# The Saha equation and the adiabatic exponent in shock wave calculations

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The purpose of this note is to comment on the calculation of equilibrium gas dynamic parameters behind strong shock waves. The writer has been aroused by the appearance of a paper by Guman (1956) presenting a generalized computing scheme for ionizing shock waves in monatomic gases. In that paper the reader is not cautioned about including excited states in the Saha equation for the computation of the degree of ionization behind shock fronts at appropriate temperatures and densities. The same paper treats the adiabatic exponent $\gamma = c_p/c_v$ as constant across strong shocks when at the same time it is implied that the computing scheme is of general validity. Hence, the unwary reader might attempt to apply the scheme in a regime where $\gamma$ is not only no longer constant but is no longer a useful quantity for characterizing the shock conditions. Other authors (see, for example, Glass, Martin & Patterson (1953)) characterize flows in which a shock has excited internal degrees of freedom in terms of a variable specific heat ratio when in fact one cannot use this quantity in calculating shock front conditions.

The following comments on some of these points are presented with apologies to those readers who are familiar with so-called real gas effects; however, the appearance of the material referred to above, as well as other examples in the literature, seems to require some comment.

Let us consider first the Saha equation. In a dilute electrically neutral gas in thermodynamic equilibrium at a temperature and density such that only neutral and singly ionized atoms are present, the concentrations (number density) of neutral atoms $N_I$, of singly ionized atoms $N_{II}$ and of electrons $N_e$, are related by the Saha equation (see, for example, Aller (1953), or Fowler (1955))

$$N_{II} N_e/N_I = 2(2\pi m_e kT/h^2)^{3/2}[B_{II}(\rho, T)/B_I(\rho, T)]\exp(-\chi_I/kT), \qquad (1)$$

where $B_I$ and $B_{II}$ are the partition functions for atoms and ions respectively, the factor 2 is the statistical weight for electrons, $\chi_I$ is the first ionization potential of the atom in question, and the other symbols have their usual meanings. At low temperatures and moderate densities, $B_{II}/B_I$ is adequately approximated by the ratio of the statistical weights of the ground states, $g_{II}/g_I$. At either higher temperatures or lower densities, significant population of excited states occurs, and $B_{II}/B_I$ must be computed more carefully. It may be noted that there appears to exist no unique and universally accepted procedure for computing $B_I$ and $B_{II}$. Since the partition functions for an isolated atom or ion diverge, one must invoke the presence of other neutral and charged particles in the gas to obtain a reasonable correction to the partition sums. The recipes suggested by various investigators range widely in complexity (Bethe 1942; Fuchs, Lynch & Peierls 1942; Ecker & Weizel 1956; Meghreblian 1953; Unsöld 1948; Woolley 1955). Perhaps the simplest approach is to consider as bound to the atom or ion, and hence as contributing to bound-state partition sums, only those electrons whose classical orbits do not exceed half the mean separation of particles in the gas. Such an assumption, together with an adjustment in the statistical weight of the outermost orbit to allow for the fact that mean particle separation is not generally an integral number of Bohr radii, yields partition functions which agree satisfactorily with more detailed analyses which involve not only this 'pressure ionization' but also electrostatic effects, modification of the more deeply bound energy levels, and correction of the partition function for free electrons (compare Fuchs, Lynch & Peierls (1942) and Bond (1954)). For example, the high temperature equation of state for argon computed by Bond (1954), using a 'pressure ionization' cut-off in the partition functions, agrees very well with shock wave measurements by Christian & Yarger (1955). We shall not attempt here to review the literature on the computation of partition functions, but rather would recommend to the reader who must deal with calculations of ionization equilibrium the representative references which have been cited.

| *Argon* | | | *Helium* | | |
|---|---|---|---|---|---|
| $\rho$(gm/cm$^3$) | $T$(°K) | $\alpha_g/\alpha_B$ | $\rho$(gm/cm$^3$) | $T$(°K) | $\alpha_g/\alpha_B$ |
| $1{\cdot}33\times10^{-3}$ | 8 000 | 1·040 | $10^{-1}$ | 50 000 | 1·11 |
| $1{\cdot}33\times10^{-3}$ | 10 000 | 1·033 | $10^{-1}$ | 75 000 | 1·26 |
| $2{\cdot}66\times10^{-3}$ | 12 000 | 1·029 | $5\times10^{-2}$ | 50 000 | 1·17 |
| $2{\cdot}66\times10^{-3}$ | 16 000 | 1·029 | $5\times10^{-2}$ | 75 000 | 1·40 |
| $4{\cdot}00\times10^{-3}$ | 20 000 | 1·065 | $10^{-2}$ | 50 000 | 1·20 |
| $5{\cdot}33\times10^{-3}$ | 23 000 | 1·154 | $10^{-2}$ | 75 000 | 1·47 |
| $5{\cdot}33\times10^{-3}$ | 25 000 | 1·225 | $10^{-4}$ | 25 000 | 1·01 |

