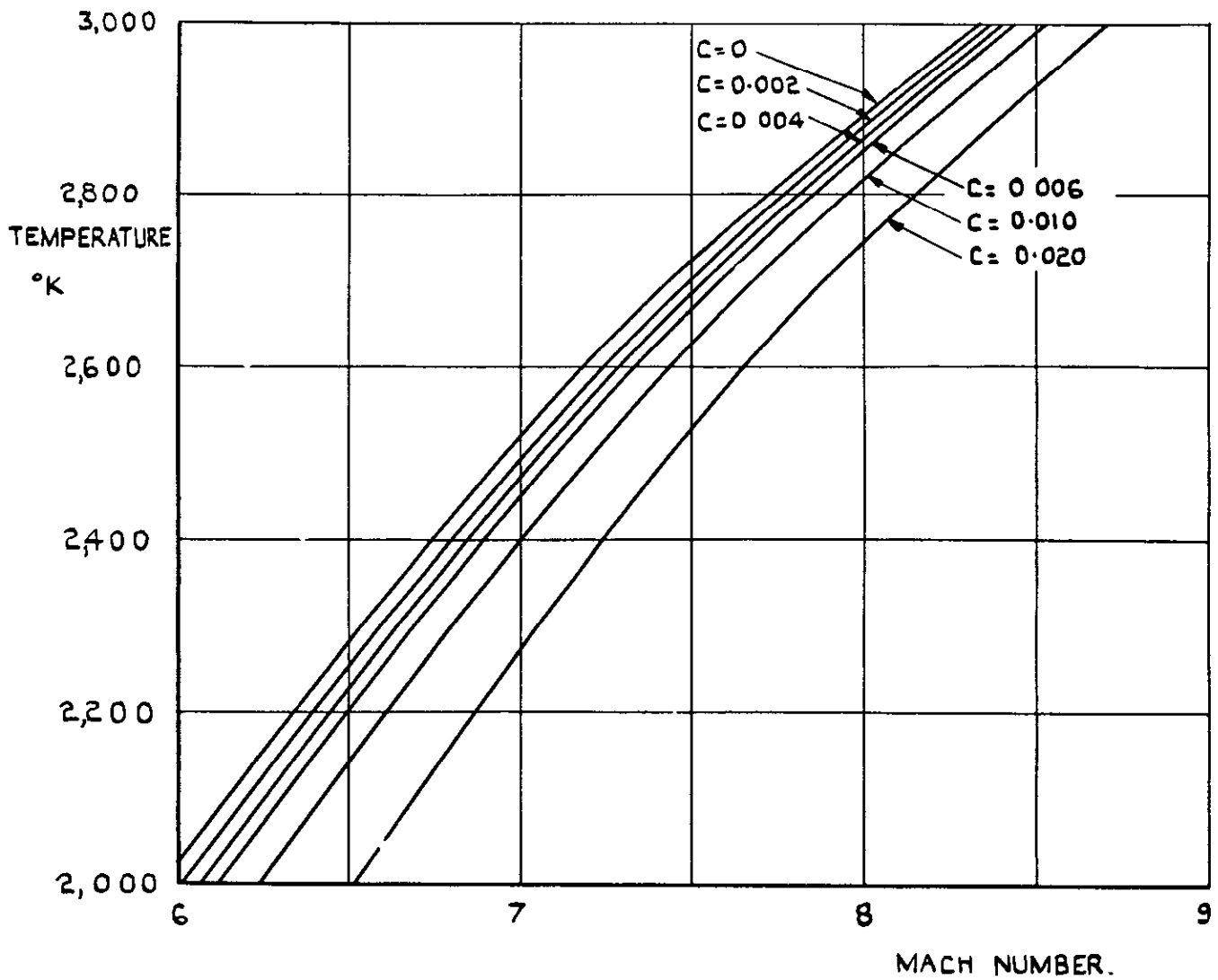
FIG. 2. TEMPERATURES BEHIND SHOCK WAVES IN VARIOUS MIXTURES OF OXYGEN WITH SODIUM IODIDE FOR INITIAL CONDITIONS $p_I = 5$ mm. Hg., $T_I = 295°$ K. THE RATIO OF THE NUMBER OF SODIUM IODIDE MOLECULES INITIALLY