Intermolecular-Force Effects on the Thermodynamic Properties of Helium with Application

EDWIN F. HARRISON*
NASA Langley Research Center, Hampton, Va.

Nomenclature

a = speed of sound, cm/sec
B = second virial coefficient, cm^3/mole
C = third virial coefficient, (cm^3/mole)^2
D = fourth virial coefficient, (cm^3/mole)^3
C_v = specific heat at constant volume, joules/mole-°K
h = enthalpy, joules/mole
p = pressure, atm
R = gas constant, 82.0567 atm-cm^3/mole-°K or 8.31436 joules/mole-°K
s = entropy, joules/mole-°K
T = temperature, °K
u = velocity, cm/sec
Z = compressibility factor
ρ = density, mole/cm^3
$\Delta E/V$ = internal energy increment transferred from an electrical discharge to each unit volume of gas, joules/cm^3

Subscripts

0 = initial reservoir conditions
3 = expansion conditions of shock tube driver gas after diaphragm rupture
i = ideal-gas conditions
r = real-gas conditions
t = stagnation reservoir conditions following an electrical discharge into a constant volume of gas. $t = 4$ for shock-tube applications

Introduction

In gasdynamic research, helium is presently being utilized as the test gas in hotshot wind tunnels at stagnation pressures as high as 1500 atm and stagnation temperatures ranging from 1000° to 4000°K. Helium is also being considered for usage as the driver gas in electrically-driven shock tubes at stagnation pressures above 1000 atm and stagnation temperatures as low as 2000°K. At these conditions, helium does not obey the ideal-gas equations that are usually assumed. In fact, the values of the thermodynamic properties of the gas will deviate from the ideal-gas data because of the effects of intermolecular forces in the gas. The actual amount of these real-gas effects on the properties of helium must be known in order to analyze accurately the experimental data obtained from the aforementioned facilities.

Some studies[1, 2] have been made which included intermolecular-force (real-gas) effects on the steady-state properties of helium. First-order estimates of these effects on the hypersonic nozzle flow parameters have been presented in Ref. 3. All of these results[1–3] are based on the Beattie-Bridgeman equation of state. However, the constants used in this equation were determined from data at temperatures up to only about 1000°K. In order to calculate real-gas effects above this temperature, the virial equation of state appeared to best represent the state properties of helium based on the results of Refs. 4–7. Thus, this equation has been utilized in the present study.

This paper presents the thermodynamic equations for enthalpy, entropy, internal energy increment, and speed of sound based on the virial equation of state. These equations have been employed to generate thermodynamic data for helium at pressures up to 3000 atm and temperatures up to 10,000°K. These real-gas results are presented along with ideal-gas results to show the contribution of intermolecular forces to the thermodynamic properties of helium. Also included in this study is an application of these data to the performance of a shock-tube driver.

Method

The virial form of the equation of state of a pure gas can be written as

$$p = \rho RT(1 + B\rho + C\rho^2 + D\rho^3) = \rho RTZ \qquad (1)$$

where B, C, and D are virial coefficients and are functions only of the temperature and the law of intermolecular force. Other general thermodynamic equations have been derived based on Eq. (1). For the derivation of these equations, the same fundamental equations and method of development as given in Ref. 3 was used with one exception. The Beattie-Bridgeman equation of state[3] was replaced by the virial equation of state. Thus, for convenience, only the final derived equations will be given here. These equations for enthalpy, entropy, internal energy increment, and the speed of sound are, respectively,

$$h = RT\left[\frac{5}{2} + \rho\left(B - T\frac{dB}{dT}\right) + \frac{\rho^2}{2}\left(2C - T\frac{dC}{dT}\right) + \frac{\rho^3}{3}\left(3D - T\frac{dD}{dT}\right)\right] \qquad (2)$$

$$s = R\left[\frac{3}{2}\ln T - \ln\rho - \rho\left(B + T\frac{dB}{dT}\right) - \frac{\rho^2}{2}\left(C + T\frac{dC}{dT}\right) - \frac{\rho^3}{3}\left(D + T\frac{dD}{dT}\right)\right] \qquad (3)$$

$$\Delta E/V = (h - h_0)\rho - (p - p_0) \qquad (4)$$

$$a^2 = \left(\frac{\partial p}{\partial \rho}\right)_T + \frac{T}{\rho^2 C_v}\left(\frac{\partial p}{\partial T}\right)_\rho^2 \qquad (5)$$

