*Emission and Absorption of the Sodium D-Line behind a Shock Wave in Argon, Nitrogen- and Carbon Monoxide-Argon Mixtures Containing a Trace of Sodium Vapor**

By Soji TSUCHIYA

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Large translational energies are given to gaseous atoms or molecules in the duration of several collisions in a shock wave. These thermal energies are transferred by atomic or molecular collisions to other degrees of freedom, such as electronic states, vibration, rotation and chemical conversion or ionization. Therefore, the shock wave technique is a powerful tool for studying the process of energy transfer and high-speed chemical reactions.

This paper will be concerned with the temperature measurement of the shock-heated gas by the simultaneous measurement of the emission and absorption of the sodium D-resonance line ; it aims at the verification of the relation of the excitation and quenching of sodium atoms to the measured temperatures. Gaydon and Hurle have studied the same problems and have concluded that the temperature observed by the sodium D-line reversal method agrees with the vibrational temperature of shock-heated diatomic molecules.[1] Also, they found that the reversal temperature of argon gas behind a shock wave was lower than the calculated value ; they explained the observed discrepancy as being due to the existence of a radiative non-equilibrium state. The present report will give a more quantitative elucidation of those problems proposed by Gaydon and Hurle, and will attempt to clarify the physical back-ground of the sodium D-line reversal method.

Sobolev and his collaborators have, using a

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* Presented at the Symposium on Photochemistry, Sendai, Oct., 1963.

[1] A. G. Gaydon and I. R. Hurle, Eighth International Symposium on Combustion, William Wilkins Pub., N. Y. (1962), p. 309 and cited references.

spectral line of barium ion, observed the reversal temperature in shock-heated argon and have obtained a value of $4\times10^{-17}\,\mathrm{cm}^2$ as an effective quenching cross-section of an argon atom.[2] Only a little is known about the quenching or exciting atomic collisions of electronic states. The shock wave technique provides an experimental method which can inform us how the excitation of electronic states of atoms occurs by slow thermal atomic or molecular collisions. Preceding shock wave works on this problem have been undertaken from the viewpoint that the excitation of the electronic states of atoms depends on collisions with electrons rather than on collisions with atoms or molecules in the shock wave.[3,4]

Experimental

The shock tube used here is constructed with steel pipe sections 10 cm. in inner diameter; the inner walls are plated with hard chromium. Some of these sections are connected to form a driver section and a low pressure section; the lengths of these sections are 160 cm. and 480 cm. respectively. The low pressure section is pumped out to pressure below 10^{-4} mmHg by an oil diffusion pump, and the leak rate of the tube is about 3 μHg/hr. Lumirror film (polyethylene terephthalate) is used as bursting diaphragms, which are ruptured spontaneously by the accumulating pressure of the driver gas of hydrogen. There are two windows 410 cm. downstream from the diaphragm position in order to make the spectroscopic measurement. Four platinum-resistance gauges are positioned at intervals 30 cm. upstream from the window. The time interval of the two signal pulses from two platinum-resistance gauges, 60 cm. apart from each other, is measured by a 1 Mc. counter, and the shock velocity is determined. One of the other gauges is used to trigger the synchroscope which records the spectroscopic data.

The real shock velocity is not constant along the entire passage through the shock tube. Simultaneous measurements of shock velocity at two positions along the tube are performed using the four platinum-resistance gauges and the synchroscope. The results show that the uncertainty of shock velocity obtained here is less than 0.5%; this corresponds to the temperature fluctuation of about 30°K in the present experimental conditions.

The sample gases are argon, nitrogen and carbon monoxide, with nominal purities of 99.99, 99.96 and 99.5% respectively. These gases are used without further purification. Gaseous mixtures which contain nitrogen or carbon monoxide of less than 1% are made by successive dilution, and the concentrations are measured by the manometric method. Complete mixing is obtained by allowing at least 2 days for diffusion. A very small amount of sodium vapor is introduced into the test gas as follows: the sample gas is fed into the shock tube through a glass tube in which a piece of sodium metal is heated to 250~350°C. By this method, roughly controlled quantities of sodium vapor, which perhaps forms colloidal dust before the passage of the shock wave, can be mixed with the shock-heated gas. The intensity of the sodium D-line is independent of the time between the shock experiment and the introduction of the sample gas, and the time required for colloidal sodium to vaporize is very short.

The emission and absorption of the sodium D-line is observed by a two-channel monochromator. This monochromator has already been described in detail in another paper.[5] The monochromator is of the Littrow type, with two glass prisms whose apex angle is 60°. The calculated spectral slit width is $8.9\,\mathrm{cm}^{-1}$ at 5890 Å when the entrance and exit slit width is 0.1 mm. The doublet lines of the sodium D-line can be resolved by the monochromator, and the experiment is performed using one of the doublet lines corresponding to the ${}^2P_{3/2}-{}^2S_{1/2}$ transition. The accuracy of the measured temperature has been discussed in the preceding paper; the maximum error is considered to be about ±50°K at 2500°K.

The Temperature Measurement of Shock-heated Gas

The gas temperature is calculated from the measured data of the emission and absorption of a resonance spectral line. In order to discuss the physical limitation of this method, the nature of the radiation from a gaseous distributed emitter should first be considered.

A gaseous atom is here assumed to have only two levels, upper and lower. When the atoms are included within an opaque enclosure, the following equilibrium is attained:

$$N_1[A_{1\to2}+B_{1\to2}\rho(\omega_{12},\ T)]-N_2B_{2\to1}\rho(\omega_{12},\ T)=0 \tag{1}$$

where N_1, N_2 are populations of atoms on the upper and lower levels respectively, where $A_{1\to2}$, $B_{1\to2}$, $B_{2\to1}$ are Einstein's coefficients for spontaneous emission, induced emission and absorption respectively, and where $\rho(\omega_{12},\ T)$ is a radiation density at the wave number of ω_{12}, which corresponds to the energy difference between upper and lower levels. The intensity of radiation in the wave number interval $(\omega,\ \omega+\mathrm{d}\omega)$ can be defined as the amount of radiant energy falling on the unit solid angle in the unit time; it is formulated as:

$$B^\circ(\omega,\ T)\mathrm{d}\omega=\frac{1}{4\pi}c\rho(\omega,\ T)\mathrm{d}\omega$$

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[2] N. N. Sobolev et al., "Proc. of Fifth International Conference on Ionization Phenomena in Gases," Ed. by H. Maecker, North-Holland Pub. Co., Amsterdam (1962), p. 2122 and cited references.

[3] T. Wilkerson, *Univ. Michigan, Technical Note*, AFOSR 1151 (1961).

[4] S. H. Bauer, J. H. Kiefer and B. E. Loader, *Can. J. Chem.*, **39**, 1113 (1961).

[5] S. Tsuchiya, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 300 (1963).

where $\boldsymbol{c}$ is the light velocity. $(1/2)\boldsymbol{B}^\circ(\omega, T)\mathrm{d}\omega$ equals the radiant energy emitted from the black body into the unit solid angle in the unit time in the wave number interval $(\omega, \omega+\mathrm{d}\omega)$. The absorption coefficient per unit optical length is formulated by the equation:

$$\begin{aligned} k(\omega_{12}) &= \boldsymbol{h}\omega_{12}(N_2\boldsymbol{B}_{2\to1} - N_1\boldsymbol{B}_{1\to2}) \\ &= \frac{\boldsymbol{h}\omega_{12}}{\rho(\omega_{12},\ T)} N_1 A_{1\to2} \end{aligned} \tag{2}$$

Equation 1 does not hold in the case of a gaseous body which is not contained in an opaque enclosure. In this case, the radiation density, $\rho'(\omega_{12}, T)$ is different from $\rho(\omega_{12}, T)$ in Eq. 1, and it is approximated as constant within the gaseous body. The intensity of radiation from the gaseous body concerned can be defined by the use of $\rho'(\omega_{12}, T)$ as follows:

$$\boldsymbol{B}(\omega_{12},\ T)\mathrm{d}\omega = \frac{1}{4\pi}\boldsymbol{c}\rho'(\omega_{12},\ T)\mathrm{d}\omega$$

The radiation intensity depends on the optical thickness of the gaseous body; this circumstance may be described in the following manner. When the radiation flux passes through the optical length $\mathrm{d}X$, the radiation intensity takes a value of $\boldsymbol{B}(\omega_{12}, T) + \mathrm{d}\boldsymbol{B}(\omega_{12}, T)$. The radiation quanta emitted in the unit time and volume are $\{N_1[A_{1\to2} + \boldsymbol{B}_{1\to2}\rho'(\omega_{12}, T)] - N_2\boldsymbol{B}_{2\to1}\cdot \rho'(\omega_{12}\ T)\}$. Therefore, the increase in radiation intensity, $\mathrm{d}\boldsymbol{B}(\omega_{12}, T)$, can be formulated as:

$$\begin{aligned} \mathrm{d}\boldsymbol{B}(\omega_{12},T) = \frac{\boldsymbol{hc}\omega_{12}}{4\pi}\{N_1[A_{1\to2} + \boldsymbol{B}_{1\to2}\rho'(\omega_{12},\ T)] \\ - N_2\boldsymbol{B}_{2\to1}\rho'(\omega_{12},\ T)\}\mathrm{d}X \end{aligned} \tag{3}$$

which is simplified by the introduction of $k(\omega_{12})$ in Eq. 2 as follows:

$$\begin{aligned} \mathrm{d}\boldsymbol{B}(\omega_{12},\ T) &= k(\omega_{12})\frac{\boldsymbol{c}}{4\pi}[\rho(\omega_{12},\ T) \\ &\qquad - \rho'(\omega_{12},\ T)]\mathrm{d}X \\ &= k(\omega_{12})[\boldsymbol{B}^\circ(\omega_{12}, T) - \boldsymbol{B}(\omega_{12}, T)]\mathrm{d}X \end{aligned}$$

Therefore, by integrating the above equation, the spectral intensity:

$$\boldsymbol{B}(\omega_{12},\ T) = \boldsymbol{B}^\circ(\omega_{12},\ T)\{1 - \exp[-k(\omega_{12})X]\} \tag{4}$$

is derived.