PRESENT TO THE TOTAL NUMBER INITIALLY PRESENT IS GIVEN BY C.
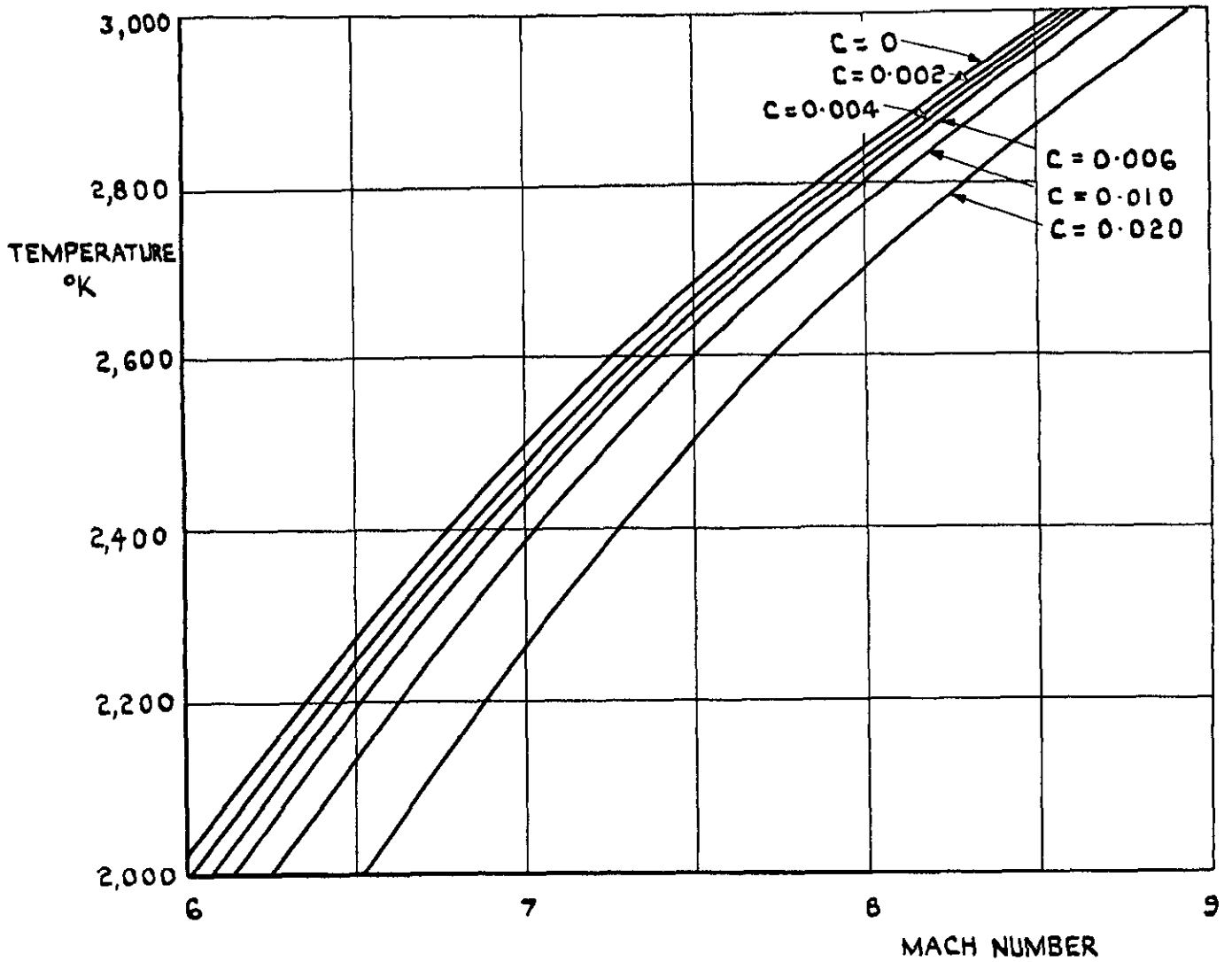
FIG. 3. TEMPERATURES BEHIND SHOCK WAVES IN VARIOUS
MIXTURES OF OXYGEN WITH SODIUM IODIDE FOR INITIAL
CONDITIONS OF p_i = 10 mm. Hg., T_i = 295°K.

