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Assessment of UF_6 Equation of State

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Assessment of UF_6 Equation of State

Summary

A common assumption in the mathematical analysis of flows of compressible fluids is to treat the fluid as a perfect gas. This is an approximation, as no real fluid obeys the perfect gas relationships over all temperature and pressure conditions. An assessment of the validity of treating the UF_6 gas flow field within a gas centrifuge with perfect gas relationships has been conducted.

The definition of a perfect gas is commonly stated in two parts: 1) the gas obeys the thermal equation of state, $p = \rho RT$ (thermally perfect), and, 2) the gas specific heats are constant (calorically perfect). Analysis indicates the thermally perfect assumption is valid for all flow conditions within the gas centrifuge, including shock fields. The low operating gas pressure is the primary factor in the suitability of the thermally perfect equation of state for gas centrifuge computations.

UF_6 is not calorically perfect, as the specific heats vary as a function of temperature. This effect is insignificant within the bulk of the centrifuge gas field, as gas temperatures vary over a narrow range. The exception is in the vicinity of shock fields, where temperature, pressure, and density gradients are large, and the variation of specific heats with temperature should be included in the technically detailed analyses. Results from a normal shock analysis incorporating variable specific heats is included herein, presented in the conventional form of shock parameters as a function of inlet Mach Number. The error introduced by assuming constant specific heats is small for a nominal UF_6 shock field, such that calorically perfect shock relationships can be used for scaling and initial analyses. The more rigorous imperfect gas analysis should be used for detailed analyses.

Introduction

Thermally perfect

No real gas obeys the perfect gas thermal equation of state, $p = \rho RT$, for all temperatures and pressures. However, all gases obey this equation of state in the limit as pressure goes to zero (and/or as temperatures increase), a consequence of a model in which the molecules are point masses—that is, they have no size—and in which there are no attractive forces between the molecules. Experimental equations of state account for the real effects of size and attractive forces, and there is an extensive array of experimentally determined equations of state for UF_6 [1,2,3,4]. This experimental data base allows evaluation of the deviations from ideal for UF_6. While the majority of the experimental data has been obtained for pressures from ~350 torr and above, published data does exist for pressures down to 50 torr. Nominal gas centrifuge operating conditions are on the

order of 100 torr and standard room temperature, and at these conditions the experimental data are in agreement such that the perfect gas thermal equation of state adequately defines the gas operating parameters. The deviations from ideal are 0.5% or less, within the range of experimental accuracy, and no benefit is gained from utilization of the more elaborate experimental equations of state. The primary driver is the low gas pressure level, with the experimental data indicating significant deviations from the ideal at higher pressures of one atmosphere and above.

Strong shocks are generated within a gas centrifuge when a blunt body is placed in the high speed gas stream. While gas pressures increase substantially across a normal shock, gas temperatures also increase and the net effect is a parameter space of low to moderate pressure (10-50 torr) and high temperature (400-600 K). Analysis indicates the perfect gas thermal equation adequately defines gas operating parameters in the shock field, with errors of less than 0.5%.

Calorically perfect

Many gases can be treated as calorically perfect, i.e., constant specific heat, as the specific heat varies weakly with temperature. Air, for example, has a nearly constant specific heat over a wide range of temperatures, allowing the widespread use of standard shock tables at a fixed value of γ, the ratio of specific heats.

The UF_6 molecule has been exhaustively studied and characterized for the past half-century, with notable amounts of experimental data on the specific heats of the gas. These data are in general agreement from experimenter to experimenter [1,3,6,7]. An analytical evaluation of specific heats using statistical mechanics is also available [5], and the experimental data are remarkably consistent with these theoretical results. The net effect is precise, reliable and consistent characterization of UF_6 specific heats. The data indicate a variation of specific heats with temperature. This variation is insignificant in computations involving the bulk of the centrifuge gas environment, as temperature variations are small. However, the effect can be significant in the strong shock fields characteristic of UF_6. Treating the gas as calorically perfect, i.e., a constant value of specific heat, can yield errors on the order of 2-3% for moderate shock inlet Mach numbers of 4 (i.e., moderate centrifuge wall speeds), with higher errors at higher wall speeds.

Results from a solution of the nonlinear Rankine-Hugoniot shock equations incorporating variable specific heats are presented below. The results are presented in the conventional format of plots of shock parameters as a function of upstream Mach Number, with comparisons to constant specific heat results. The rigor of the nonlinear Rankine-Hugoniot computation is recommended for precise analyses of shock effects in gas centrifuge flow fields. The error associated with use of constant specific heat analyses, however, is small, and the calorically perfect analysis can be useful in scoping studies and initial evaluations of shock effects.