It is important to notice that the equilibrium condition is admitted into Eq. 4 inexplicitly by introducing the absorption coefficient $k(\omega_{12})$, which is defined in condition 1 of the radiation equilibrium. This means that the Boltzmann distribution between the upper and lower levels is maintained;

$$N_1/N_2 = (g_1/g_2)\exp(-\boldsymbol{hc}\omega_{12}/\boldsymbol{k}T) \tag{5}$$

where g_1 and g_2 are the statistical weights of the upper and lower levels respectively. In Eq. 4, the factor $\{1-\exp[-k(\omega)X]\}$ is a spectral emissivity, and an emission from any body may be represented by such an emissivity and the radiation density of "hohlraum radiation." The emissivity is the function of the concentration of atoms or molecules emitting a spectral line and of the optical length of the gaseous system. The assumption that the emission from the gaseous body is the thermal radiation originates from the acknowledgement of equilibrium relation 5 in the gas.

It is convenient to define the effective emissivity, E_ω, since the emission from the gaseous body is measured by the monochromator, which has a finite spectral resolving power. If $g(\omega', \omega)$ is a spectral slit function when the monochromator is set at a certain wave number, ω, an effective emissivity is:

$$E_\omega = \int g(\omega',\ \omega)\{1 - \exp[-k(\omega')X]\}\mathrm{d}\omega'/\overline{\Delta\omega} \tag{6}$$

and,

$$\overline{\Delta\omega} = \int g(\omega',\ \omega)\mathrm{d}\omega'$$

where $\overline{\Delta\omega}$ is a spectral slit width expressed in wave numbers.

The observed intensity of the sodium D-line from the high-temperature gas containing sodium atoms is;

$$\begin{aligned} I_d &= \int g(\omega',\ \omega_d)\boldsymbol{B}^\circ(\omega',\ T_g) \\ &\qquad \times\{1 - \exp[-k(\omega')X]\}\mathrm{d}\omega'\cdot\Delta\Omega\cdot\Delta s \\ &= E_d\boldsymbol{B}^\circ(\omega_d,\ T_g)\overline{\Delta\omega}\cdot\Delta\Omega\cdot\Delta s \end{aligned} \tag{7}$$

where ω_d is the wave number of the sodium D-line, T_g is the temperature of a gas, E_d is the effective emissivity of the sodium D-line, and $\Delta\Omega$ and Δs are the solid angle of a light-flux incident on the monochromator and the area of the slit respectively. Also, the intensity of the light beam from the standard light source, whose spectral radiancy is the same as the black body of the temperature, T_0, is represented as a sum of emission and absorption terms that is,

$$\begin{aligned} I_l = [&E_d\boldsymbol{B}^\circ(\omega_d,\ T_g) \\ &+ (1-E_d)\boldsymbol{B}^\circ(\omega_d,\ T_0)]\overline{\Delta\omega}\cdot\Delta\Omega\cdot\Delta s \end{aligned} \tag{8}$$

The light beam from the standard light source without an absorption by the gaseous body has an intensity of

$$I_0 = \boldsymbol{B}^\circ(\omega_d,\ T_0)\overline{\Delta\omega}\cdot\Delta\Omega\cdot\Delta s \tag{9}$$

The following relation can be derived from Eqs. 7, 8 and 9:

$$\frac{I_l - I_0}{I_d} = 1 - \frac{\boldsymbol{B}^\circ(\omega_d,\ T_0)}{\boldsymbol{B}^\circ(\omega_d,\ T_g)} \tag{10}$$

If Wien's radiation formula is applied to Eq. 10, the relation between the temperatures of gas and the light source is shown by the equation:

$$\frac{1}{T_g}=\frac{1}{T_0}+\frac{k}{\boldsymbol{hc}\omega_d}\ln\left(1-\frac{I_l-I_0}{I_d}\right) \tag{11}$$

Thus, the temperature of the gas can be obtained by the measurement of I_l and I_d; this temperature is the same as the so-called reversal temperature. The physical meaning of the temperature is given by Eq. 5;[6] that is,

$$\frac{[\mathrm{Na}(^2\mathrm{P})]}{[\mathrm{Na}(^2\mathrm{S})]}=\frac{g_{^2\mathrm{P}}}{g_{^2\mathrm{S}}}\exp\left(-\frac{\boldsymbol{hc}\omega_d}{\boldsymbol{k}T_g}\right) \tag{12}$$

It is necessary to remember that the temperature observed in the simultaneous measurement of emission and absorption is not always the gaseous temperature; it is defined as the population temperature in the upper and lower levels concerned. This population temperature, of course, agrees with the thermodynamic temperature when the whole system is in thermal equilibrium.

In order to clarify the assumption that the sodium D-line in the shock-heated gas containing a trace of sodium vapor is thermal radiation, the relative intensities of the sodium D-line were measured in the cases of various shock velocities.

The effective emissivity of the sodium D-line may be obtained by the relation;

$$E_d=\frac{I_d}{I_0}\left(1-\frac{I_l-I_0}{I_d}\right) \tag{13}$$

Further, the following relation can be derived from Eqs. 9, 11 and 13;

$$\ln\frac{I_d}{E_d}=-\frac{\boldsymbol{hc}\omega_d}{\boldsymbol{k}T_g}+\mathrm{const.} \tag{14}$$

If the complete equilibrium between sodium atoms and shock-heated gas is maintained (see below), the temperature, T_2, calculated from the shock velocity equals the temperature, T_g, obtained by the present method. Therefore, the observed emission intensity is expected to be illustrated by the temperature T_2.

The graphic plot of I_d/E_d vs. $1/T_2$ are shown in Fig. 1. The data used are the mean values of the intensities in the steady region behind the shock fronts. (As to the profiles of emission, a more detailed description will be given in the next section). It may be seen in Fig. 1 that the experimental points accord with the theoretical linear slope. It is reasonable that the emission of the sodium D-line in the present experiments arises from a thermal mechanism but not from the other sources, e.g., a chemical luminescence.

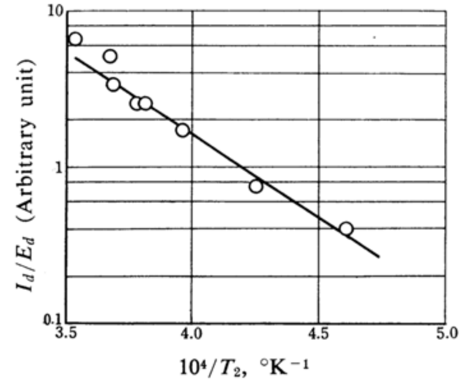

Fig. 1. Relation of sodium D-line emission intensity to reciprocal of the temperature T_2 calculated from shock velocity. The experimental points are the data from shock-heated 1% N_2-99% Ar mixture. The solid line shows the theoretical slope, $-\boldsymbol{hc}\omega_d/\boldsymbol{k}$.

Results

Figure 2 shows the emission and the emission-plus-absorption profiles of the sodium D-line in argon gas behind the shock wave; the temperatures calculated from these two curves are also given. The intensity of the emission rises very fast in less than 10 μsec. (lab. time) after the passage of the shock front, and it is almost constant in the high temperature region between the shock front and the intermixing zone. It is found that the emission becomes more intense near the intermixing zone; this may be attributable to the diffusional mixing of the driver hydrogen and argon gas. These phenomena are also found in the case of argon gas containing less than 0.1% of nitrogen or carbon monoxide. To avoid the confusion

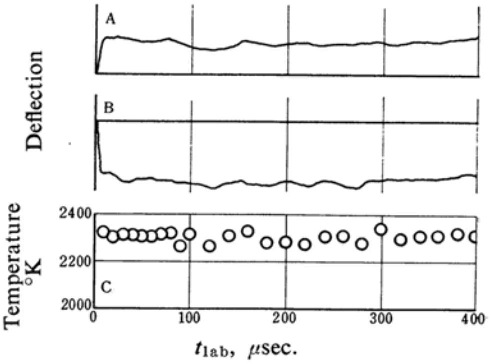

Fig. 2. Emission (A), emission-plus-absorption (B), and temperature (C) profiles behind the shock wave in pure argon gas.
Run No. 012, $v_s=1.724$ mm./μsec., $T_2^{\mathrm{calc}}=$ 2921°K, $p_2^{\mathrm{calc}}=1017$ mmHg, $T_0=2583$°K.