FIG. 4. TEMPERATURES BEHIND SHOCK WAVES IN VARIOUS MIXTURES OF OXYGEN WITH SODIUM IODIDE FOR INITIAL CONDITIONS $p_i = 20$ mm. Hg., $T_i = 295°K$.
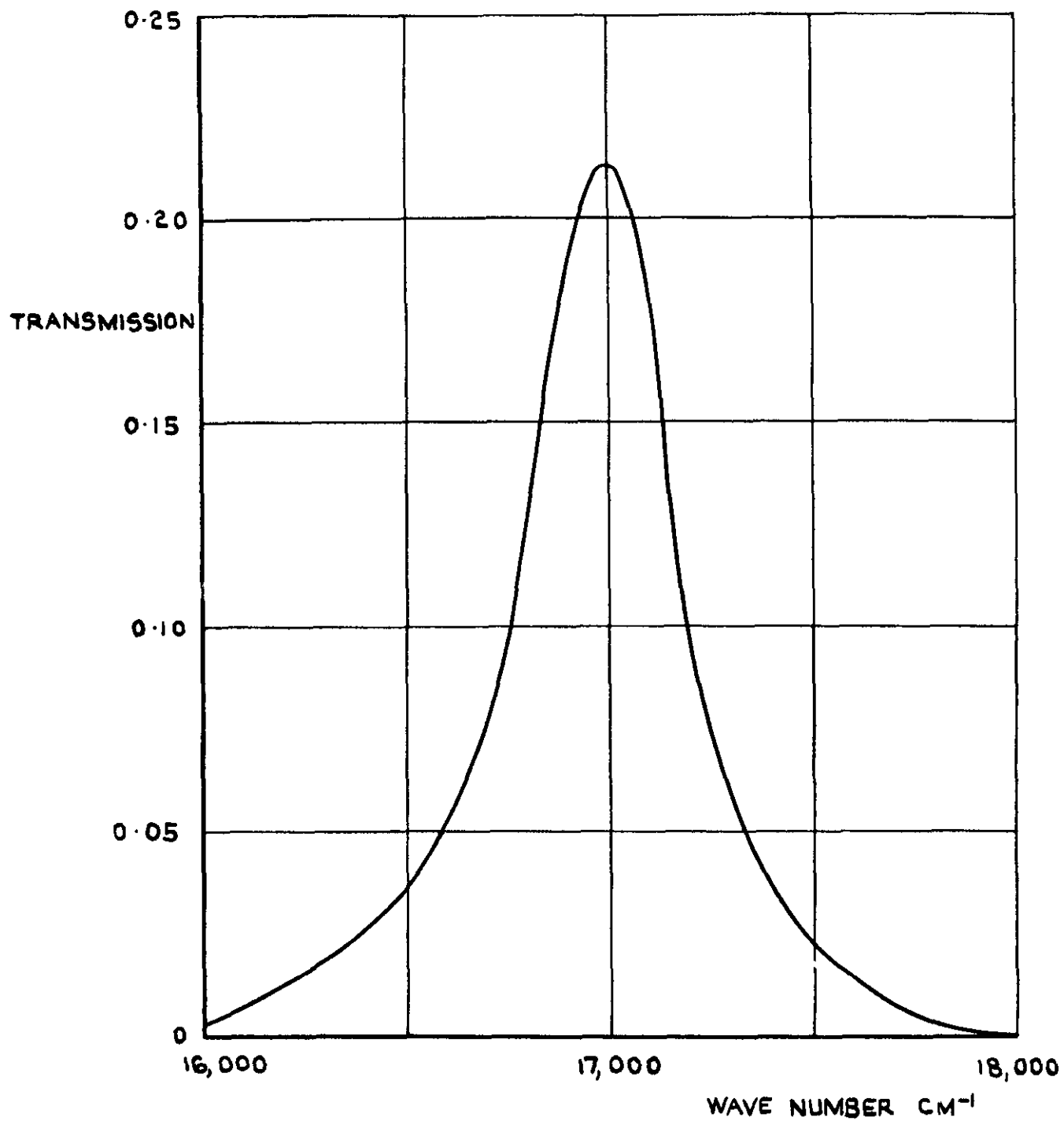
FIG. 5. TRANSMISSION OF THE INTERFERENCE FILTER.