Discussion

Thermally perfect

Experimental observations indicate that a low density the behavior of gases is closely given by the ideal gas equation of state

$$p = \rho RT \tag{1}$$

At higher pressures or lower temperatures the behavior of gases deviates from this relationship, with proposed formulations of

$$\frac{p}{\rho RT} = 1 + B'p + C'p^2 + \ldots. \tag{2}$$

sometimes stated as

$$\frac{p}{\rho RT} = 1 + B\rho + C\rho^2 + \ldots \tag{3}$$

The values of the virial coefficients *(B* and *C*) depend on temperature and are determined experimentally. Another common formulation and one of the first proposed, is the van der Waals equation of state,

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \tag{4}$$

A comprehensive document on UF_6 gas properties is Dewitt [1], which presents a number of experimental equations of state. Much of the data presented in Dewitt derives from an interest in gaseous diffusion parameter ranges, typically a pressure on the order of one atmosphere (760 torr). Later work by Malyshev [2] specifically addresses the low pressure range appropriate to gas centrifuge operation, with data acquired at pressures as low as 50 torr, and temperatures as low as 290 K. More recent work by Anderson [3] reviews and critiques the available data; however, the subject of interest is UF_6 cylinder fires, and Anderson develops equations of state covering a wide range of operation, but pressures no lower than about 0.5 atm.

Three equation of state formulations were chosen for evaluation: Malyshev, Weinstock [4], and the van der Waals formulation. Malyshev is considered the most relevant to gas centrifuge conditions; Weinstock is representative of the numerous correlations in Dewitt; and the van der Waals formula is of historical interest and general application. The three equation of state models are summarized in Table 1 and the results presented in

Figure 1, in the form of a comparison of the difference in density computed by the experimental equation of state and the thermally perfect equation of state.

Table 1. UF_6 equations of state

Malyshev	$\frac{p}{\rho RT} = 1 + B(T)\rho$	$B(T) = 3.94 - \frac{2197}{T}$
Weinstock	$\frac{p}{\rho RT} = 1 + B'(T)p$	$B'(T) = \frac{-1810}{T^3}$
Van der Waals	$p = \frac{RT}{v-b} - \frac{a}{v^2}$	$a = \frac{27}{64}\frac{R^2T_c^2}{P_c} \quad b = \frac{RT_c}{8P_c}$

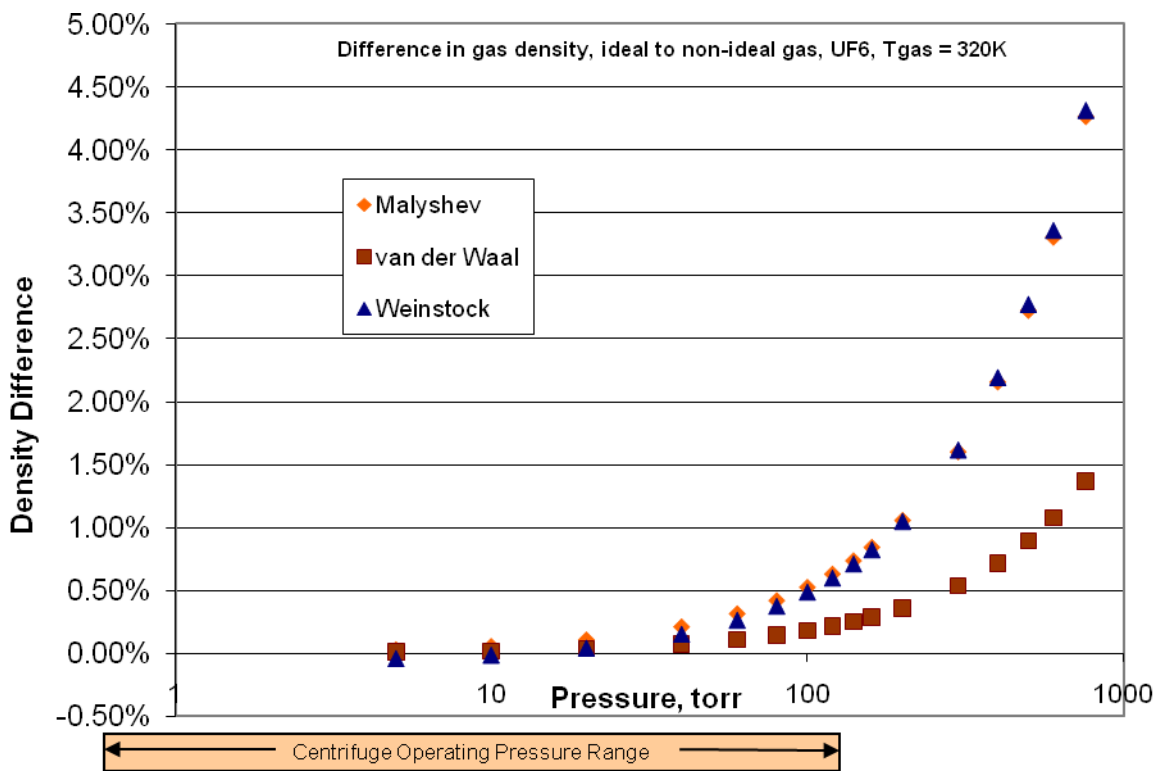

Figure 1. Difference in density in use of perfect gas law compared to use of experimental equations of state

All three correlations exhibit significant errors at pressures on the order of one atmosphere (760 torr), and all three exhibit errors on the order of 0.5% or less at pressures of 100 torr and less. The experimental data error band is on the order of 0.5%; there is no benefit to the experimental correlations in the centrifuge operating pressure range, and the perfect gas thermal equation of state adequately describes gas properties.

