

Excitation Temperature of Chromium in the Shock Tube*

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THIS is a preliminary report of excitation temperature measurements on CrI in shock-heated gases. These measurements represent an extension of earlier work done in this laboratory^{1,2} relating to the use of the shock tube as a spectroscopic source. Of particular interest to astrophysicists is the application of this technique to the measurement of atomic³ and molecular radiative transition probabilities. One hopes to be able to assume that the excitation temperatures of all radiating species are the same as the kinetic temperature computed from hydrodynamic theory. We find that (i) the distribution of CrI over its excited states is a steady Boltzmann distribution but that (ii) the temperature T_E describing the distribution is in general not equal to the kinetic temperature T of the shock tube gas. T_E is only about 0.6 T for $T \sim 10^4$ °K, whereas T and T_E agree to within 10% for $T \sim 5 \times 10^3$ °K.

We derive excitation temperatures by measuring relative intensities of CrI emission lines whose wavelengths lie between 4500 and 5000 Å. Relative oscillator strengths of these lines have previously been measured by Hill and King,³ so that a set of observed relative intensities serves to specify the distribution of atoms over their excited states. The multiplets used by us are $^3G^\circ \rightarrow ^5G$, $^5P^\circ \rightarrow ^5D$, $^3F^\circ \rightarrow ^3G$, $^5F^\circ \rightarrow ^5G$, $^5P^\circ \rightarrow ^3G$, $^3H^\circ \rightarrow ^3G$, and $^7D \rightarrow ^7F^\circ$, the energies of whose upper levels are 3.68 to 5.80 eV above the ground state. The spectral lines are recorded on Kodak 103-D film by an $f/7$ grating spectrograph and revolving drum camera. The processed film is traced with a recording microdensitometer. Relative line intensities are measured by the procedures of heterochromatic photometry,⁴ using a flash lamp and step-filter for determining the characteristic curve of the emulsion at any wavelength and a standard carbon arc^{5,6} for determining the variation of emulsion response with wavelength. Considerable care has been exercised in eliminating those errors such as vignetting and reciprocity-law failure to which spectrophotometric systems can fall prey.

The region of shock tube flow which we are studying is the stationary gas behind the reflected shock. The spectrographic line of sight traverses the shorter dimension of the 4.13×6.67 cm tube cross section 2 cm from the end wall of the tube. The shock tube test gas is a premixture of neon and a small amount of $\text{Cr}(\text{CO})_5$ vapor, the fractional abundance of the latter varying from 10^{-3} to 10^{-4} . Initial expansion chamber pressures of this mixture are 5 to 50 mm Hg. Mach 4 to 7 primary shock waves are generated in this gas by the expansion of high-pressure hydrogen from the compression chamber. The shocks are reflected at the end of the tube leaving a stationary gas sample ($T \sim 5 \times 10^3$ to 10^4 °K., $p \sim 1$ to 10 atmos.) in the spectrographic line of sight for at least 100 μsec . During this time, the spectral lines are

of constant intensity. The motion of the spectrograph film enables one to distinguish this radiation from preceding and subsequent radiations at the same tube position. The gaseous state behind the reflected shock is computed from observed primary shock speeds and the properties of the atomic and molecular constituents. For our experimental conditions, one can neglect all but the translational degrees of freedom if a 2% determination of the thermodynamic state is all that is required. In spite of the nonideal hydrodynamical effects which occur in the shock tube, the state of the twice-compressed gas near the end wall is certainly within 10% of the state computed from the primary shock speed. This conclusion is drawn from our direct measurements of gas pressure, flow speed, and reflected shock speed.

The problem is then the general disparity between the CrI excitation temperature and the gas-kinetic temperature; according to a private communication from L. R. Doherty, a similar discrepancy has been observed for hydrogen and NeI. Our photometric system measures relative intensities with 10% accuracy, whereas the relative intensity corrections necessary for bringing T_E into agreement with T are of the order of 500 to 1000%. We have examined the assumption of "optical thinness" used in the data analysis; correction of the observed line intensities for the largest conceivable optical depths has a negligible effect on the derived T_E .

We are currently considering three possible causes of the phenomenon.

(I) The electron gas may be non-Maxwellian by virtue of (i) inelastic collisions at high energy with CrII, CI, CII, OI, etc., and (ii) elastic collisions at low energy predominantly with NeI. Preferential degrading of high-velocity electrons may considerably reduce the over-all efficiency of the electrons in exciting CrI to high-energy levels.

(II) L. R. Doherty has suggested that we examine the manner in which a steady excitation distribution is established through the interplay of excitation and de-excitation by collision and radiation. An instructive example is a gas of two-state atoms wherein one neglects collisional de-excitation and assumes the optical depth to be so small that radiative excitation is also negligible. A steady relative population of the two states is maintained only if the numbers per second of collisional excitations and radiative de-excitations are equal. Thus the population ratio is dictated primarily by the relative sizes of the Einstein emission coefficient and the collisional excitation cross section, and only indirectly by the kinetic temperature of the exciting particles.

(III) We are studying the effects of heat conduction in developing a sheath of cold, high-density gas near the shock tube wall. Such a layer would have some effect on the radiation field as observed from outside the shock tube.