where

$$(\partial p/\partial \rho)_T = RT(1 + 2B\rho + 3C\rho^2 + 4D\rho^3)$$

$$\left(\frac{\partial p}{\partial T}\right)_\rho = R\rho\left[1 + \rho\left(B + T\frac{dB}{dT}\right) + \rho^2\left(C + T\frac{dC}{dT}\right) + \rho^3\left(D + T\frac{dD}{dT}\right)\right]$$

$$C_v = \frac{3}{2}R - RT\left[\rho\left(2\frac{dB}{dT} + T\frac{d^2B}{dT^2}\right) + \frac{\rho^2}{2}\left(2\frac{dC}{dT} + T\frac{d^2C}{dT^2}\right) + \frac{\rho^2}{3}\left(2\frac{dD}{dT} + T\frac{d^2D}{dT^2}\right)\right]$$

The virial coefficients for helium over a wide temperature range of 300° to 10,000°K may be expressed in the following manner:

$$B = 1.3436 \times 10^{-2}[15.8922 - \ln T]^3 - 4.39\exp[-(2.4177 \times 10^{-3})T] \qquad (6)$$

where the term $4.39\exp[-(2.4177 \times 10^{-3})T]$ is negligible for $T \geq 2000$°K, and

$$C = 9.0263 \times 10^{-5}\,[15.8922 - \ln T]^6 \qquad (7)$$

$$D = 7.0341 \times 10^{-7}\,[15.8922 - \ln T]^9 \qquad (8)$$

All of these coefficients for helium were determined by Amdur and Mason[4] except for the expression B at temperatures between 300° and 2000°K. In this region the equation for B was slightly modified by the addition of a negative exponential term in order to make it agree more closely with some experimental results.[5–7] However, the equations for C and D agreed reasonably well with the available experimental data[5] even at temperatures as low as 300°K. It should be noted that the coefficient equations (6–8) are applicable for

---

Received June 29, 1964.

* Aerospace Engineer. Member AIAA.

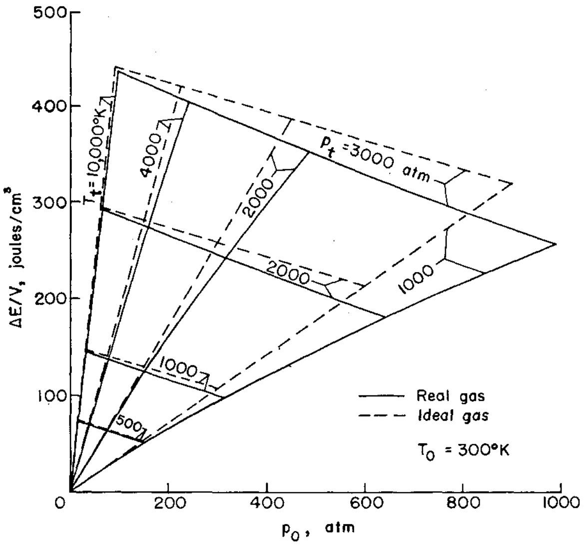

Fig. 1 Effect of internal energy additions on helium reservoir conditions.

temperatures up to 15,000°K, although the calculations contained in this paper are limited to only 10,000°K. Since the virial cofficients are expressed as a simple function of temperature, the derivatives required in Eqs. (2–5) were easily determined by direct differentiation.

The ideal-gas equations used in this study were taken from Ref. 8. These equations were based on the assumptions that the compressibility factor in the equation of state had a value of one, and the ratio of the specific heats equaled $\frac{5}{3}$ for helium.

Results and Discussion

Figure 1 shows the stagnation temperature and pressure that may be anticipated for real and ideal helium systems for a range of internal energy increments and a range of initial pressures. It may be seen that the energy required to produce a given stagnation temperature and pressure is considerably less for the real gas than for the ideal gas. However, in this case, the real-gas initial pressure must be slightly increased. For example, assume $(T_t)_r = (T_t)_i = 1000°K$ and $(p_t)_r = (p_t)_i = 2000$ atm, then $(\Delta E/V)_r = 0.84\ (\Delta E/V)_i$ and $(p_0)_r = 1.06\ (p_0)_i$. Shown in Fig. 2 is the real-gas compressibility factor and in Fig. 3 is the ratio of the real-to-ideal gas speed of sound as a function of pressure for various temperatures. Here it can be seen that at low temperatures and high pressures, which correspond to high densities, the real-gas compressibility factor as well as the real-gas speed of sound may be up to 25% larger than the ideal-gas results. Hence, Figs. 1–3 illustrate the significance of real-gas effects, caused by intermolecular forces, on the thermodynamic properties of helium.