Table 1

To emphasize the effect of using only ground state statistical weights in the Saha equation, let us consider the calculation of the degree of ionization $\alpha$, where

$$\alpha = N_{II}/(N_I+N_{II}) = N_e/(N_I+N_{II}). \tag{2}$$

Let $\alpha_B$ denote the ionization fraction calculated with corrected partition functions $B_{II}$ and $B_I$, and $\alpha_g$ the ionization computed using ground state statistical weights $g_{II}$ and $g_I$. Then, if we write

$$B_I/B_{II} = (1+f)g_I/g_{II}, \tag{3}$$

it follows that

$$\alpha_g/\alpha_B = [1+(1-\alpha_g^2)f]^{\frac{1}{2}} = [(1+f)/(1+\alpha_B^2 f)]^{\frac{1}{2}}. \tag{4}$$

This quantity is tabulated in table 1 at several values of $\rho$ and $T$ for argon, based on partition functions computed by Bond (1954), and for helium, based on calculations by the author and colleagues. Both involve the simple 'pressure ionization' correction. Clearly a deliberate decision is required before neglecting excited states in applying the Saha equation to strong shock calculations.

Let us now turn to the use of the adiabatic exponent $\gamma$ in the Rankine–Hugoniot relations. This index is usually introduced into the equations of conservation across a shock front by noting that the internal energy of an ideal gas is written

$$E = \int_{1/\rho}^{\infty} p\, d(1/\rho) = \frac{1}{\gamma-1}\frac{p}{\rho}, \tag{5}$$

if $p = k\rho^{\gamma}$ and $\gamma$ is a constant. If (5) is valid across the shock, the Hugoniot condition may be written

$$\begin{aligned}\tfrac{1}{2}(p_2-p_1)\left(\frac{1}{\rho_1}+\frac{1}{\rho_2}\right) &= E_2\left(1+\frac{p_2}{\rho_2 E_2}\right)-E_1\left(1+\frac{p_1}{\rho_1 E_1}\right)\\ &= (E_2-E_1)\gamma. \end{aligned}\tag{6}$$

However, if the gas is vibrationally or electronically excited, dissociated, or otherwise changed in composition, or ionized by the shock, the internal energy is no longer a simple function of $p$ and $\rho$ as in (5), and the usual simplification of the shock front conservation relations by the introduction of $\gamma$ is no longer possible. One can discuss the strongly shocked gas in terms of a new quantity $\beta$, as used by Bethe & Teller (1940), viz.

| | $\rho$(gm/cm$^3$) | $10^{-5}$ | $10^{-4}$ | $10^{-3}$ | $10^{-2}$ | $10^{-1}$ |
|---|---|---|---|---|---|---|
| Helium, 25 000°K | $\gamma$ | – | 1·46 | 1·52 | 1·58 | 1·62 |
| | $\gamma'$ | – | 1·65 | 1·65 | 1·66 | 1·66 |
| Helium, 50 000°K | $\gamma$ | – | 1·22 | 1·16 | 1·17 | 1·26 |
| | $\gamma'$ | – | 1·53 | 1·42 | 1·44 | 1·50 |
| Air (dry), 3000°K | $\gamma$ | 1·17 | 1·18 | 1·21 | 1·23 | – |
| | $\gamma'$ | 1·24 | 1·27 | 1·30 | 1·30 | – |

Table 2. The data for air are taken from Gilmore (1955) and Hirschfelder & Curtiss (1948).

$$\beta = 1+\rho E/p, \tag{7}$$

or an 'effective specific heat ratio' $\gamma'$, as used by Gilmore (1955) and Sänger-Bredt (1955), viz.