Another method of characterizing the non-ideality of gases is with the compressibility factor, Z, defined as

$$Z = \frac{p}{\rho RT} \tag{5}$$

An ideal gas has a value of 1.0 for Z, with deviations from 1.0 indicating deviations from the ideal gas assumption. Table 2 presents values of Z for the Malyshev correlation over the nominal gas centrifuge operating range of both temperature and pressure. Malyshev is considered the most applicable correlation for gas centrifuges. Errors over the entire parameter space are nominally below 0.5%.

Table 2. Compressibility factor Z for Malyshev equation of state

Temp	Pressure, torr				
K	5	25	50	75	100
300	.9997	.9984	.9968	.9952	.9936
320	.9997	.9987	.9974	.9961	.9948
400	.9999	.9995	.9989	.9984	.9978
500	1.0000	.9999	.9997	.9996	.9995
600	1.0000	1.0001	1.0001	1.0001	1.0003

Calorically perfect

The specific heats of UF_6 vary with temperature, and this variation must be considered in analyses involving the strong shocks which appear within a gas centrifuge. There is an impressive array of experimental data available on the specific heats of UF_6, and this gas property can be assigned with great precision. Dewitt presents data and correlations from a number of sources. Anderson improved on the Dewitt correlations, by virtue of additional data and a more generalized correlation. The Anderson correlation is

$$c_p = \left[a + bT + cT^2 + dT^{0.5} + \frac{e}{T} + f \ln T + g \arctan \frac{T}{h} \right] * 1.0e-06 \tag{6}$$

$$a = 1.7043E + 06$$

$$b = -170.5c = 3.90e - 03$$

$$d = 2.9511e + 04$$

$$e = -1.643e + 07$$

$$f = -4.0663e + 05$$

$$g = 5.736e + 05$$

$$h = 189.1$$

with units of kJ/kg. While somewhat cumbersome, the Anderson correlation provides the most comprehensive and complete capture of the available data.

Thermodynamic properties of a gas can be computed from molecular energy modes using statistical mechanics principles. Gentry [5] performed this computation in the 1980s, and the work is replicated in Appendix A in an expanded format. Yet another approach was taken by Kirshenbaum [6], deriving a functional relationship for specific heat from thermodynamic functions and the vapor-pressure relationships of the condensate, yielding the relationship

$$c_p = 32.43 + (7.936e - 3)T - \frac{32.068e4}{T^2} \tag{7}$$

with units of cal/mole K. The Kirshenbaum correlation has seen use within the centrifuge community.

Table 3a compares specific heats from the three sources mentioned above, together with a data set from Beirlesium [7]. Beirlesium is referenced in Anderson and is representative of the large amount of experimental data available on this topic.

Table 3a. Heat Capacity of UF_6 vapor, c_v, cal/mole K

Temp K	Bigeleisen Data set	Anderson Data Corrleation	Gentry Stat. mech.	Kirshenbaum Thermo functions
273	30.13	30.12	30.06	30.27
298	31.00	30.98	30.93	31.16
300		31.04	31.00	31.22
320		31.63	31.60	31.81
323	31.75	31.72	31.68	31.89
348	32.38	32.35	32.32	32.52
350		32.40	32.37	32.56

373	32.93	32.91	32.88	33.06
400	33.46	33.42	33.40	33.57
500	34.80	34.80	34.76	35.09
600		35.64	35.59	36.27
750	36.35	36.37	36.31	37.78
1000	36.94	36.97	36.91	40.01

The most notable feature of Table 3a is the precise agreement amongst the first three sources. The last source, Kirshenbaum, agrees well over the lower temperature ranges, but deviates at higher temperatures. Either the Anderson correlation or the Gentry computation is recommended for UF_6 specific heat, both yielding essentially the same values. Table 3a highlights the high precision in the values for specific heat.

Table 3b presents values for γ, the ratio of specific heats. This is computed from the specific heat value and the relationship

$$c_p - c_v = R \tag{8}$$

valid for a gas that obeys Equation 1.