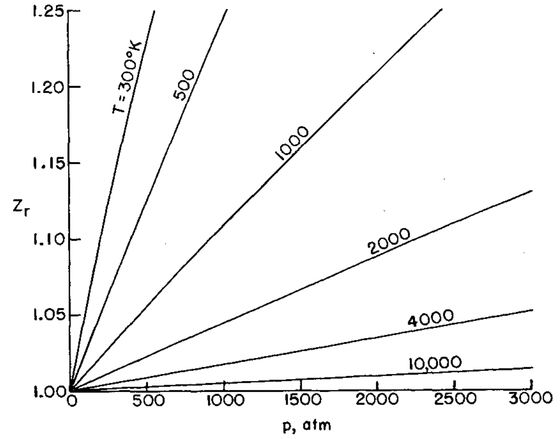

Fig. 2 Effect of pressure and temperature on the compressibility factor of helium.

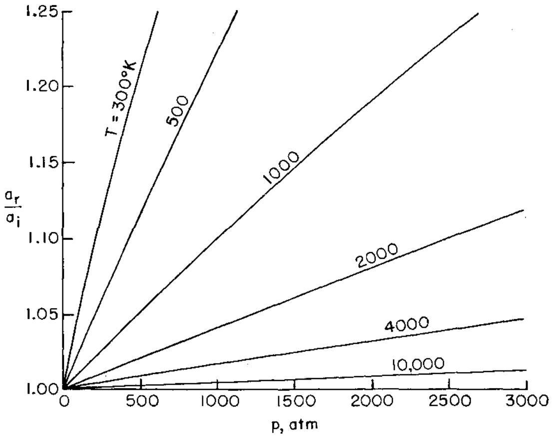

Fig. 3 Effect of pressure and temperature on the speed of sound of helium.

A very interesting application of these results can be made considering helium as a driver gas in a shock tube. In this case, the helium expands isentropically and the velocity[8] is generally expressed as

$$u_3 = \int_4^3 \left(\frac{dp}{\rho a}\right)_{s_4 = s_3} \tag{9}$$

Although Figs. 2 and 3 show that Z_r and a_r/a_i can have values considerably larger than 1, it should be noted that, for a first-order approximation,

$$(a_r/a_i)/Z_r \cong 1 \quad \text{for} \quad p_r = p_i \quad \text{and} \quad T_r = T_i \tag{10}$$

Using the fact that $Z_r = \rho_i/\rho_r$ for these same pressure and temperature conditions, Eq. (10) may be expressed as

$$\rho_r a_r \cong \rho_i a_i \tag{11}$$

Thus, assuming a given reservoir of helium for which $(p_4)_r = (p_4)_i$ and $(T_4)_r = (T_4)_i$ are isentropically expanded to $(p_3)_r = (p_3)_i$ according to Eqs. (3) and (9) and the ideal-gas entropy equation, then the results are $(u_3)_r \cong (u_3)_i$. In this case, the main reason that $(u_3)_r \cong (u_3)_i$ is because Eq. (11) may be utilized in Eq. (9).

In practice, however, the initial pressure and stagnation pressure are measured instead of the stagnation temperature and pressure. Under these conditions, it was determined that the intermolecular forces caused a slight effect on the value of T_4, and a larger effect on the value of u_3 than in the previous case. These effects still caused the real-gas results to be only about 3% greater than the ideal-gas values for reservoir conditions of $p_0 \leq 150$ atm and $p_4 \leq 2000$ atm and reasonable expansion conditions.

However, real-gas effects become more appreciable for higher initial and stagnation pressures. For example, assume $(p_0)_r = (p_0)_i = 600$ atm and $(p_4)_r = (p_4)_i = 3000$ atm, then $(T_4)_r = 1.10(T_4)_i$ and $(u_3)_r \geqq 1.07(u_3)_i$ for $(p_3)_r = (p_3)_i$, depending on the expansion length. Hence, real-gas effects should probably be included in application of helium at very high initial pressures (i.e., high densities) and high stagnation pressures.

References

[1] Akin, S. W., "The thermodynamic properties of helium," Trans. Am. Soc. Mech. Engrs. **72**, 751–757 (1950).

[2] Wilson, M. P., Jr., "Thermodynamic and transport properties of helium," Electric Boat Div., General Dynamics Corp. Rept. MGCR-PR-60-1550 (1960).

[3] Erickson, W. D., "An extension of estimated hypersonic flow parameters for helium as a real gas," NASA TN D-1632 (1963).