$$\gamma' = \beta/(\beta-1) = 1+p/\rho E. \tag{8}$$

These quantities require appropriate calculation of the high temperature thermodynamic properties of the gas. Note that for an ideal gas $\gamma'$ reduces to the usual $\gamma$. Using (8) one may develop shock front relations involving $\gamma_1'$ for the unshocked gas ($\gamma_1' = \gamma_1$ ordinarily) and $\gamma_2'$ for the shocked gas ($\gamma_2' \neq \gamma_2$) which will formally resemble relations one might write down with $\gamma_1$ and $\gamma_2$. Thus the usual Hugoniot relation can be written in terms of $\gamma'$ in the form

$$\tfrac{1}{2}[(p_2-p_1)(1/\rho_1+1/\rho_2)] = E_2\gamma_2'-E_1\gamma_1'. \qquad (9)$$

Solution of this for $\rho_1/\rho_2$ will give an erroneous result if $\gamma_2'$ is taken as the specific heat ratio. To illustrate the errors possible, we present in table 2 some comparisons of $\gamma$ and $\gamma'$.

Alternatively one may evaluate numerically the gas parameters behind a strong shock without introducing any special functions (see Resler, Lin & Kantrowitz (1952) and Romig (1956)). Evidently the principal use of the adiabatic index $\gamma$ in describing the thermodynamic state of a strongly shocked gas appears to be in calculating one of the sound velocities which may be defined (see Bethe & Teller (1940)).

## REFERENCES

ALLER, L. H. 1953 *Astrophysics—The Atmospheres of the Sun and Stars.* New York: Ronald Press.

BETHE, H. A. 1942 The specific heat of air up to 25 000° C, *Office of Scientific Research and Development, Rep* no. 369.

BETHE, H. A. & TELLER, E. 1940 Deviations from thermal equilibrium in shock waves, *Ballistic Research Laboratories, Aberdeen Proving Ground, Maryland, Rep.* no. X117.

BOND, J. W. 1954 The structure of a shock front in Argon, *Los Alamos Scientific Laboratory, Rep.* no. LA 1603.

CHRISTIAN, R. H. & YARGER, F. L. 1955 *J. Chem. Phys.* **23**, 2042.

ECKER, G. & WEIZEL, W. 1956 *Ann. d. Phys.* **17**, 126.

FOWLER, R. H. 1955 *Statistical Mechanics.* Cambridge University Press. (In this book the earlier work on Fermi, Urey and Planck on the computation of partition functions is also discussed.)

FUCHS, K., LYNCH, G. J. & PEIERLS, R. 1942 The equation of state of air at high temperature, *British Ministry of Supply, Department of Atomic Energy,* BDDA 16, *Rep.* no. MS61 (*U.S. Dept of Commerce* PBL 87018).

GILMORE, F. R. 1955 Equilibrium composition and thermodynamic properties of air to 24 000° K, *Rand Corporation, Santa Monica, California, Rep.* no. RM1543.

GUMAN, W. J. 1956 *J. Appl. Phys.* **27**, 663.

GLASS, I. I., MARTIN, W. & PATTERSON, G. N. 1953 A theoretical and experimental study of the shock tube, *University of Toronto Institute of Aerophysics, Rep.* no. 2.

HIRSCHFELDER, J. L. & CURTISS, C. F. 1948 Thermodynamic properties of air at high temperatures, *University of Wisconsin, Rep.* no. CM–518.

MEGHREBLIAN, R. V. 1953 Thermodynamic functions of poly-electronic atoms at very high temperatures, *California Institute of Technology, Ph.D. Thesis.*

RESLER, E. L., LIN, S. C. & KANTROWITZ, A. 1952 *J. Appl. Phys.* **23**, 1390.

ROMIG, M. L. 1956 *J. Aero. Sci.* **23**, 185.

SÄNGER-BREDT, I. 1955 *Z. angew. Math. Phys.* **6**, 35. (This paper is a very thorough discussion of the role of the adiabatic index in gas dynamics. The author specifically discusses isentropic flows which are generalized by means of an index $\sigma$, equivalent to $\gamma'$ in equation (8).)

UNSÖLD, A. 1948 *Z. Astrophys.* **24**, 355.

WOOLLEY, H. W. 1955 Thermodynamic functions of atomic ions. I. Fundamental theory, *National Bureau of Standards, Washington, Rep.* no. 4089.