Further experiments on excitation temperature are now under way. In addition, we hope to be able to derive new information about absolute line intensities for CrI and CrII. Complete reports of this work will be prepared in the near future.

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On the Dilatational Viscosity of Simple Dense Fluids

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THE diminution in intensity of the amplitude of a planar longitudinal wave traversing a liquid is, neglecting radiation losses, due to the conversion of the organized collective motion of the sonic pulse into random thermal motion. The total attenuation may be separated into contributions due to thermal conductivity and viscous loss. This latter contribution is itself separable into two components: that due to shear viscosity η and that due to dilatational viscosity Φ , with η and Φ defined by the Newtonian stress tensor

$$\sigma = \left[-p + \left(\Phi - \frac{2\eta}{3} \right) \nabla \cdot \mathbf{u} \right] \mathbf{1} + 2\eta \dot{\epsilon}. \quad (1)$$

The bulk viscosity, η_B , is commonly defined as the coefficient of $\nabla \cdot \mathbf{u}$ in Eq. (1) and thereby related to η and Φ .

For polyatomic fluids the dilatational viscosity can be related to intramolecular relaxation phenomena.¹ Indeed, two-state or similar models provide the basis for many calculations of sonic attenuation.² On the other hand, for monoatomic fluids, the dilatational viscosity has thus far eluded measurement. In view of the extensive investigations of relaxation and energy transfer phenomena in liquid media, it is of importance to establish the magnitude to be expected for the intrinsic dilatational viscosity and to determine whether or not substantial corrections must be applied to the multiple state models of intramolecular relaxation.

There have been a number of investigations directed at the calculation of the dilatational viscosity of a monoatomic fluid. Kirkwood³ and Nettleton⁴ linked the dissipative effects to the perturbation of the distribution function in pair space. Kirkwood's calculation is valid for dense fluids and leads to a value of Φ of 0.36×10^{-3} poise for liquid argon at 89°K, whereas Nettleton's calculation is valid only in the gaseous range and predicts bulk viscosities of the order of 10^{-6} poise. Herzfeld⁵ has computed the dilatational viscosity by starting from a result of M. S. Green⁶ which relates the autocorrelation function of the virial to Φ . The autocorrelation function is calculated from a fluctuation distribution function expressed

in terms of thermodynamic derivatives. It is necessary to carry the second-order derivatives to obtain a non-vanishing contribution. Herzfeld's calculation presents the bulk viscosity in terms of known thermodynamic functions and an unknown correlation time and length. Kirkwood's and Nettleton's analyses lead to inconvenient formulas which require extensive calculation to obtain numerical values.

It is the purpose of this note to present a calculation of the dilatational viscosity in terms of the coefficient of self-diffusion and thermodynamic properties of the fluid. The assumptions made in the calculation are the following⁷:

- (1) The process of diffusion in a dense fluid medium involves many displacements small relative to the internuclear spacing.
- (2) The distribution function may be adequately approximated as corresponding to local equilibrium in configuration space and locally Maxwellian in momentum space.
- (3) The pair diffusion tensor may be approximated as the direct sum of singlet diffusion tensors.

It is then possible to show that

$$\Phi = \frac{m}{18\zeta} \left(\frac{N}{v} \right)^2 \int R^2 \left[\frac{d^2 V}{dR^2} + \frac{1}{R} \frac{dV}{dR} \right] g_0^{(2)}(R) d^3 R, \quad (2)$$

$$\zeta^2 = \frac{Nm}{3v} \int \nabla^2 V(R) g_0^{(2)}(R) d^3 R,$$

with m the mass, N the number of molecules, v the volume, $V(R)$ the intermolecular pair potential, and $g_0^{(2)}(R)$ the local equilibrium pair correlation function. By introduction of the Lennard-Jones form of the pair potential and use of the equation of state and the potential energy of the fluid, L ,¹

$$L = -\frac{N^2}{2v} \int V(R) g_0^{(2)}(R) d^3 R, \quad (3)$$

$$\frac{pv}{NkT} = 1 - \frac{N}{6vkT} \int R \frac{dV}{dR} g_0^{(2)}(R) d^3 R,$$

it is easily shown that

$$\Phi = \frac{2mD}{vkT} [4L - 3RT + 3pv], \quad D = \frac{kT}{\zeta}. \quad (4)$$

Equation (4) has the correct behavior in the ideal gas limit. For, when the density is very low, $pv \rightarrow RT$ and $L \rightarrow 0$ so that, $\Phi \rightarrow 0$. This is in complete agreement with the observation that the bulk viscosity arises from collisional transfer of momentum and has no kinetic component.

Equation (4) may be compared with the corresponding expression from this theory for the intermolecular force contribution to the shear viscosity,⁷

$$\eta_v = \frac{3mD}{5vkT} [8L - 5RT + 5pv], \quad (5)$$

whence $\Phi/\eta_v \approx 5/3$, a result rather larger than that predicted by Kirkwood ($\Phi/\eta_v \approx \frac{1}{2}$). For liquid argon at 89°K and one atmosphere, Eq. (4) gives $\Phi = 1.8 \times 10^{-3}$