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[6] A. G. Gaydon and H. G. Wolfhard, "Flames," Chapman and Hall, London (1960) p. 234.

which arises from the intermixing of argon and hydrogen, the present observations and discussion are limited to the region of about 300 μsec. after the passage of the shock front.

The observed profile of emission behind the shock front confirms that the vaporization of the colloidal sodium introduced into the argon gas occurs in less than 30 μsec. (gas time), and that the concentration of sodium vapor is almost constant throughout the shock-heated gas. In the later section, the concentration of sodium atoms is calculated to be $10^{12}\sim10^{13}$ atoms/cc. The observed temperature profile is the same as the emission intensity, about 600°K lower than the theoretical temperature calculated from the shock velocity. Gaydon and Hurle have observed that the reversal temperature in the shock-heated argon is 100～200°K lower than the calculated value.[1)] Their observed temperature is much higher than the present results; this discrepancy may be attributed to the existence of impurities in their argon gas or to a less efficient vacuum in their shock tube.

An example of the experimental results in the case of nitrogen-argon mixtures is shown in Fig. 3. The emission of the sodium D-line rises gradually after the shock front and reaches a steady value of intensity which is much larger than that observed in the case of pure argon gas shocked to the same shock velocity. The rise of the emission intensity just behind the shock front seems to indicate an induction time or a relaxation process. The observed emissivity profile shows that the concentration of sodium vapor is almost constant behind the shock front, even if the emission intensity is low compared with the steady state. In the profile of emission-plus-absorption in Fig. 3, a remarkable intensity decrease is observed just behind the shock front. This decrease is due to low excitation temperature behind the shock front. However, the observed temperature in the steady region agrees well with the theoretical temperature. The difference between these results and those in pure argon can be attributed to the existence of a small amount of nitrogen gas in the mixture.

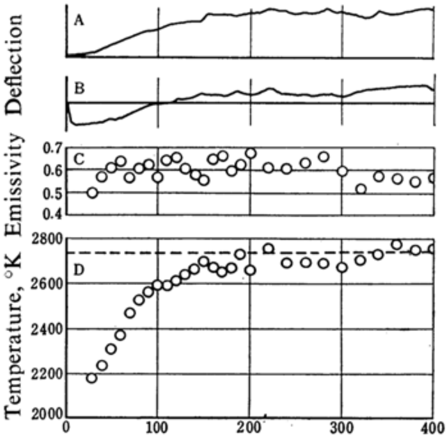

Fig. 3. Profiles of emission (A), emission-plus-absorption, (B), effective emissivity (C), and temperature (D) behind the shock wave in 1% N_2-99% Ar mixture. The dotted line in (D) shows the temperature T_2 calculated from shock velocity. Run No. 1101, $v_s=1.662$ mm./μsec., $T_2^{\mathrm{calc}}=2714$°K, $p_2^{\mathrm{calc}}=766$mmHg, $T_0=2583$°K.

The time required to reach the steady value of the emission intensity is independent of the concentration of nitrogen in the range of 1～0.1%, and it becomes shorter as the temperature or pressure is raised. On the contrary, the mean temperature in the steady region far from the shock front drops in the shock-heated argon containing less nitrogen. This circumstance is shown in Fig. 4. These findings confirm that, rather than argon atoms, nitrogen molecules in the mixture, even if their concentration is very small, play an important role in the excitation of sodium atoms.

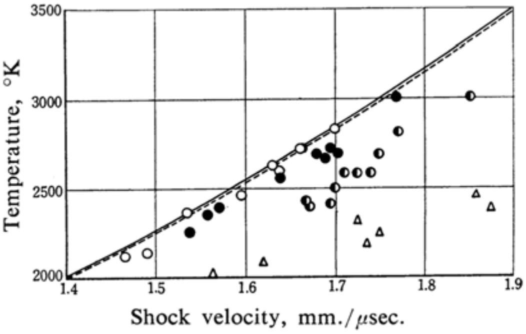

Fig. 4. Temperature obtained from the simultaneous measurement of emission and emission-plus-absorption in the steady regions far from shock front in the case of N_2-Ar mixtures.

——: Calculated temperature for pure argon
----: Calculated temperature for 1% N_2-99% Ar mixture
○: 1.03% N_2 ●: 0.09% N_2
◐: 0.04% N_2 in argon △: pure argon

The same observations have been made in the carbon monoxide-argon mixture behind the shock wave. The only difference between the experimental results of the carbon monoxide- and nitrogen-argon mixtures is that the emission of the sodium D-line in the carbon monoxide-argon mixture behind the shock front rises a little faster than in the case of the nitrogen-argon mixture. Figure 5 shows one of the experimental observations in the case of the carbon monoxide-argon mixture.

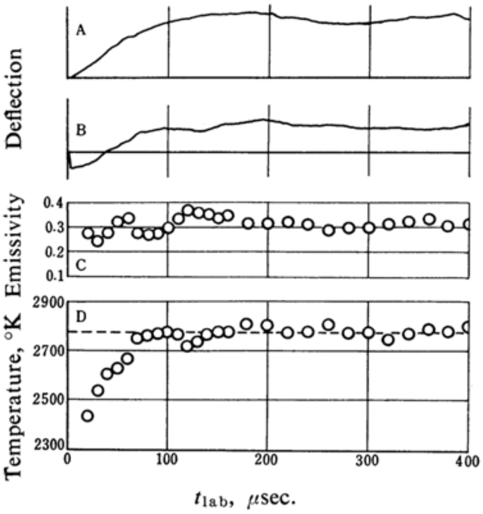

Fig. 5. Profiles of emission (A), emission-puls-absorption (B), effective emissivity (C), and temperature (D) behind the shock wave in 0.5% CO-99.5% Ar mixture. The dotted line in (D) shows the temperature calculated from shock velocity. Run No. 2203, $v_s=1.675$ mm./μsec., $T_2^{\text{calc}}=2774$°K, $p_2^{\text{calc}}=1010$ mmHg, $T_0=2583$°K.

The Excitation and Quenching of Sodium Atoms

It has been described that the temperature observed by the present method determines the populations of the ^{2}P and ^{2}S states of sodium atom, provided that the populations are distributed by Boltzmann's law. The experimental findings that the measured temperatures are about 600°K lower than the theoretical temperatures calculated from shock velocity in the shock-heated argon and agree with the theoretical temperatures in the nitrogen-argon mixtures, are to be explained by the aforementioned nature of the measured temperature. That is, sodium atoms in the pure argon gas do not attain a thermal equilibrium with argon atoms since the effective cross-section of collisions between sodium and argon atoms is very small. The existence of nitrogen molecules, which have a large cross section in collision with a sodium atom, can excite sodium atoms to ^{2}P states, thus resulting in the thermal equilibrium of the whole system. These conclusions will be more quantitatively treated in the latter part of this section.

The populations of sodium atoms in the ^{2}P and ^{2}S states are supposed to be determined by the following reaction scheme:

$$\begin{aligned} &\mathrm{Na}(^2\mathrm{S}) + \mathrm{M}^* \rightarrow \mathrm{Na}(^2\mathrm{P}) + \mathrm{M} \\ &\mathrm{Na}(^2\mathrm{P}) + \mathrm{M} \rightarrow \mathrm{Na}(^2\mathrm{S}) + \mathrm{M}^* \\ &\mathrm{Na}(^2\mathrm{P}) \rightarrow \mathrm{Na}(^2\mathrm{S}) + hc\omega_d \end{aligned} \tag{15}$$

where M may be either an atom, a molecule and an electron, and M* is an M which possesses enough energy to excite a sodium atom to the ^{2}P state. The ionization via the ^{2}P state of sodium is disregarded in the above scheme. The ionization from the excited electronic state occurs by means of the collisions with electrons, whose content is expected to be too small to make effective collisions with excited atoms (see the latter part of this paper).

As a mean of determining the populations of the ^{2}P and ^{2}S states, however, the scheme is not a perfect one. The light quanta emitted spontaneously from ^{2}P sodium atoms are re-absorbed by the neighboring atoms, re-emitted, and so on. This phenomenon is characteristic of the resonance spectral line, and is called the "radiation imprisonment."