[4] Amdur, I. and Mason, E. A., "Properties of gases at very high temperatures," Phys. Fluids **1,** 370–383 (1958).

[5] Michels, A. and Wouters, H., "Isotherms of helium between 0° and 150°C up to 200 amagat," Physica **8,** 923 (1941).

[6] Schneider, W. G. and Duffie, J. A. H., "Compressibility of gases at high temperatures II. The second virial coefficient of helium in the temperature range of 0° to 600°C," J. Chem. Phys. **17,** 751 (1949).

[7] Yntema, J. L. and Schneider, W. G., "Compressibility of gases at high temperatures III. The second virial coefficient of helium in the temperature range of 600° to 1200°C," J. Chem. Phys. **18,** 641 (1950).

[8] Liepmann, H. W. and Roshko, A., *Elements of Gasdynamics* (John Willey and Sons, Inc., New York, 1957), pp. 8–51, 71–83.

Chaplygin's Transformation Applied to Magnetogasdynamics

E. V. Laitone*
University of California, Berkeley, Calif.

THE studies[1–6] concerning two-dimensional magnetogasdynamics with infinite conductivity and either an aligned or a transverse magnetic field seem to have missed the fact that all of their exact solutions can be derived more easily by applying the fundamental relations developed by Bers and Gelbart[7] and, even more important, the fact that the analytic continuation through the sonic line should be expressed in terms of the Chaplygin[8] transformation σ rather than the canonical transformation S introduced by Christianovich.[9]

Following Bers and Gelbart,[7] we note that if we can write the following expressions in the physical (x, y) plane

$$
\begin{aligned}
Q(q)\cos\theta &= \partial\phi/\partial x = P(q)(\partial\psi/\partial y) \\
Q(q)\sin\theta &= \partial\phi/\partial y = -P(q)(\partial\psi/\partial x)
\end{aligned}
\tag{1}
$$

where P and Q are analytic functions of the velocity magnitude (q) only, then a solution in the hodograph (q, θ) plane may be written as

$$
\begin{aligned}
\psi(q, \theta) &= \sum_{m=0}^{\infty} C_m \psi_m(q, \theta) \\
\psi_{n+1} &= \int \psi_n d\theta + \int (PQ)^{-1} \phi_n dQ \\
\phi_{n+1} &= \int \phi_n d\theta + \int Q \frac{d(P/Q)}{dQ} \psi_n dQ
\end{aligned}
\tag{2}
$$

where ψ_n and ϕ_n represent any solutions of the generalized hodograph equations

$$
\frac{\partial\phi}{\partial\theta} = PQ \frac{\partial\psi}{\partial Q} \qquad \frac{\partial\phi}{\partial Q} = Q \frac{d(P/Q)}{dQ} \frac{\partial\psi}{\partial\theta}
\tag{3}
$$

For example, taking $\psi_0 = 0$ and $\phi_0 = \text{const}$ means that ψ_1 corresponds to a generalized vortex flow, whereas $\phi_0 = 0$ and $\psi_0 = \text{const}$ yield the equivalent of a source or a sink. Then a superposition of the two solutions gives a spiral type flow, and so on. The flow about an infinite half-plane, corresponding to the Ringleb[10] solution, is given by

$$
\psi = CQ^{-1} \sin\theta \qquad \phi = CPQ^{-1} \cos\theta
\tag{4}
$$

In this same general form the Chaplygin[8] transformation may be written as

$$
\begin{gathered}
\frac{d\sigma}{dQ} = -\frac{1}{PQ} \qquad \frac{\partial\phi}{\partial\theta} = -\frac{\partial\psi}{\partial\sigma} \qquad \frac{\partial\phi}{\partial\sigma} = K \frac{\partial\psi}{\partial\theta} \\
\frac{\partial^2\psi}{\partial\sigma^2} + K \frac{\partial^2\psi}{\partial\theta^2} = 0 \\
K(\sigma) = -PQ^2 \frac{d(P/Q)}{dQ}
\end{gathered}
\tag{5}
$$

On the other hand, the canonical transformation becomes

$$
\begin{gathered}
\frac{dS}{dQ} = -\frac{K^{1/2}}{PQ} \qquad \frac{\partial\phi}{\partial\theta} = -K^{1/2} \frac{\partial\psi}{\partial S} \\
\frac{\partial\phi}{\partial S} = +K^{1/2} \frac{\partial\psi}{\partial\theta} \qquad \frac{\partial^2\psi}{\partial S^2} + \frac{\partial^2\psi}{\partial\theta^2} = -\frac{1}{K^{1/2}} \frac{dK^{1/2}}{dS} \frac{\partial\psi}{\partial S}
\end{gathered}
\tag{6}
$$