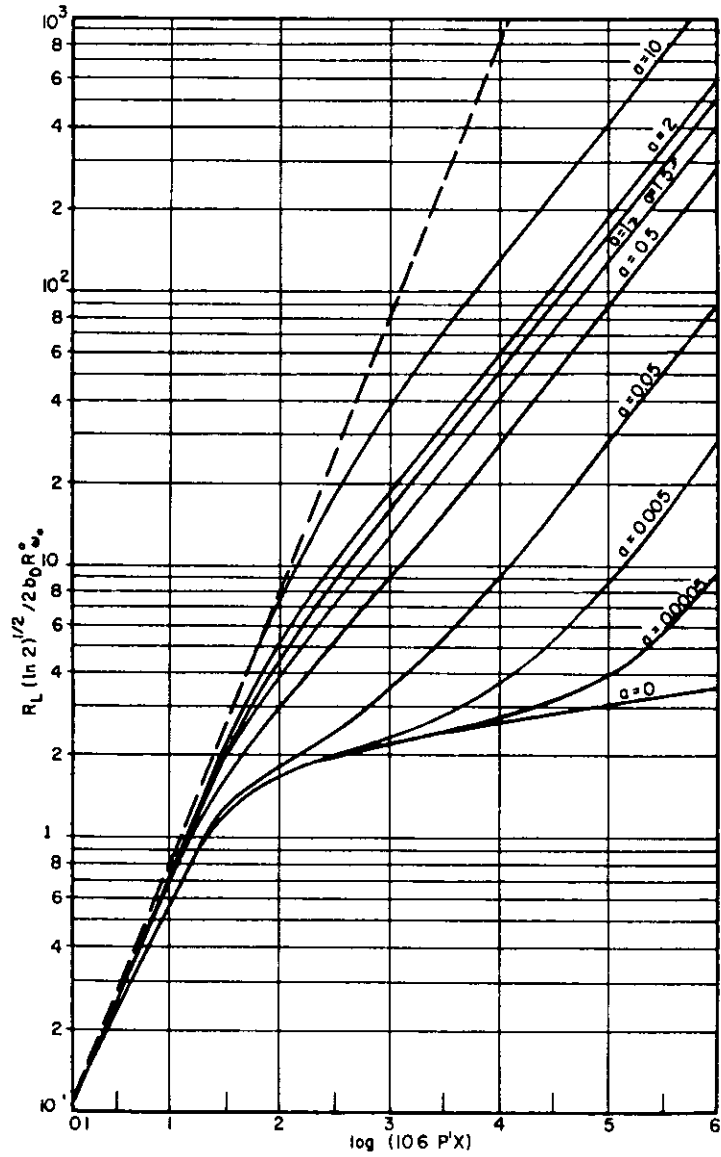
FIG.6. THE "CURVES OF GROWTH" REPRODUCED FROM QUANTITATIVE MOLECULAR SPECTROSCOPY AND GAS EMISSIVITIES BY S S. PENNER 1959, PUBLISHED BY ADDISON-WESLEY PUBLISHING Co. INC., READING, MASS.