Radiation Imprisonment. — The theoretical treatment of the imprisonment of resonance radiation has been made by Bieberman[7] and Holstein.[8] Their method of analysis may be applied to the present problem. Let $N_1(\boldsymbol{r})$ and $N_2(\boldsymbol{r})$ represent the concentration of sodium atoms in the ^{2}P and ^{2}S states respectively at a position, $\boldsymbol{r}$, within the gaseous body. If the reactions 15 represent the mechanism of the excitation or quenching of sodium atoms, $N_1(\boldsymbol{r})$ obeys the following integro-differential equation:

$$\frac{\partial N_1(\boldsymbol{r})}{\partial t} = Z_E N_2(\boldsymbol{r}) - Z_Q N_1(\boldsymbol{r}) - \gamma N_1(\boldsymbol{r}) + \gamma \int N_1(\boldsymbol{r}') G(\boldsymbol{r}', \boldsymbol{r}) \mathrm{d}\boldsymbol{r}' \tag{16}$$

where Z_E, Z_Q are collision frequencies per unit time of the excitation and quenching respectively, where γ is the reciprocal of the radiative life time, and where the last term expresses the imprisonment of the resonance radiation. $G(\boldsymbol{r}', \boldsymbol{r})$ represents the probability that a light quantum emitted from the $\boldsymbol{r}'$ position in the gaseous body is re-absorbed in the volume element, d$\boldsymbol{r}$, at the $\boldsymbol{r}$ position, and the integration in Eq. 16 is accomplished over the whole volume of the gaseous body.

Since the present problem concerns the steady state behind the shock wave, $\partial N_1(\boldsymbol{r})/\partial t=0$. Two extreme cases are expected to occur in Eq. 16.

(i) In the case of Z_E, $Z_Q \gg \gamma$, the third and fourth terms in Eq. 16 can be disregarded, and

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[7] L. M. Bieberman, *J. Exptl. Theoret. Phys.* (*U. S. S. R.*), **17**, 416 (1946).

[8] T. Holstein, *Phys. Rev.*, **72**, 1212 (1947); **83**, 1159 (1951).

the following relation is derived;

$$(N_1/N_2)^{\text{equil}} = Z_E/Z_Q = (g_1/g_2)\exp(-\boldsymbol{hc}\omega_{12}/\boldsymbol{k}T) \qquad (17)$$

The exciting or quenching collisions are predominant over the transitions due to the spontaneous emission; therefore, the thermal equilibrium between the atoms emitting the resonance line and the surrounding gaseous particles is maintained.

(ii) In the case of $G(\boldsymbol{r}', \boldsymbol{r})=0$, i.e., when the concentration of atoms is too low to reabsorb the light quanta emitted, Eq. 16 may be arranged to the relation:

$$(N_1/N_2) = Z_E/(Z_Q+\gamma) \qquad (18)$$

This formula is an analogous form of the Stern-Volmer equation which is frequently used in the photochemical experiment of the quenching.

For the analysis of the present results, it is convenient to introduce the parameter $y(\boldsymbol{r})$:

$$y(\boldsymbol{r}) = \frac{N_1(\boldsymbol{r})}{N_2(\boldsymbol{r})} \Big/ \frac{Z_E}{Z_Q} \qquad (19)$$

which represents a degree of non-equilibrium between the atoms emitting the resonance line and the gaseous particles; i.e., a value of y is 1 in the complete thermal equilibrium and less than 1 in the radiative non-equilibrium state, where the insufficient energy transfer from the gaseous particles to the atoms results in the lean populations in the upper electronic state.

The mean value of the parameter y, is obtained in the present experiment in the following manner. The physical meaning of the observed temperature, T_g, has already been described by Eq. 12. When the complete equilibrium between sodium atoms and gaseous particles is maintained behind the shock wave, T_g equals T_2 calculated from the shock velocity; i.e.,

$$\left\{\frac{[\mathrm{Na}(^2\mathrm{P})]}{[\mathrm{Na}(^2\mathrm{S})]}\right\}_{\text{equil}} = (g_{^2\mathrm{P}}/g_{^2\mathrm{S}})\exp(-\boldsymbol{hc}\omega_d/\boldsymbol{k}T_2) = Z_E/Z_Q$$

Therefore, the experimental value of the parameter y is expressed as:

$$y = \frac{[\mathrm{Na}(^2\mathrm{P})]}{[\mathrm{Na}(^2\mathrm{S})]} \Big/ \left\{\frac{[\mathrm{Na}(^2\mathrm{P})]}{[\mathrm{Na}(^2\mathrm{S})]}\right\}_{\text{equil}} = \exp\left[-(\boldsymbol{hc}\omega_d/\boldsymbol{k})\left(\frac{1}{T_g}-\frac{1}{T_2}\right)\right] \qquad (20)$$

The introduction of $y(\boldsymbol{r})$ into Eq. 16 gives the equation:

$$1-\left(1+\frac{\gamma}{Z_Q}\right)y(\boldsymbol{r}) + \frac{\gamma}{Z_Q}\int y(\boldsymbol{r}')G(\boldsymbol{r}', \boldsymbol{r})\mathrm{d}\boldsymbol{r}' = 0 \qquad (21)$$

where $N_2(\boldsymbol{r})$ is approximated as equal to N of the total concentration of the emitting atoms. The dependence of $y(\boldsymbol{r})$ upon the position, $\boldsymbol{r}$, in the gaseous body is disregarded in Eq. 21. Therefore, y may be formulated as:

$$y = 1\Big/\left[1+\frac{\gamma}{Z_Q} < 1-\int G(\boldsymbol{r}, \boldsymbol{r}')\mathrm{d}\boldsymbol{r}' >_{Av}\right] \qquad (22)$$

where the symmetric property of the function G, i.e., $G(\boldsymbol{r}', \boldsymbol{r}) = G(\boldsymbol{r}, \boldsymbol{r}')$ is used. $\left[1-\int G(\boldsymbol{r}, \boldsymbol{r}')\mathrm{d}\boldsymbol{r}'\right]$ is described as the probability that the light quanta emitted at the $\boldsymbol{r}$ position escape from the enclosure of the gas. Though this probability is dependent on the coordinate $\boldsymbol{r}$, mean probability is adopted here:

$$< 1-\int G(\boldsymbol{r}, \boldsymbol{r}')\mathrm{d}\boldsymbol{r}' >_{Av} = \int\left[1-\int G(\boldsymbol{r}, \boldsymbol{r}')\mathrm{d}\boldsymbol{r}'\right]\mathrm{d}\boldsymbol{r}\Big/\int \mathrm{d}\boldsymbol{r}$$

By the use of the escaping probability of the resonance light quanta, the effective radiative life time may be defined;

$$\tau_{eff} = \tau/< 1-\int G(\boldsymbol{r}, \boldsymbol{r}')\mathrm{d}\boldsymbol{r}' >_{Av} \qquad (23)$$

τ_{eff} depends on the absorption coefficient of the gas and the geometrical shape of the gaseous body. y is represented from Eq. 22 as;

$$y = 1\Big/\left(1+\frac{\gamma_{eff}}{Z_Q}\right) \qquad (24)$$

where

$$\gamma_{eff} = 1/\tau_{eff}$$

The assumption that $y(\boldsymbol{r})$ does not depend on the $\boldsymbol{r}$ coordinate contradicts the expectation that the concentration of the emitting atoms in the upper state at the border of the gaseous body is less than in the center part, because the light quanta emitted from the atoms at the border have a great possibility of escaping from the gaseous body. However, in the case of the dense concentration of the atoms, this treatment is satisfactory for the present purpose. The situations may be explained by the following consideration. The light quanta emitted from the atoms can travel only a very short distance because of the great possibility of capture by the neighboring atoms, and at the border of the gaseous body, there is only a thin layer of atoms which have lower value of y than the atoms in the center part have. In addition to this, the experimental value of y obtained from the measured temperature is a mean value, since it is assumed that the radiation density, $\rho'(\omega_{12}, T)$, is constant over the gaseous body in Eq. 3. Walsh confirmed the suitability of the approximation by more detailed calculations.[9]

The Derivation of the Escaping Probability. —The quantity $G(\boldsymbol{r}', \boldsymbol{r})$ is formulated in terms of the distance, $x=|\boldsymbol{r}'-\boldsymbol{r}|$, and the absorption coefficient of the gas. Holstein shows

$$G(|\boldsymbol{r}'-\boldsymbol{r}|)=\frac{1}{4\pi x^2}\frac{\partial T(x)}{\partial x} \tag{25}$$

where $T(x)$ is the probability that the radiation quantum travels the distance x without absorption; this can be explained by the equation:

$$T(x)=\int_{-\infty}^{+\infty}\varepsilon(\omega)e^{-k(\omega)x}\mathrm{d}\omega \tag{26}$$

The factor $\varepsilon(\omega)$ in Eq. 26 is the distribution function which represents the wave number profile of the emitted line; it is assumed to be proportional to $k(\omega)$. Holstein has given the approximate formula for $T(x)$ as follows:

$$T(x)=1/k_0x(\pi\ln k_0x)^{1/2}, \quad \text{for the Doppler line shape} \tag{27}$$

$$T(x)=1/(\pi k_cx)^{1/2}, \quad \text{for the collision-broadened line shape} \tag{28}$$

where k_0 and k_c are the peak absorption coefficients in the Doppler and collision-broadened lines respectively.