Table 3b. Ratio of heat capacities of UF_6 vapor, γ, c_p/c_v

Temp K	Bigeleisen Data set	Anderson Data Corrleation	Gentry Stat. mech.	Kirshenbaum Thermo functions
273	1.0706	1.0706	1.0707	1.0702
298	1.0684	1.0685	1.0686	1.0681
300		1.0684	1.0685	1.0679
320		1.0670	1.0671	1.0666
323	1.0667	1.0668	1.0669	1.0664
348	1.0653	1.0654	1.0655	1.0650
350		1.0653	1.0654	1.0649
373	1.0642	1.0642	1.0643	1.0639
400	1.0631	1.0632	1.0632	1.0629
500	1.0605	1.0605	1.0606	1.0600
600		1.0590	1.0591	1.0579
750	1.0578	1.0578	1.0579	1.0555
1000	1.0568	1.0568	1.0569	1.0522

Gentry used the nonlinear variation of specific heat with temperature from Table 3a, together with the ideal equation of state (equation 1) and the Rankine-Hugoniot shock relationship

$$e_2 - e_1 = \frac{(p_1 + p_2)}{2} * \left(\frac{1}{\rho_1} - \frac{1}{\rho_2} \right) \tag{9}$$

to compute shock parameters for UF_6. Figure 2 presents results from this computation, in a conventional form for shock results. As a gas centrifuge generality, a shock inlet Mach number of 3 would be characteristic of a low speed machine, values of 4-5 characteristic of moderate speed machines, and a Mach number of 6 and above is associated with very high speed machines.

Normal shock relations for a perfect gas are also presented in Figure 2, for comparison to the Gentry non-ideal computations. The normal shock relationships from Shapiro [8], summarized in Equations 10-12 below, were used for this computation.

$$\frac{T_2}{T_1} = \frac{(1 + \frac{\gamma - 1}{2} M_1^2)(\frac{2\gamma}{\gamma - 1} M_1^2 - 1)}{\frac{(\gamma + 1)^2}{2(\gamma - 1)} M_1^2} \tag{10}$$

$$\frac{p_2}{p_1} = \frac{2\gamma}{\gamma + 1} M_1^2 - \frac{\gamma - 1}{\gamma + 1} \tag{11}$$

$$\frac{\rho_2}{\rho_1} = \frac{\frac{p_2}{p_1}}{\frac{T_2}{T_1}} \tag{12}$$

Errors associated with the use of ideal gas shock parameters are moderate, such that the ideal solution provides useful insight into shock effects. For precise computations, particularly at higher Mach numbers, the rigor of the Gentry nonlinear Rankine-Hugonoit computation is recommended.

An interesting observation concerns the sensitivity of the ideal gas computation to the choice of γ, the ratio of specific heats. A value of 1.067 was chosen for the constant value of γ, using Table 2 data at a shock inlet temperature of 320 K. This is a conventional choice, as the inlet temperature is known or specified in a shock analysis, and the calorically ideal assumption specifies a constant value for γ. The ideal gas computations in Figure 2 were repeated with a value of 1.062 for γ, a value roughly equivalent to the mean shock temperature (average of upstream and downstream shock temperature) at a nominal Mach number of 5. Results are show in Figure 3. This new choice for γ yielded errors less than 1% between Gentry and ideal computations over all but the uppermost end of the Mach number range. This is certainly an interesting result, indicating that the choice of a value for γ based on mean shock temperature rather than upstream temperature yields a more accurate representation of actual (Gentry) shock conditions. There is some justification for a use of mean parameters, as Equation 9 states that the increase in internal energy across a shock is the work done by the mean pressure in compressing the flow from inlet density to outlet density. A caution is noted that this approach lacks rigor, but does provide a path for more accurate scoping and initial shock evaluations.