SHOCK
ARRIVAL
↓

ARRIVAL OF
MIXING REGION
↓

0 05
VOLTS/CM
↓

50 MICROSEC/CM

FIG.7. OSCILLOGRAM OF EMISSION SIGNAL BEHIND
SHOCK WAVE AT M = 7 04 INTO 10 mm. Hg
OF OXYGEN CONTAINING ABOUT 0 2% SODIUM

SHOCK
ARRIVAL
↓

ARRIVAL OF
MIXING REGION
↓

$T_1 = 2,330°K$

$T_2 = 2,500°K$

FIG.8. OSCILLOGRAM OF DOUBLE-BEAM SIGNALS FOR
SHOCK WAVE AT M = 6 7 INTO 10 mm. Hg OF
OXYGEN CONTAINING ABOUT 0 2% SODIUM
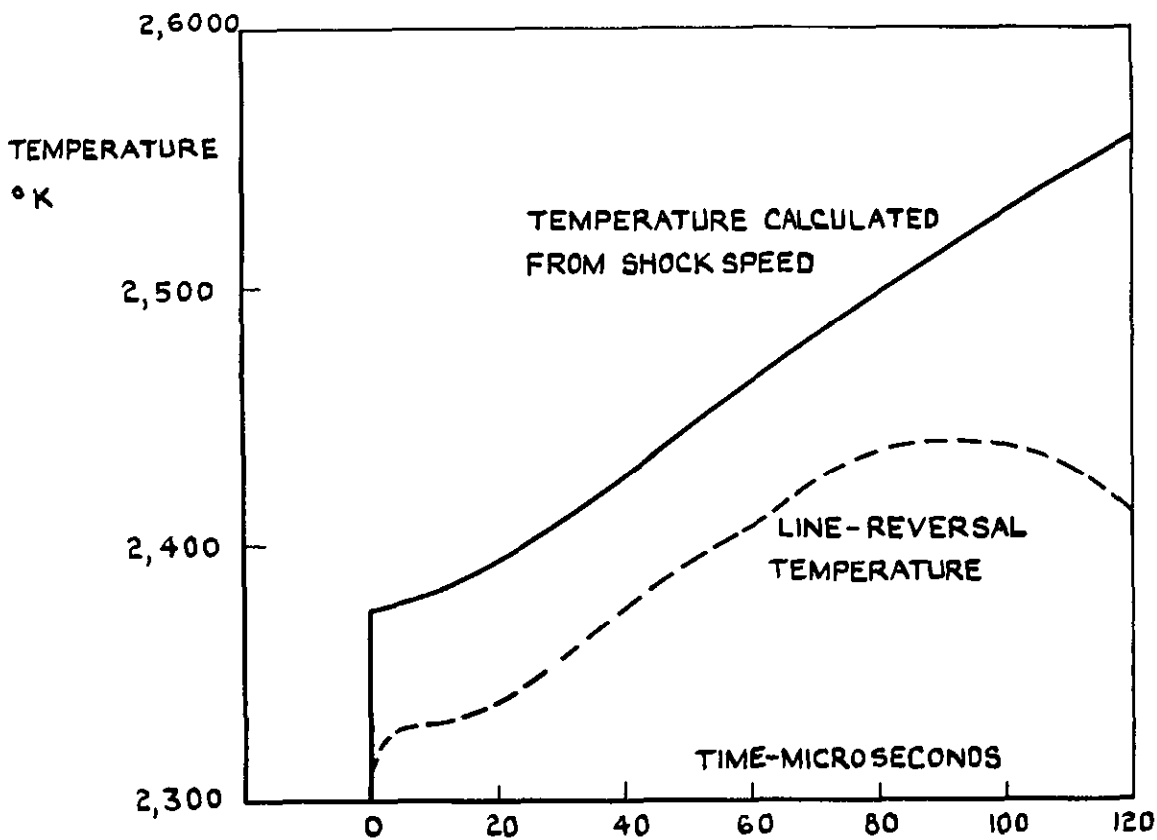
FIG. 9.(a) TEMPERATURES MEASURED DIRECTLY,
AND CALCULATED FROM SHOCK SPEED MEASUREMENTS,
AT A GIVEN STATION IN THE SHOCK TUBE
AGAINST TIME AFTER SHOCK PASSAGE.