In order to calculate the numerical value of the escaping probability, it is necessary to know the geometry of the gaseous body emitting the resonance line. Under present experimental conditions, sodium vapor in the shock-heated gas is enclosed in a cylinder whose diameter and height are the radius of the shock tube and the distance between the shock front and the contact discontinuity respectively. Here, the solution in the enclosure of an infinite slab with the thickness L is applied to the present problem. Though the infinite cylinder is expected to be a better approximation to the real geometry than the infinite slab, Holstein has shown that the escaping probability is nearly equal in these two cases. The above approximation is also based on the the same conditions which are introduced into the definition of the mean escaping probability; in other words, the light quanta emitted from atoms travels only a small distance before absorption.

According to Holstein's calculation, the escaping factor in the case of an infinite slab is as follows:

for a Doppler-broadened spectral line,

$$<1-\int G(\boldsymbol{r}, \boldsymbol{r}')\mathrm{d}\boldsymbol{r}'>_{Av}=\frac{1}{k_0L}\left(\frac{1}{\pi}\ln\frac{k_0L}{2}\right)^{1/2} \tag{29}$$

for a collision- or dispersion-broadened spectral line,

$$<1-\int G(\boldsymbol{r}, \boldsymbol{r}')\mathrm{d}\boldsymbol{r}'>_{Av}=\frac{4}{3(\pi k_cL)^{1/2}} \tag{30}$$

The Determination of the Absorption Coefficient. — The absorption coefficient may be derived from the effective emissivity obtained from the experiment. The spectral shape of the sodium D-line is considered to be a combined form of the Doppler and the collision broadening in the present shock wave experiment. The absorption coefficient has already been given as a function of parameter a, which is defined as $a=(\ln 2)^{1/2}(\Delta\omega_N+\Delta\omega_c)/\Delta\omega_D$, where $\Delta\omega_N$, $\Delta\omega_c$, $\Delta\omega_D$ are the half-widths of the natural and collision and Doppler-broadened lines respectively.[10] The total absorption of the spectral line is given by the integration:

$$A=\int_{-\infty}^{+\infty}\{1-\exp[-k(|\omega-\omega_0|)L]\}\mathrm{d}\omega \tag{31}$$

where ω_0 is the wave number at the center of the spectral line. The value of A has been calculated numerically in the case of various values of a and is given by the "curves of growth". Since the spectral slit width, $\overline{\Delta\omega}$, is much wider than the half-width of a pure Doppler- or collision-broadened line (e.g., in the present case, $\overline{\Delta\omega}=8.9\,\mathrm{cm}^{-1}$ against $\Delta\omega_D$ or $\Delta\omega_c=0.1\sim0.15\,\mathrm{cm}^{-1}$), the total absorption can be obtained from the observed effective emissivity by the relation:

$$E_d=\int g(\omega,\omega_d)\{1-\exp[-k(\omega)L]\}\mathrm{d}\omega\Big/\int g(\omega,\ \omega_d)\mathrm{d}\omega\doteqdot A_d/\overline{\Delta\omega} \tag{32}$$

For the numerical evaluation of k_0 by the use of the curves of growth*, the collision half-width, $\Delta\omega_c$, is necessary. This is given by the classical collision-damping theory[11]:

$$\Delta\omega_c=\sigma^2\bar{v}N'/\boldsymbol{c}$$

where N' is the concentration of perturbing atoms or molecules, $\bar{v}$, the gas kinetic mean velocity, and σ^2, the optical cross-section of collisions with perturbing particles. Hinnov measured the total absorption of the sodium D_2-line in the acetylene-air flame and obtained

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[9] P. J. Walsh, *Phys. Rev.*, **107**, 338 (1957).

[10] S. S. Penner, "Quantitative Molecular Spectroscopy and Gas Emissivities," Addison-Wesley Pub. Co., Mass. (1959), p. 38.

* The relation $k_c=k_0/\sqrt{\pi}\ a$ can be derived, since in any shape of the spectral line, $\int k(|\omega-\omega_0|)\mathrm{d}\omega=(\pi e^2/mc^2)Nf$, where e and m are the electron's charge and mass respectively, and f is the f-number of the concerned spectral line. In the latter part of this paper, the absorption coefficient, k_0, will be used as a measure of optical thickness instead of k_c, because the total absorption is given in terms of k_0L in the curves of growth.

[11] S. Chen and M. Takeo, *Rev. Mod. Phys.*, **29**, 20 (1957).

TABLE I. CALCULATED QUENCHING CROSS SECTION OF NITROGEN AND CARBON MONOXIDE FROM SHOCK WAVE DATA

Test gas	N_2 0.05%-Ar 99.95%					CO 0.03%-Ar 99.97%				
Run No.	1802	1803	1805	1809	1811	2401	2403	2404	2406	2408
T_1 (°K)	303	303	303	303	303	302	302	302	302	302
v_s (mm./μsec.)	1.657	1.649	1.700	1.690	1.675	1.648	1.657	1.675	1.680	1.680
T_2^{calc} (°K)	2737	2713	2868	2837	2792	2709	2736	2791	2806	2806
p_2^{calc} (mmHg)	839	834	886	943	894	881	865	880	879	876
T_g^{steady} (°K)	2430	2395	2330	2440	2590	2405	2530	2450	2325	2270
E_d	0.44	0.35	0.115	0.18	0.95	0.41	1.0	0.44	0.14	0.14
y^{steady}	0.32	0.31	0.14	0.25	0.51	0.32	0.48	0.29	0.17	0.13
k_0L	460	280	40	62	1770	360	2040	300	43	38
Z_Q ($\times 10^6$ sec^{-1})	1.40	1.46	1.43	2.35	1.39	1.43	1.65	1.36	1.68	1.33
σ^2_{eff} ($\times 10^{-15}$ cm^2)	1.4	1.5	1.4	2.1	1.3	2.1	2.5	2.1	2.5	2.0
σ^2_{eff}*	14 Å^2 for nitrogen					28 Å^2 for carbon monoxide				

* Effective cross section from Norrish and Smith's data.

value of σ^2 as 64 Å^2 for nitrogen-sodium collisions.[12a] Margenau and Watson observed the absorption profile of the sodium D$_1$- and D$_2$-lines in the atmosphere of nitrogen and argon[12b] and found that the half-width of the absorption line in argon at high pressure was larger than that in nitrogen. However, half-widths at less than 1 atm. are almost the same in both cases, as is shown in Fig. 4 of their paper. The difference between half-widths in argon and nitrogen at high pressure may be considered to be due to the fact that the degrees of assymmetrical broadening and the shift of the spectral line are different in argon and in nitrogen. The value of σ^2 obtained by Hinnov is used in the present case, since the present experimental conditions, i. e., high temperature and about 1 atm., resemble Hinnov's case and the sodium D-line is expected to be broadened equally by nitrogen- and argon-sodium collisions.

Effective Collision Cross-section.—The aforementioned procedures make it possible to calculate the numerical value of the quenching collision frequency, Z_Q, by the use of an experimental y value. Table I shows the experimental results of the temperature measurement in the cases of shock-heated nitrogen- and carbon monoxide-argon mixtures, and it also gives the calculated values of k_0L and Z_Q. The value of k_0L is obtained from the curves of growth using the total absorption estimated from the observed emissivity. Z_Q is calculated by Eq. 24, where the value of γ_{eff} is obtained from Eq. 30. Here the value of 1.6×10^{-8} sec. is adopted as the radiative lifetime of the Na$^2P_{3/2}-^2S_{1/2}$ transition.[13] In the above calculation, the spectral line, which has a shape combining the Doppler and the collision brandening, is considered to be a pure collision-broadened line, and k_0L is converted to k_cL using the relation $k_cL=k_0L/\sqrt{\pi a}$. This approximation is reasonable taking into account the fact that the spectral shape of the sodium D-line is close to the collision-broadened line in the present experimental conditions.

The calculated Z_Q's have an order of 10^6 sec^{-1} in the cases of both the 0.05% nitrogen and 0.03% carbon monoxide mixtures. This Z_Q should be interpreted from the viewpoint that some particles in the shock-heated heated nitrogen- or carbon monoxide-argon mixture have large efficiencies in exciting or quenching collisions with sodium atoms. The effective collision cross-section, σ^2_{eff}, is defined by the equation;

$$Z_Q=\sigma^2_{eff}\left[8\pi RT\left(\frac{1}{M_{\mathrm{Na}}}+\frac{1}{M_q}\right)\right]^{1/2}N_q \qquad (33)$$

where M_{Na} and M_q are the atomic or molecular weights of sodium and the quencher respectively, and N_q is the number of quenchers per unit volume.

In order to explain the obtained value of Z_Q in nitrogen- and carbon monoxide-argon mixtures, it is assumed that the collisional excitation and quenching of sodium atoms are performed by nitrogen or carbon monoxide molecules involved in the shock-heated mixtures. The values of σ^2_{eff} for nitrogen or carbon monoxide in collisions with sodium atoms can be calculated on the above assumption; they are shown in Table I. These values agree well with the experimental values given by Norrish and Smith,[14] even though many approximations are made in the process of the

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[12a] E. Hinnov, *J. Opt. Soc. Am.*, **47**, 151 (1957).