The well-known relations for isentropic perfect gas flow are immediately given by writing

$$
\left.
\begin{aligned}
&Q = q \qquad P = \frac{\rho_0}{\rho_0} \qquad \frac{d(P/Q)}{dQ} = -\frac{\rho_0}{\rho q^2}(1 - M^2) \\
&K = -\frac{\rho_0 q^2}{\rho} \frac{d(\rho_0/\rho q)}{dq} = \left(\frac{\rho_0}{\rho}\right)^2 (1 - M^2) = \\
&\qquad\qquad 2\left(\frac{\gamma + 1}{2}\right)^{(\gamma+2)/(\gamma-1)} \sigma + 0(\sigma^2) \\
&\frac{1}{K^{1/2}} \frac{dK^{1/2}}{dS} = \frac{\gamma + 1}{2} \frac{M^4}{(1 - M^2)^{3/2}} = -\frac{1}{3S} + O(S^{-1/3})
\end{aligned}
\right\}
\tag{7}
$$

The magnetogasdynamic flow with an aligned magnetic field, wherein the magnetic field lines are everywhere coincident with the streamlines, may be written by following Iur'ev,[2] for a gas with infinite conductivity, as

$$
\begin{gathered}
\mathbf{B} = \alpha\rho\mathbf{q} \qquad \mathbf{q} \times (\nabla \times \mathbf{q}) = (\rho\mu)^{-1}\mathbf{B} \times (\nabla \times \mathbf{B}) \\
\frac{\partial}{\partial x}[v(1 - m\rho)] = \frac{\partial}{\partial y}[u(1 - m\rho)]
\end{gathered}
\tag{8}
$$

where $m = \alpha^2/\mu = \text{const}$. These relations correspond to Eq. (1) if we write

$$
\begin{aligned}
Q &= (u^2 + v^2)^{1/2}(1 - m\rho) = q(1 - m\rho) \\
P &= (\rho_0/\rho)(1 - m\rho) = (\rho_0/\rho)(Q/q)
\end{aligned}
\tag{9}
$$

so that Eq. (5) reduces to

$$
\frac{d\sigma}{dq} = \frac{\rho_0}{\rho q}(1 - m\rho)^{-2}[1 - m\rho(1 - M^2)]
$$

$$
K(\sigma) = \left(\frac{\rho_0}{\rho}\right)^2 (1 - M^2) \left[\frac{(1 - m\rho)^3}{1 - m\rho(1 - M^2)}\right] = K(S)
\tag{10}
$$

where K is in agreement with the resuts first given by Iu'rev[2] and later by Smith.[6] The effect of a weak magnetic field is clearly shown by the series expansion

$$
K(\sigma) = \left(\frac{\rho_0}{\rho}\right)^2 (1 - M^2) \left[1 - \frac{\alpha^2\rho}{\mu}(2 + M^2) + 0\left(\frac{\alpha^2\rho}{\mu}\right)^2\right]
\tag{11}
$$

Similarly, for the vortex flow we obtain from Eqs. (3) and (9)

$$
\begin{gathered}
\phi = \theta \qquad \psi = \sigma \qquad (a_0/a_*)^2 = (\gamma + 1)/2 \\
\psi = \int \frac{\rho}{\rho_0} \left[\frac{1 - m\rho(1 - M^2)}{(1 - m\rho)^2}\right] \frac{dq}{q} = \\
\left(1 + \frac{\alpha^2\rho_0}{\mu}\right) \ln\left[\left(\frac{\gamma - 1}{2}\right)^{1/2} \frac{q}{a_0}\right] - \frac{1}{4}\left(\frac{q}{a_0}\right)^2 + \ldots
\end{gathered}
\tag{12}
$$

and from Eq. (4) we obtain the equivalent of the Ringleb[10] flow as

$$
\begin{gathered}
\phi = (\rho_0/\rho_q)\cos\theta \\
\psi = q^{-1}\left(1 - \frac{\alpha^2\rho}{\mu}\right)^{-1} \sin\theta = \frac{\sin\theta}{q}\left[1 + \frac{\alpha^2\rho}{\mu} + 0\left(\frac{\alpha^2\rho}{\mu}\right)^2\right]
\end{gathered}
\tag{13}
$$

When the same procedure is applied to the transverse magnetic field that is assumed to remain everywhere normal to the

---

Received June 17, 1964.

* Professor and Chairman of the Division of Aeronautical Sciences. Associate Fellow Member AIAA.