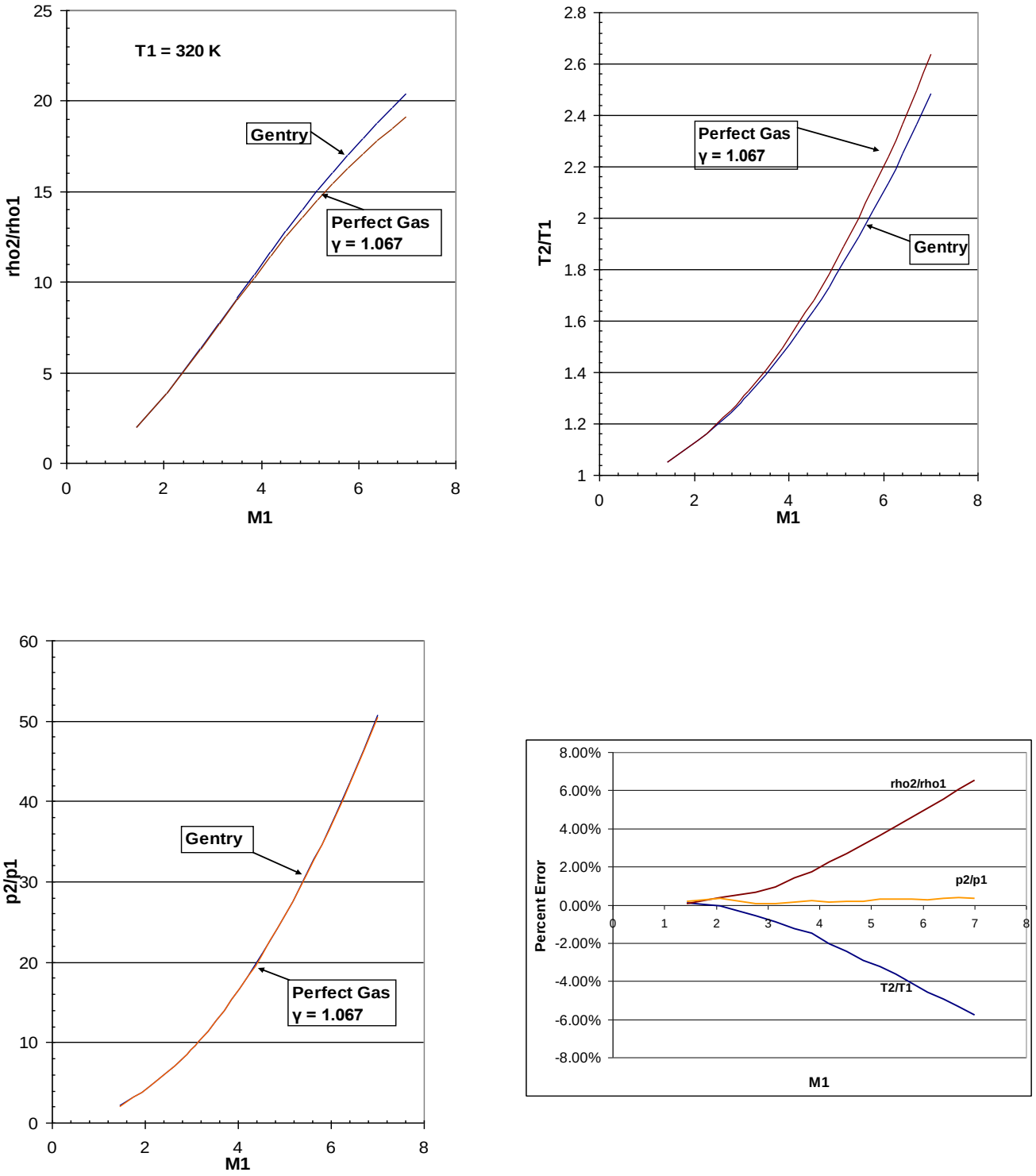

Figure 2. Comparison of normal shock computations for perfect gas and the non-ideal Gentry gas, inlet temperature 320 K, γ=1.067.