[12b] H. Margenau and W. W. Watson, *Phys. Rev.*, **44**, 92 (1933).

[13] A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," Cambridge University Press, London (1934), p. 146.

[14] R. G. W. Norrish and W. MacF. Smith, *Proc. Roy. Soc.* (*London*), **176A**, 295 (1945).

calculation. However, the value of σ^2_{eff} obtained here has only one significant figure, i. e., σ^2_{eff} (for N_2) = $(1.4\pm0.5)\times10^{-15}\,\mathrm{cm}^2$, because of the uncertainty in the estimation of the absorption coefficient and because of the approximation used in the analysis of the radiation imprisonment. The agreement of σ^2_{eff} with Norrish and Smith's value leads to the conclusion that molecular collisions with sodium atoms are dominant in quenching Na(^{2}P), that is, in exciting Na(^{2}S) in the nitrogen- and carbon monoxide-argon mixtures even if the concentration of nitrogen or carbon monoxide is less than 0.1%. The present values of σ^2_{eff} are obtained in the gas with a high temperature of about 2800°K. On the other hand, the experiment of Norrish and Smith was performed at room temperature. The agreement of the present values with their experimental values shows that the activation energy of the quenching process is zero. Mori has calculated quantum-mechanically the potential surface of the sodium-nitrogen system; the calculated potentials have no activation energy.[15]

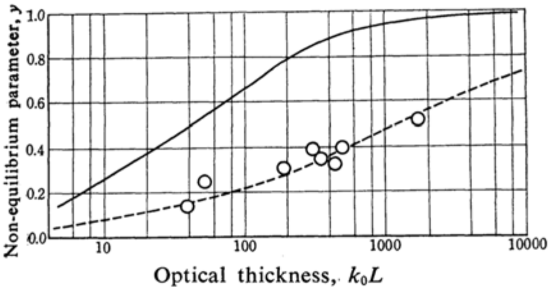

Fig. 6. Relation of non-equilibrium parameter y to optical thickness k_0L. The calculation is carried out in the case of $Z_Q=1.53\times10^6$ sec^{-1} which corresponds to the quenching collision frequency of nitrogen in 0.05%N_2-99.95%Ar mixture at 900 mmHg and 2800°K. In this case, $y=0.0239$ at $k_0L\to0$. Solid and dotted lines shows values of y calculated in the case of Doppler- and collision-broadened spectral lines, respectively. Experimental points are adopted from Table I.

The graphical representation of the theoretical y value vs. the optical thickness, k_0L, is shown in Fig. 6. The theoretical curves are calculated by Eq. 24 in the case of $Z_Q=1.53\times10^6\,\mathrm{sec}^{-1}$. This value of Z_Q is the collision frequency of quenching by nitrogen molecules in a 0.05% nitrogen - 99.95% argon mixture, which is shocked to the temperature of 2800°K and the pressure of 900 mmHg. Experimental results are also given in Fig. 6, although the experimental shock conditions are not precisely the same as the conditions used in the calculation. The experimental points lie on the curve of y calculated in the case of the collision-broadened line shape.

It is seen in Fig. 6 that the values of y increases as the optical thickness, k_0L, becomes larger. This is due to the radiation imprisonment. If all the light quanta emitted spontaneously from sodium atoms escape from the gaseous enclosure, i. e., if $\tau_{eff}=\tau$ and $k_0L=0$, expected value of y is 0.0239 as calculated from Eq. 25. Gaydon and Wolfhard have explained the radiative non-equilibrium state between sodium atoms and a high temperature medium by the use of τ rather than of τ_{eff}.[16] However, the populations of the ^{2}P state of sodium atoms are much closer to the values of the thermal equilibrium state than those without the imprisonment of resonance radiation.

Vibrational-Electronic Energy Exchange

In this section, the rise of the emission behind the shock wave will be discussed. The results show that a lab. time of 50~100 μsec. after the passage of the shock front is required for the emission intensity to attain a steady value in the nitrogen- or the carbon monoxide-argon mixture. On the contrary, the emission rises in less than 10 μsec. (lab. time) in the shock-heated argon.

Gaydon has described that the excitation of sodium atoms occurs by collision with vibrationally-excited molecules, because the quenching cross-sections of the fluorescence are large when the quenchers are molecules and extremely small when they are inert monoatomic gases.[17] He obtained the vibrational relaxation time on the assumption that the reversal temperature equals the vibrational temperature of diatomic gases.[1] Karl and Polanyi investigated the infrared emission of carbon monoxide, which quenched electronically-excited mercury, and found that the electronic energy of the mercury atom was transferred to the vibrational freedom of carbon monoxide by collisions of second kind.[18] Their findings can be applied to the present problem.

The mechanism of the collisional excitation of the sodium atom may be represented by the following scheme:

$$\begin{aligned} &N_2(v=0) + \mathrm{Ar} \rightleftarrows N_2(v=1) + \mathrm{Ar} \\ &\qquad \rightleftarrows N_2(v=2) + \mathrm{Ar} \rightleftarrows \end{aligned} \qquad (34)$$

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[15] Y. Mori, This Bulletin, **35**, 1591 (1962).

[16] A. G. Gaydon and H. G. Wolfhard, *Proc. Phys. Soc.* (*London*), **65**, 19 (1952).

[17] A. G. Gaydon, "Energy Transfer in Hot Gases," Natl. Bur. Standards, Circular 523, Washington (1954), p. 1.

[18] G. Karl and J. C. Polanyi, *J. Chem. Phys.*, **38**, 271 (1963).

$$\begin{aligned} &\mathrm{Na}(^2\mathrm{S}) + \mathrm{N}_2(v \geqq v^*) \\ &\quad \rightleftarrows \mathrm{Na}(^2\mathrm{P}) + \mathrm{N}_2(v < v^*) \end{aligned} \tag{35}$$

The successive excitation or de-excitation of vibrational states of carbon monoxide has been recently experimentally ascertained.[19] This has been predicted by Landau-Teller's classical theory of vibrational relaxation, and Eq. 34 reflects this mechanism. Equation 35 represents how the excitation of sodium atoms occurs in collisions with nitrogen of a high vibrational state ($v^* \geqq 8$).

First, it will be shown that the process of Eq. 35 is much faster than that of Eq. 34. Equation 16 represents the concentration of $\mathrm{Na}(^2\mathrm{P})$ and is formulated by the use of γ_{eff} as follows:

$$\mathrm{d}N_1/\mathrm{d}t = Z_E N_2 - (Z_Q + \gamma_{eff}) N_1 \tag{16'}$$

where the exciting collision frequency, Z_E, is a function of a concentration of vibrationally-excited nitrogen molecules. If Eq. 34 keeps complete equilibrium, that is, if nitrogen molecules are in equilibrium with argon atoms at any moment after the passage of the shock front, Z_E is constant throughout the high temperature region behind the shock front, and the rate of the process of Eq. 35 is represented by Ep. 16′. On the assumption that $N_2 \fallingdotseq N$, Eq. 16′ may be integrated to give the relation:

$$N_1 = N_1^{\text{steady}} \{1 - \exp[-(Z_Q + \gamma_{eff})t]\} \tag{36}$$

$$N_1^{\text{steady}} = N Z_E / (Z_Q + \gamma_{eff})$$

where the integration is carried with the initial condition, $N_1 = 0$ at $t = 0$, and N_1^{steady} is a value of N_1 at the steady region far from the shock front.

Since the emission intensity of the sodium D-line is proportional to the concentration of excited sodium atoms, the profiles of the emission intensity behind the shock front is expressed by Eq. 36. In the case of a 1% nitrogen-99% argon mixture, the time required for N_1 to reach 90% of N_1^{steady} is estimated by Eq. 36; this corresponds to the rise time of the emission intensity behind the shock front. Under the present experimental conditions, $\gamma_{eff} \fallingdotseq 10^6\ \mathrm{sec}^{-1}$ and $Z_Q \fallingdotseq 10^7\ \mathrm{sec}^{-1}$. The corresponding rise time of the emission intensity is calculated to have an order of 10^{-7} sec., which is much shorter than the rise time observed in the experiment. The discrepancy between this argument and the experimental findings is due to the assumption that Eq. 34 keeps complete equilibrium. Therefore, it can be concluded that the process of Eq. 34 rather than that of Eq. 35 is the rate-determining step of the excitation of sodium atoms; i. e., the distribution of sodium atoms in the ^{2}S and ^{2}P states are always in equilibrium with nitrogen molecules in the various vibrational states.