$$\frac{R_L}{R^\circ_{\omega_o}} = \int E_\omega \, d\omega$$

ARBITRARY UNITS

TIME – MICROSECONDS
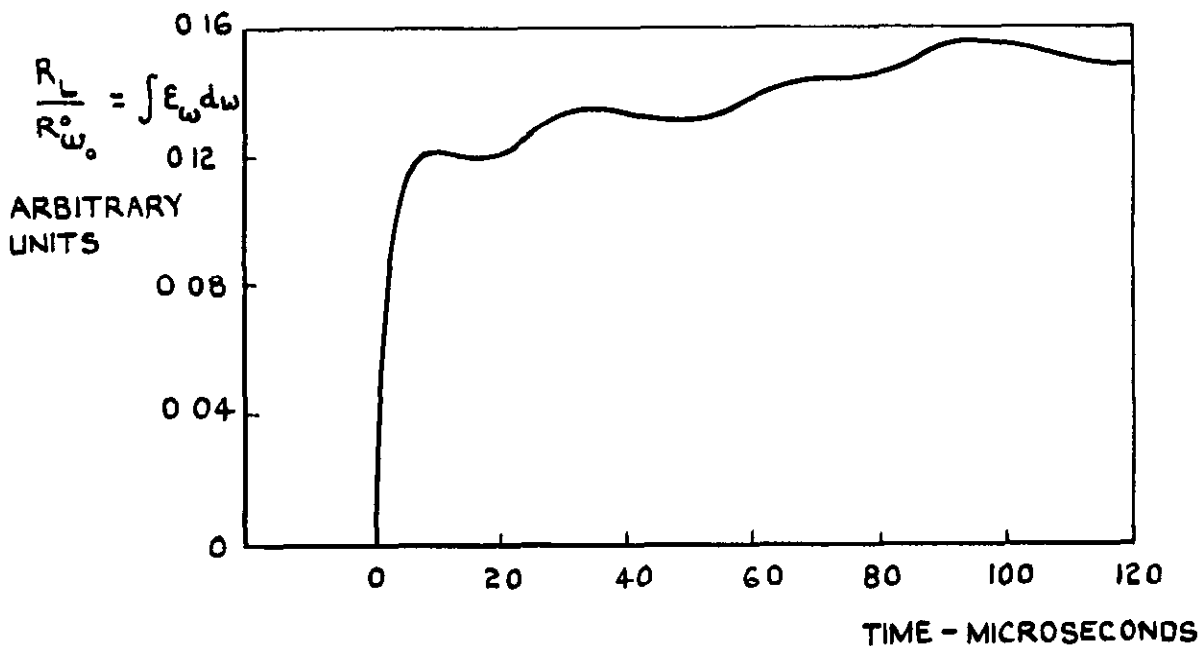
FIG 9 (b) THE LINE RADIANCY OBSERVED IN THE
SHOCK TUBE (IN ARBITRARY UNITS) AGAINST TIME
AFTER SHOCK PASSAGE.
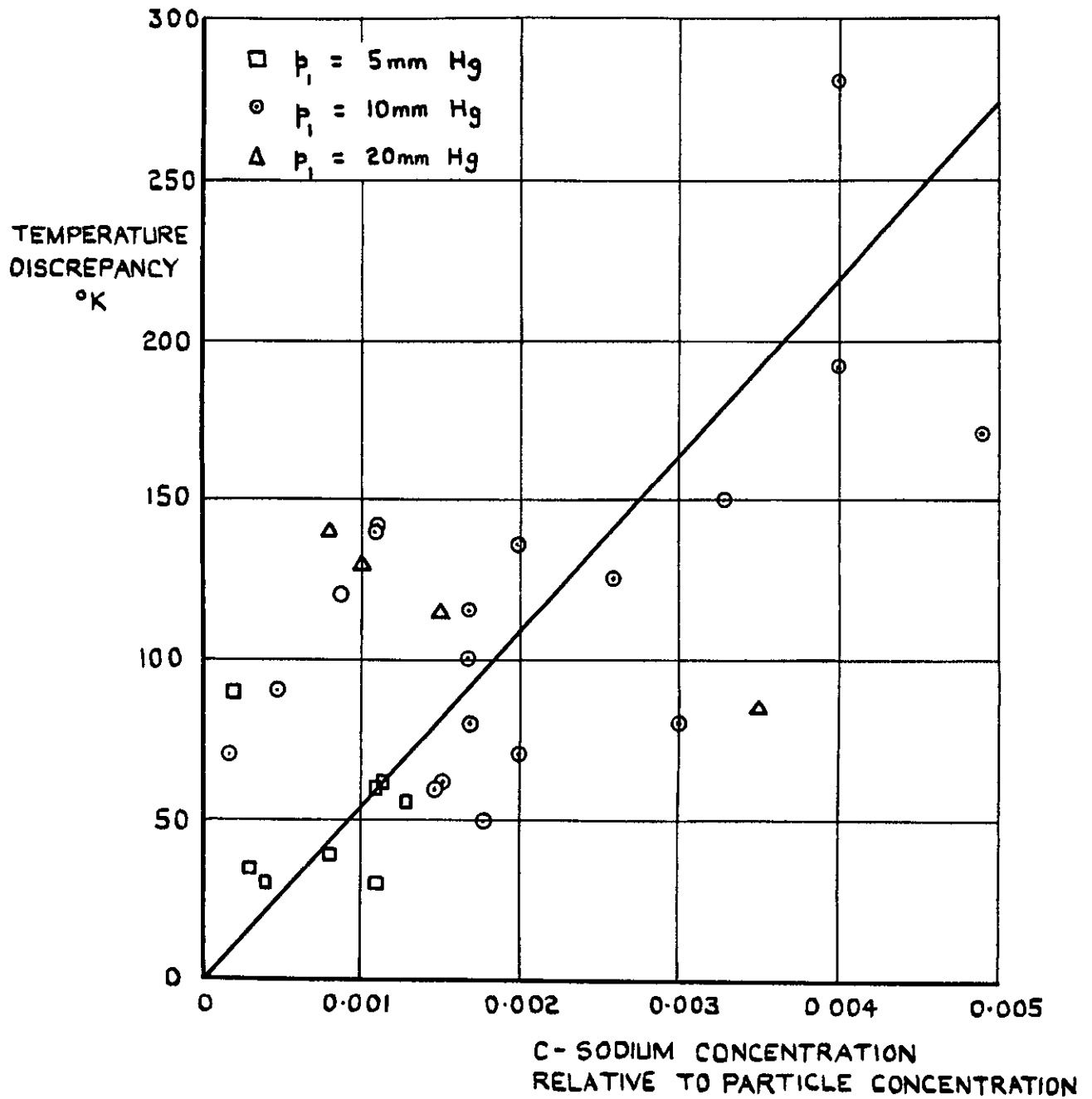
FIG.IO. THE OBSERVED DISCREPANCY BETWEEN MEASURED & CALCULATED TEMPERATURES AGAINST THE RATIO OF THE SODIUM CONCENTRATION TO THE TOTAL PARTICLE CONCENTRATION BEFORE THE SHOCK.

A.R.C. C.P. No. 712

533.6.011.72:
533.6.011.6:
536.55

DISCREPANCIES BETWEEN THEORETICAL AND EXPERIMENTAL VALUES OF TEMPERATURES
BEHIND A SHOCK WAVE. Wilson, J. March, 1963.

In using the sodium-line reversal technique for measuring temperature,
a discrepancy between calculated and measured temperatures behind shock
waves has been observed. Possible reasons for this discrepancy are dis-
cussed. These include (i) boundary layer effects, (ii) reduction of the
shock speed caused by dissociation of Na I, (iii) collision-limiting and
non-equilibrium effects on the radiation from the Na.