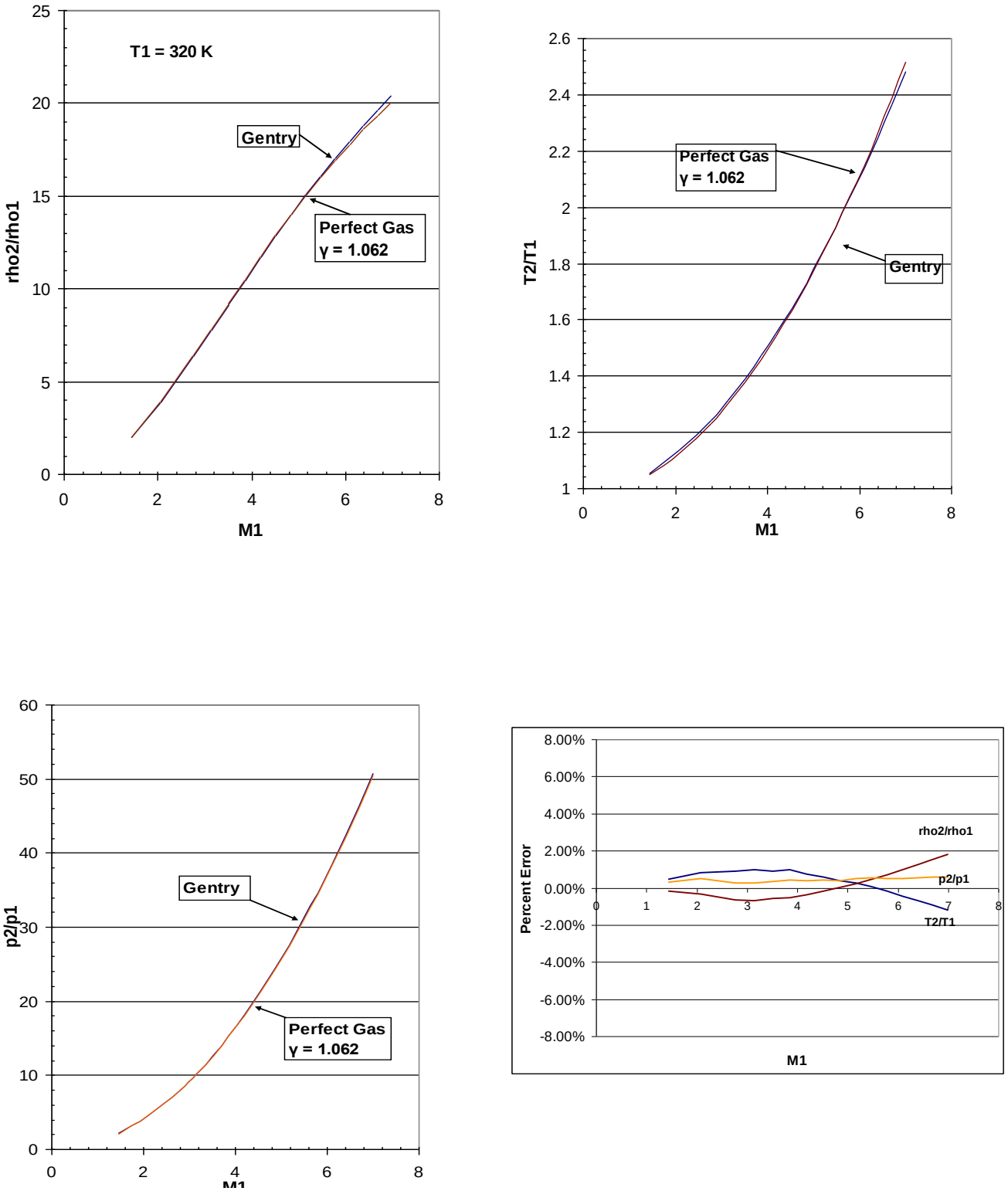

Figure 3. Comparison of normal shock computations for perfect gas and the non-ideal Gentry gas, inlet temperature 320 K, γ=1.062.

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Appendix
Derivation of the thermodynamic properties of UF_6

The following work details the derivation of the internal energy and specific heats for UF_6 as outlined in Gentry [5]. Statistical mechanics can be used to calculate the thermodynamic properties of a gas from its molecular energy modes, i.e.translational, rotational, vibrational and electronic motion. Each energy mode has an associated partition function, q, which is obtained from the quantitized molcular energy levels, ϵ_i, of the mode. Additionally, if an energy level is degenerate the degeneracy, g_i, must be included (in general $g_i = 1$). The molecular partition function for each mode is then:

$$q = \sum_{i}^{\infty} g_i \, e^{\frac{-\epsilon_i}{kT}} \tag{1}$$

When $\epsilon_i \approx kT$ or $\epsilon_i < kT$ quantum effects are significant and the summation in equation (1) must be maintained. When $\epsilon_i > kT$ all of the energy levels are assumed to be accessible to the molecule, thus enabling the discrete summation of the partition function to be replace by an integral approximating the continuim. This leads to the classical representation of the system, i.e. the kinetic theory of gases, where the equipartition theorm states that at equilibrium each degree of freedom contributes, on average, $\frac{kT}{2}$ of energy per molecule. Another way of determining whether the quanitized or continium representation of the partition function should be used is to calculate the characteristic temperature, Θ, for each mode. For some modes multiple characheristic temperatures may be calculated due to molecular degeneracies, in which case the characteristic temperature closest to the to temperature range of interest is commonly quoted. The characteristic temperature simply defines what is met by "high" and "low" temperatures for the system, i.e. systems with temperatures at or below the characteristic temperature must use the quanitized form of the partition function.

$$\Theta = \frac{\epsilon}{k} \tag{2}$$

In the following sections the transational, rotational, vibrational and electronic energy levels of UF_6 will be examined.

Using q for partition funciton of an individual molecule the overall canonical ensemble partion function for N independent molecules Q, can be calculated. The N! associated with the translational term is necessary to account for the N! ways of permuting N molecules.

$$Q = \frac{q_{trans}^{N}}{N!} \, q_{rot}^{N} \, q_{vib}^{N} \, q_{elec}^{N} \tag{3}$$

Because the modes are assumed to be decoupled the thermodynamic properties of a moledule can be calculated by summing the individual contributions from each mode. For instance the total internal energy of a moledule, U_{Tot}, is given below along with the thermodynamic functions relating the canonical partition functions derived

from statitistcal mechanics to the relevant thermodynamic properties .

$$U_{Tot} = U_{trans} + U_{rot} + U_{vib} + U_{elec} \tag{4}$$

$$U = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N} \tag{5}$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} \tag{6}$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_{P,N} \text{ where } H = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N} + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N} \text{ assuming an ideal gas } C_P = U + R \tag{7}$$