Montroll and Shuler have calculated the relaxational process of harmonic oscillators which are involved in a heat bath with a constant temperature.[20] Their calculations are based on the Landau-Teller-type relaxation, and the solution is applicable to the present problem. Their calculations show that when the temperature of a heat bath is suddenly raised, as in the shock wave, the initial Boltzmann distribution of harmonic oscillators goes to the final distribution, maintaining the Boltzmann distribution at any moment of the relaxation process. Therefore, the vibrational temperature, $T(t)$, of oscillators can be defined as a function of the time, t, after the sudden increase in the temperature of the heat bath. At a large value of t, Montroll and Shuler gave the equation;

$$\Theta - \theta \fallingdotseq e^{-t/\tau} \left[\frac{(1 - e^{-\theta})}{(1 - e^{-\theta_0})} (1 - e^{\theta - \theta_0}) \right] - O(e^{-2t/\tau}) \tag{37}$$

In this equation, τ is the vibrational relaxation time of $v = 1 \rightarrow v = 0$; $O(e^{-2t/\tau})$ is a function of terms higher than $e^{-2t/\tau}$, and $\Theta = \boldsymbol{hc}\omega_{vib}/\boldsymbol{k}T(t)$, $\theta_0 = \boldsymbol{hc}\omega_{vib}/\boldsymbol{k}T(0)$, $\theta = \boldsymbol{hc}\omega_{vib}/\boldsymbol{k}T(\infty)$, where $T(0)$ and $T(\infty)$ are the initial and final temperatures of the system of oscillators, and ω_{vib} is the fundamental vibration frequency of the oscillator. Equation 37 can be arranged to give the relation;

$$\ln \left[\frac{1}{T(t)} - \frac{1}{T(\infty)} \right] \fallingdotseq -\frac{t}{\tau} + \text{const.} \tag{38}$$

As a results of the preceding consideration of the energy transfer between sodium atoms and nitrogen molecules, the observed excitation temperature of the sodium D-line may be concluded to correspond to $T(t)$ of the vibrational temperature of nitrogen. The emission intensity of the sodium D-line is described by Eq. 4, and if the concentration of sodium is constant behind the shock wave, the ratio of the intensities at any time, t, and at the steady state of $t = \infty$ is represented by;

$$\frac{I(t)}{I(\infty)} = \exp\left\{ -\frac{\boldsymbol{hc}\omega_d}{\boldsymbol{k}} \left[\frac{1}{T(t)} - \frac{1}{T(\infty)} \right] \right\}$$

therefore,

$$\ln \left[\ln \frac{I(\infty)}{I(t)} \right] \fallingdotseq -\frac{t}{\tau} + \text{const.} \tag{39}$$

Figure 7 shows the experimental determination of τ from the measured temperature and the emission intensity profiles behind the shock wave in the case of the 1% nitrogen-99%

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[19] W. J. Hooker and R. C. Millikan, ibid., **38**, 214 (1963).

[20] E. W. Montroll and K. E. Shuler, ibid., **26**, 454 (1957).

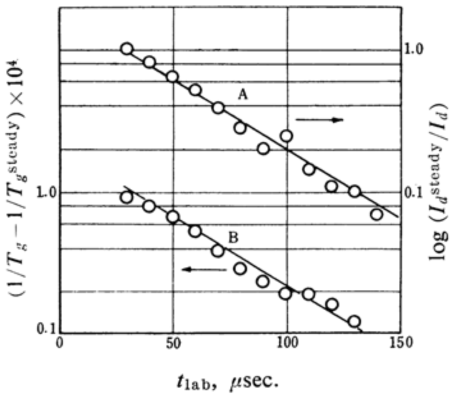

Fig. 7. Determination of vibrational relaxation time from the measured emission intensity (A) and temperature (B) profiles behind shock wave in 1% N_2 - 99% Ar mixture. Both linear slopes give the same relaxation time. Run No. 1101.

argon mixture. Two methods, i. e., Eqs. 38 and 39, of obtaining the vibrational relaxation time give the same value. In Figs. 8 and 9, the obtained vibrational relaxation times at 1 atm. are given. Since the measurements are made in 1% and 0.1% nitrogen or carbon monoxide in argon, the contribution of nitrogen-nitrogen or carbon monoxide-carbon monoxide collisions to the relaxation time is negligible. The results of the relaxation time measured by the present method in pure nitrogen behind the shock wave agree with the extrapolated value of Blackman's data,[21] as has already been pointed out by Gaydon.[1] On the other hand, the relaxation times in the 1% nitrogen - 99% argon mixture are about three times longer than in the pure nitrogen. This is consistent with Camac and Vaughan's measurement in an oxygen-argon mixture,[22] and Hooker and Millikan's data on a carbon monoxide-argon mixture.[19] The plots of the relaxation time vs. $T^{-1/3}$ give the relation;

$$\log_{10}\tau_{N_2-Ar} = 85T^{-1/3} - 9.8$$

$$\log_{10}\tau_{N_2-N_2} = 81T^{-1/3} - 10$$

where τ is described in sec. The results obtained in carbon monoxide-argon mixtures are the same as Hooker and Millikan's data:

$$\log_{10}\tau_{CO-Ar} = 101T^{-1/3} - 11.45$$

$$\log_{10}\tau_{CO-CO} = 69.3T^{-1/3} - 9.64$$

It is reasonable to expect a longer vibrational relaxation time in nitrogen-argon collisions than in nitrogen-nitrogen collisions, since only a translational-vibrational energy exchange, and novibrational-vibrational one, occurs in nitrogen-argon collisions.

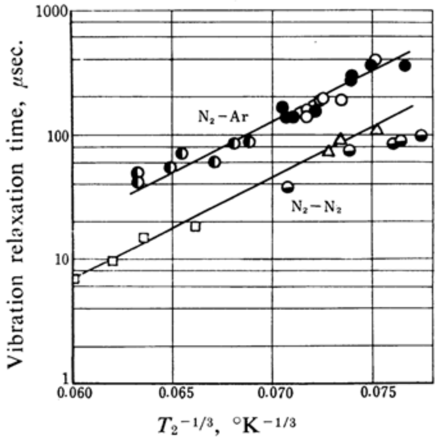

Fig. 8. Obtained vibrational relaxation time at 1 atm. in N_2-Ar and N_2-N_2 collisions.

- ○: 1.0% N_2 in argon, data obtained from temperature profile
- ◐: 1.0% N_2, from emission profile
- ●: 0.09% N_2, from temperature profile
- △: data obtained from temperature profile in shocked nitrogen
- □: Blackman's data[21]
- ◒: Gaydon and Hurle's data

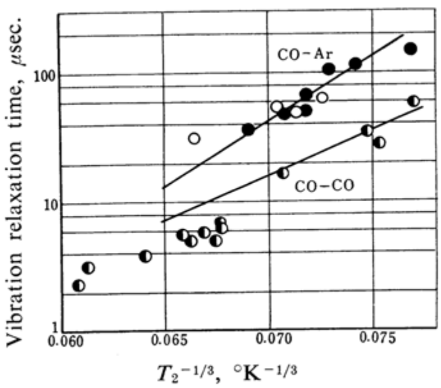

Fig. 9. Vibrational relaxation time in CO-Ar collisions.

- ○ : 1.16% CO in argon
- ● : 0.12% CO in argon
- ◐ : Matthew's data[23]
- ——: Hooker and Millikan's data

The Excitation of the Sodium Atom in Argon behind the Shock Wave

In order to discuss the mechanism of the excitation of sodium atoms in the shock-heated argon, the method of analysis already described will be applied to the experimental results. Table II shows that the quenching collision frequency, Z_Q, derived from the measured tem-

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[21] V. Blackman, *J. Fluid Mech.*, **1**, 61 (1956).

[22] M. Camac and A. Vaughan, *J. Chem. Phys.*, **34**, 448 (1961).

[23] D. L. Matthews, ibid., **34**, 639 (1961).

TABLE II. CALCULATED QUENCHING COLLISION FREQUENCIES OF ARGON ATOMS WITH SODIUM ATOM FROM SHOCK WAVE DATA

Run No.	012	022	025	036	040	053	057	058
T_1 (°K)	282	282	282	296	297	297	297	297
v_s (mm./μsec.)	1.724	1.749	1.734	1.929	1.874	1.618	1.562	1.522
T_2^{calc} (°K)	2921	3000	2953	3609	3422	2616	2456	2342
p_2^{calc} (mmHg)	1017	852	773	556	242	1031	1053	1074
T_g^{steady} (°K)	2320	2250	2170	2390	2385	2085	2020	1925
E_d	0.73	0.61	0.48	0.28	0.078	0.71	0.66	0.53
y^{steady}	0.11	0.064	0.050	0.032	0.045	0.093	0.12	0.10
k_0L	580	810	470	140	51	930	800	510
N_{Na} ($\times 10^{13}$ atoms/cc.)	3.8	5.3	3.1	0.92	0.33	6.1	5.2	3.3
Z_Q ($\times 10^5$ sec^{-1})	3.1	1.3	1.2	1.1	1.8	2.2	1.6	3.4
σ^2_{eff} ($\times 10^{-19}$ cm^2)	1.3	0.69	0.73	1.1	3.6	0.93	0.55	1.3

perature has an order of 10^5 sec^{-1}. By the use of this value, it can be determined what sort of particles in the shock-heated argon performs the excitation and de-excitation by collisions with sodium atoms.

First, the collisions between sodium and argon atoms will be discussed. The effective cross sections can be calculated from the obtained Z_Q's; the values are shown to be about $10^{-19}\sim 10^{-20}$ cm^2 in Table II. Laidler has discussed the physical quenching of an excited sodium atom by considering the potential surface between a sodium atom and a quencher;[24] he has concluded that the inert atoms would be poor quenchers, since the potential curves of the $\mathrm{Na}^+ + \mathrm{M}^-$ (M=inert atom) system do not cross the curves of the $\mathrm{Na}(^2\mathrm{P}) + \mathrm{M}$ and $\mathrm{Na}(^2\mathrm{S}) + \mathrm{M}$ systems. A very small effective cross-section obtained from the present data reflects these circumstances. Gaydon has proposed the possibility of quenching by an inert atom;[25] though both $\mathrm{Na}(^2\mathrm{S}) + \mathrm{Ar}$ and $\mathrm{Na}(^2\mathrm{P}) + \mathrm{Ar}$ have potential curves of a repulsive type, the $\mathrm{Na}(^2\mathrm{P}) + \mathrm{Ar}$ system is less repulsive than $\mathrm{Na}(^2\mathrm{S}) + \mathrm{Ar}$, and the intersection of the two potential curves occurrs at a high energy point, as Fig. 10 shows. The same discussions were cited by Herzberg.[26] In this mechanism, an activation energy is necessary for quenching.

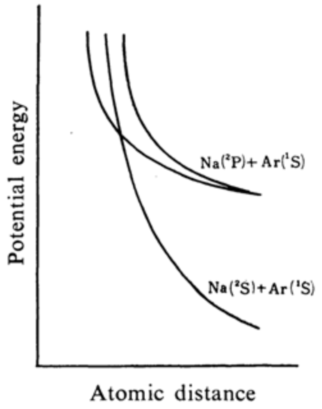

Fig. 10. Potential curves explaining the excitation of sodium atom by collision with argon atom. Two states $^2\Sigma$, $^2\Pi$ are considered in the system $\mathrm{Na}(^2\mathrm{P}) + \mathrm{Ar}(^1\mathrm{S})$.

The present data may be interpreted by the above scheme. It is reasonable that the crossing point of the two potential curves, $\mathrm{Na}(^2\mathrm{P}) +$ Ar and $\mathrm{Na}(^2\mathrm{S}) + \mathrm{Ar}$, lies at an atomic distance of about 10^{-8} cm. Therefore, the collision cross-section is expected to have an order of 10^{-16} cm^2; the $10^{-3}\sim 10^{-4}$ factor might come from the necessity of the activation energy for quenching, i. e., the energy difference between the crossing point of two potential curves and the energy level of $\mathrm{Na}(^2\mathrm{P}) + \mathrm{Ar}$ at a large atomic distance. This activation energy may be expected to be $40\sim 60$ kcal. from the results of the present experiment. If the above explanation correctly accounts for the excitation of the sodium atom by collisions with argon atoms, the effective cross-section is strongly dependent on the temperature of the shock wave. The temperature dependency is not certain in the present experiments. Moreover, the constant cross-section is not obtained from the experiments carried out at the various pressures behind the shock wave. These negative facts appear to deny the possibility of the excitation of a sodium atom by collisions with argon atoms.

The collisional excitation of the sodium atom by other particles in argon gas behind the shock wave should also be examined. When the concentration of sodium atoms in the shock-heated argon is calculated from the obtained value of k_0, it is shown to be

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[24] K. J. Laidler, ibid., 10, 34 (1942).

[25] A. G. Gaydon and I. R. Hurle, "The Shock Tube in High Temperature Chemical Physics," Chapman and Hall London (1963), p. 230.

[26] G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules," D. Van Nostrand Co., N. Y. (1950), p. 463.

$10^{12} \sim 10^{13}$ atoms/cc. (cf. Table II). The collisions between sodium atoms cannot take a dominant role in the shock wave unless the effective cross section for a sodium atom is extraordinarily large. There is no possibility of the excitation by Na_2 molecules, which exist in a small concentration because of the low dissociation energy. The other possibility is collision with the nitrogen or oxygen which is involved in argon gas as an impurity. The Z_Q of 10^5 sec^{-1} at 1000 mmHg and 3000°K requires the contamination of about 0.003% nitrogen in argon. The argon gas used in the present experiment contains nitrogen, oxygen, hydrogen and water vapor as follows: $N_2 < 0.007\%$, $O_2 < 0.001\%$, $H_2 < 0.001\%$, $H_2O < 0.001\%$. Therefore, the excitation of sodium atoms by these impurities must be taken into consideration; the observed Z_Q can be explained by this scheme. However, there is a phenomenon which contradicts the reality of the excitation by the impurity whose main component is nitrogen; i. e., the rise time of the emission intensity just behind the shock front is very short compared with that in the case of the 1% nitrogen-99% argon mixture. The following explanation of this fact is possible. The proportion of oxygen, hydrogen or other impurities to the amount of nitrogen is much larger than that of the 1% nitrogen - 99% argon mixture. The vibrational relaxation times of oxygen, hydrogen and water vapor are much shorter than that of nitrogen. This is the probable reason why the emission of the sodium D-line rises rapidly behind the shock front. In order to gain a more rigid conclusion, however, it is necessary to perform the experiment using highly pure argon and a highly-evacuated shock tube.

Bauer, Kiefer and Loader have measured the temperature dependency of the emission rise of the chromium line in the 10% nitrogen-90% argon mixture behind the shock wave[4)] and have concluded that chromium atoms are excited predominantly by collisions with electrons. Since the large cross-section for the excitation of sodium atoms is expected in collisions with electrons, electrons which are produced by the ionization of sodium atoms can make the quenching collisions of $Z_Q \fallingdotseq 10^5$ sec^{-1} if the equilibrium ionization is attained. However, the ionization is known to occur after some delay in the inert gas behind the shock wave. Haught has observed the delayed luminosity in the shock wave of a cesium-argon mixture[27)] and has described that the ionization by atom-atom collisions is less effective by a factor of 10^{-3} than electron-atom collisions, and that atom-atom collisions occur only just behind the shock front in argon. In the shocked gas higher than 3500°K, the delayed rise of the emission is observed 100~300 μsec. (lab. time) later behind the passage of the shock front; this is perhaps attributable to the ionization of sodium atoms. A detailed investigation of this phenomenon will be discussed in another place. Therefore, the emission of the sodium D-line in the shock-heated argon is not due to the ionization of sodium atoms.

The above arguments lead to the conclusions that the excitation of sodium atoms in the shock-heated argon does not occur by sodium-argon collisions in the 2500~3500°K temperature range, and that molecular impurities such as nitrogen, oxygen and hydrogen, rather than electrons play a dominant role as to the excitation of sodium atoms. This conclusion is compatible with the fact that the translational-electronic energy exchange in nitrogen-sodium collisions cannot occur in the case of a shock-heated nitrogen-argon mixture.

Conclusion

The so-called reversal temperature can be obtained by simultaneous measurements of the emission and of the absorption of the sodium D-line. The physical meaning of the temperature is such that the obtained temperature determines the distribution of populations in the ^2P and ^2S states of the sodium atom according to the Boltzmann distribution. The measured temperatures in argon containing a trace of sodium vapor are about 600°K lower than the values calculated from the shock velocity. However, in the shock-heated 1% nitrogen-99% argon mixture, the measured temperatures agree with the calculated ones, and a complete equilibrium between sodium atoms and the gaseous particles is attained.

These results can be explained by the fact that the effective cross-section for the excitation of the sodium atom in collisions with argon atoms is too small to maintain the thermal equilibrium. The collision frequencies of the second kind can be obtained with the correction of radiation imprisonment, and the calculations show that sodium-nitrogen collisions rather than sodium-argon collisions play a dominant role in the shock wave of a temperature between 2000~3000°K, even if the concentration of nitrogen is 0.05%. Quite the same conclusions are obtained in the case of a carbon monoxide-argon mixture. The present shock wave experiment may provide a method for obtaining the effective cross-section of collison for quenching an excited atom.

Concerning the feature of the emission rise

[27)] A. F. Haught, *Phys. Fluid*, 5, 1337 (1962).

in the nitrogen-argon mixture just behind the shock front, the observed temperature follows the vibrational temperature of nitrogen defined by Montroll and Shuler; that is, the electronic excitation occurs in collisions with vibrationally-activated nitrogen molecules. The vibrational relaxation time in nitrogen-argon collisions has a value about three times greater than the value in nitrogen-nitrogen collisions in the temperature range of 2000∼3000°K.

The effective quenching cross-section of $Na(^2P)$ for the argon atom has been calculated to be $10^{-19}\sim10^{-20}\,cm^2$ at 2500∼3500°K from the measured temperatures in the shock-heated argon. However, collisions with other impurities, e. g., nitrogen, electrons etc., must be taken into consideration. It has been concluded that molecular impurities, such as nitrogen or oxygen, rather than argon atoms or electrons make exciting collisions with sodium atoms in the shock-heated argon.

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Aeronautical Research Institute
The University of Tokyo
Meguro-ku, Tokyo