<u>TRANSLATIONAL CONTRIBUTION:</u>

The transational contribution the molecular energy is caclulated by examing the translational energy levels that are available to a molecule confined to a cubic box of volume V=a^3. The quantized translational energy in three dimensions is

$$\epsilon_i = \frac{h^2 \left(n_x^2 + n_y^2 + n_z^2 \right)}{8\, m\, a^2} \tag{8}$$

where $n_$ are the transational quantum numbers, h is Planck's constant ($6.626 * 10^{-34}$J sec) and m is the mass of the molecule. The characteristic rotational energy per mole of UF_6 is:

$$\Theta_{trans} = \frac{\frac{h^2}{8\, m\, a^2}}{k} = \frac{h^2}{8\, mkV^{2/3}} \text{ (assume one mole of ideal gas) so } \Theta_{trans} = \frac{h^2}{8\, m\ k^{5/3}\, T^{2/3}\, P^{-2/3}\, N_A^{2/3}} \text{ (combining } \Theta_{trans} \text{ and T) } \Theta_{trans} = \left(\frac{h^3}{N_A\, (8 * m)^{3/2} * k^{5/2} * P^{-1}} \right)^{2/5} \tag{9}$$

For a UF_6 having a mass of 352 amu at an assumed pressure of 10^5 Pa, the characteristic translational temperature is $\Theta_{trans} = 1.8 * 10^{-25}\, K$ per mole of UF_6. For the temperatures currently under consideration, 300 K-1000 K, the translational contributions to the thermodynamic properties of UF_6 can clearly be treated classically. This translational characteristic temperature is higher than most due to the large mass of UF_6. Using the expression for the quanitized translational energy given in Equation (7), the definition of the partion function given in Equation (1) and the fact that there is no translational degeneracy (g=1)

$$q_{trans} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{\frac{-\frac{h^2 \left(n_x^2 + n_y^2 + n_z^2 \right)}{8\, m\, a^2}}{kT}} \tag{10}$$

Because Θ_{trans} is less than the temperatures of interest the summations in the above equation may be replaced by integrals (see "Statistical Mechanics and Thermodynamics of Matter" by Joachim Lay for details) to give the following translational partition function for a molecule

$$q_{trans} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \tag{11}$$

For N molecules the total translational contribution to the partition function is

$$Q = \frac{q_{trans}{}^N}{N!} = \frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2} = \frac{V^N e^N}{VN^N}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \text{ (using the Sterling approximation)} \tag{12}$$

Using the Equations (4-6), the thermodynamic relationships are given below. Note that each degree of freedom (translation in x,y and z) contributes $\frac{kT}{2}$ per molecule, thereby showing agreement with the results obtained from the classical kinetic theory of gases.

$$U[trans] = \frac{3\,NkT}{2} \tag{13}$$

$$C_V[trans] = \frac{3\,NkT}{2} \tag{14}$$

$$C_P[trans] = \frac{5\,NkT}{2} \tag{15}$$

<u>ROTATIONAL CONTRIBUTION:</u>

The quantized rotaional energy is given by

$$\epsilon_i = \frac{h^2\,J\,(J+1)}{8\pi^2\,I_{A,B,C}} \tag{16}$$

where J is the rotational quantum number and $I_{A,B,C}$ the princple moments of interia of the molecule. The characteristic rotational temperature of a molecule is

$$\Theta_{rot} = \frac{A\,h}{k} \text{ where } A = \frac{h^2}{8\pi^2\,I_A} \tag{17}$$

UF_6 is a sherical top molecule, therefore the principal moments of inertia are equal, $I_A = I_B = I_C$ or $A = B = C$. By taking the F-U-F line as the inertial axis the moment of intertia, $I_A = \sum_{i=1}^{4} m_i\, r_i^2$, as well as a F-U bond length of $1.9993*10^{-10}\,m$ and the mass of F as 18.998 amu the characteristic rotational temperature for UF_6 is $\Theta_{trans} = 0.08\,K$. Because all of the principal moments of inertia are the same for UF_6, there is only one character-

istic temperature. Typically $\Theta_{trans}$is of the order of 0.1K for heavy molecules to 100K for light molecules. The quanitized rotational partition is given by

$$q_{rot} = \sum_{J=0}^{\infty} (2\,J + 1)\, e^{-\frac{\frac{h^2 J(J+1)}{8\pi^2 I}}{kT}} \tag{18}$$

Because Θ_{rot} is less than the temperatures of interest the summations in the above equation may be replaced by integrals to give the following translational partition function for a molecule

$$q_{rot} = \frac{\left(\frac{kT}{h}\right)^{3/2} \pi^{1/2}}{\sigma\,(ABC)^{1/2}} \tag{19}$$

UF_6 belongs to the O_h symmetry point group meaning the the rotational symmetry number is σ=24. For N molecules the total rotational partition function, energy, and heat capacities given below. Note that the symmetry parameter does not enter the calculations below as it only appears in thermodynamic functions involving the entropy of the molecule.

$$Q = q_{rot}{}^{N} = \left(\frac{\left(\frac{kT}{h}\right)^{3/2} \pi^{1/2}}{\sigma\,(ABC)^{1/2}}\right)^{N} \tag{20}$$

$$U[rot] = \frac{3\,NkT}{2} \tag{21}$$

$$C_V[rot] = \frac{3\,NkT}{2} \tag{22}$$

$$C_P[rot] = \frac{3\,NkT}{2} \tag{23}$$

<u>VIBRATIONAL CONTRIBUTION:</u>

The quantized vibrational energy is given by

$$\epsilon_i = h\nu_i \tag{24}$$

where ν_i is a fundamental vibrational frequency. Note that the vibrational energy is measured relative to the ground state (ν=0) as opposed to the bottom of the energy well. The characteristic vibrational temperature of a molecule is

$$\Theta_{vib} = \frac{h\nu c}{k} \tag{25}$$

As seen in Table I of Gentry [5], there are six experimentally obtained fundamental frequencies for UF_6. Using

this information the characteristic vibrational temperatures from from 205 K - 959 K. Thus indicating the the quantized model of the vibrational contributions to the thermodynamic properties of UF_6 must be used.

$$q_{vib} = \sum_{\nu=1}^{\infty} g_\nu \, e^{\frac{-\Theta_i}{T}} \tag{26}$$

Expanding the partiation function as a geometric series the partition function for each vibrational frequency can be written as follows

$$q_i = \frac{g_i}{1 - e^{\frac{-\Theta_i}{T}}} \tag{27}$$

For N molecules the total vibrational partition function is

$$Q = \prod_{i=1}^{6} \left(\frac{g_i}{1 - e^{\frac{-\Theta_i}{T}}} \right)^N \tag{28}$$

$$U[vib] = R \sum_{i=1}^{6} \frac{g_i \, \Theta_i \, e^{\frac{-\Theta_i}{T}}}{1 - e^{\frac{-\Theta_i}{T}}} \tag{29}$$

$$C_V[vib] = R \sum_{i=1}^{6} \frac{g_i \, \Theta_i^2 \, e^{\frac{\Theta_i}{T}}}{T^2 \left(1 - e^{\frac{\Theta_i}{T}}\right)^2} = R \sum_{i=1}^{6} \frac{g_i \, x_i^2 \, e^{-x_i}}{(1 - e^{-x_i})^2} \text{ where } x_i = \frac{\Theta_i}{T} \text{ as in Gentry} \tag{30}$$

$$C_P[vib] = R \sum_{i=1}^{6} \frac{g_i \, \Theta_i^2 \, e^{\frac{\Theta_i}{T}}}{T^2 \left(1 - e^{\frac{\Theta_i}{T}}\right)^2} = R \sum_{i=1}^{6} \frac{g_i \, x_i^2 \, e^{-x_i}}{(1 - e^{-x_i})^2} \tag{31}$$

<u>ELECTONIC CONTRIBUTION:</u>

Typical characteristic temperatures for electronic contributions to the thermodynamic properties of a molecule are on the order of 10^5 *K* and therefore will not be considered in this derivation.

<u>SUMMARY:</u>

In summary the total thermodynamic properties of one mole of UF_6 are as follows:

$$U_{Tot} = \frac{3\,NkT}{2} + \frac{3\,NkT}{2} + R \sum_{i=1}^{6} \frac{g_i \, \Theta_i \, e^{\frac{-\Theta_i}{T}}}{1 - e^{\frac{-\Theta_i}{T}}} = 3\,RT + R \sum_{i=1}^{6} \frac{g_i \, \Theta_i \, e^{\frac{-\Theta_i}{T}}}{1 - e^{\frac{-\Theta_i}{T}}} \tag{32}$$

$$C_V = \frac{3\,NkT}{2} + \frac{3\,NkT}{2} + R \sum_{i=1}^{6} \frac{g_i \, x_i^2 \, e^{-x_i}}{(1 - e^{-x_i})^2} = 3\,RT + R \sum_{i=1}^{6} \frac{g_i \, x_i^2 \, e^{-x_i}}{(1 - e^{-x_i})^2} \tag{33}$$

$$C_P = \frac{5\,NkT}{2} + \frac{3\,NkT}{2} + R\sum_{i=1}^{6}\frac{g_i\,x_i^2\,e^{-x_i}}{(1-e^{-x_i})^2} = 4\,RT + R\sum_{i=1}^{6}\frac{g_i\,x_i^2\,e^{-x_i}}{(1-e^{-x_i})^2} \tag{34}$$