Gas Property Equations for the NIST Fluid Flow Group Gas Flow Measurement Calibration Services

John D. Wright

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In January of 2003, the NIST Fluid Flow Group began using a new set of equations to calculate properties of gases. The goal was to unify the property correlations across all of the gas flow calibration services (26 m^3 *PVTt*, 34 L and 677 L *PVTt*, and piston and bell provers) and have them traceable to a single, modern, and reliable reference, a NIST properties database called Refprop.[1] We also want to expand our repertoire of gases from dry air and nitrogen to argon, helium, and carbon dioxide. The fitting process described below be easily applied to any other gases available in Refprop or for which a reliable table of values can be generated. The properties needed for calibrations of laminar flowmeters and critical nozzles are: molecular weight, specific heat ratio, density (2nd virial coefficient *B*, 3rd virial coefficient *C*), viscosity, and the critical flow factor, *C**.

Heretofore, our properties have been based on fits to NBS Circular 564 [2] and to Johnson.[3] In some cases (e.g. viscosity of air), these are correlations taken directly from the parent document, in other cases they are fits done by predecessors at NIST. The previously used equations used for air flow calibrations are documented in a previous publication.[4]

The new algorithms use a set of equations of the following form to fit the (generally) *P* and *T* dependent property data. Using viscosity as an example:

$$\mu = a_0 + a_1 T + a_2 T^2 + a_3 T^3 \qquad (1)$$

where the polynomial coefficients, a_i are in turn polynomial functions of pressure:

$$a_i = b_0^i + b_1^i P + b_2^i P^2 + b_3^i P^3 \qquad (2)$$

where *P* is in kPa and *T* is in K. Examining Eq. 1 and 2 shows that 4 x 4 =16 coefficients are required for each property correlation. The coefficients for the five gases are arranged in Table 1 in the following order: 1) nitrogen, 2) air, 3) argon, 4) helium, and 5) carbon dioxide. For each gas, the property coefficients are in the order: 1) *B*, 2) *C*, 3) *Cp*/*Cv*, and

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[1] Lemmon, E., McLinden, M., and Huber, M., 2002, Refprop 23: Reference Fluid Thermodynamic and Transport Properties, NIST Standard Reference Database 23, Version 7.0, 7/30/02, National Institute of Standards and Technology, Boulder, Colorado.

[2] Hilsenrath, J., Beckett, C. W., Benedict, W. S., Fano, L., Hoge, H. J., Masi, J. F., Nuttall, R. L., Touloukian, Y. S., and Woolley, H. W., *Tables of Thermal Properties of Gases*, NBS Circular 564, 1955.

[3] Johnson, Robert C., *Real Gas Effects in Critical Flow through Nozzles and Tabulated Thermodynamic Properties*, NASA Technical Note D-2565, January, 1965.

[4] Wright, J. D., *The Long Term Calibration Stability of Critical Flow Nozzles and Laminar Flow Meters*, NCSL Conference Proceedings, Albuquerque, NM (1998), 443-462.

4) viscosity. The 2nd and 3rd virial coefficients given by Refprop are functions of temperature alone, not pressure. Therefore, only the b_0^i coefficients are non-zero, it is not necessary to evaluate Eq. 2, and the b_0^i values can be taken as the a_i values. However, it also does no harm to use the full polynomial evaluation scheme either, and it may be more convenient to apply the same polynomial evaluation algorithm to all of the properties. *B* has dimensions $cm^3/gmol$, *C* has dimensions $cm^3/gmol^2$, and viscosity has dimensions g/(cm s). *Cp*/*Cv* is dimensionless.

Molecular weights, *M*, and the universal gas constant, *R*, are not found in Table 1 and the following values should be used: nitrogen = 28.01348, air = 28.9646431, argon = 39.948, helium = 4.0026, carbon dioxide = 44.0098 (all in g/gmol), and $R = 8314.471 (m^2\ g)/(s^2\ K\ gmol)$.[5] These are the values found in Refprop, with the exception of air.

The CO2 free air pre-defined mixture found in Refprop has a molecular weight that is about 250 parts per million (PPM) different from the molecular weight used by NBS Circular 564 and that this resulted in differences of the same magnitude between the old and new density equations. Refprop was therefore used to define our own mixture that included CO2. The following mole fractions were used: N2 = 0.78084, O2 = 0.209476, Ar = 0.00934, CO2 = 0.000314, Ne = 0.00001818, and CH4 = 0.000002.[6] (This totalizes to within 0.00000018 of 1.0 and the "normalize to 1.0" feature of Refprop was used). The change in coefficients in Table 1 resulting from the change in mixture definition has little impact; the main source of change is the molecular weight.

The coefficients in Table 1 were determined as follows. The matrix of pressure values 100, 200,…,700, 800 (in kPa) and temperature values 270, 280,…,320, 330 (all in K) were entered into Refprop for each gas and the resulting 56 values for each gas property were tabulated in a data file. This data file was used as the input to program that performs a polynomial fit of the data for a particular temperature value. The 7 sets of values of the a_i's were then fit to a polynomial in temperature to give the *b* coefficients. This process was repeated for each of the 4 gas properties. Although the fitted parameter space has a minimum pressure of 100 kPa, the virial coefficients (and hence *Z* and density) are applicable down to vacuum conditions since the virial coefficients are functions of *T* alone (not *P*). This is not true of the specific heat ratio and viscosity: they should only be used within the previously given parameter space.

Programs that evaluate the gas properties in Mathcad, Excel, and Labview have been written and a printed version of the Mathcad program is in Figure 1. In these programs, the pertinent section of the coefficient array is used depending upon which gas is being worked with. Polynomial evaluation functions calculate the value of *B*, *C*, *Cp*/*Cv* and viscosity. The gas compressibility, *Z*, is evaluated from the 2nd and 3rd virial coefficients and the molar density using the equation,

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[5] Moldover, M. R., Trusler, J. P. M., Edwards, T. J., Mehl, J. B., and Davis, R. S., *Measurement of the Universal Gas Constant R Using a Spherical Acoustic Resonator*, NIST J. of Res., 93, (2), 85–143, 1988.

[6] The mole fractions are from the *CRC Handbook of Chemistry and Physics*, David R. Lide, editor in chief, 1997.

$$Z = 1 + B\left(\frac{P}{R\,T\,Z}\right) + C\left(\frac{P}{R\,T\,Z}\right)^2 . \qquad (3)$$

The quantity in parentheses is the gas *molar* density. The gas density is calculated with the equation,

$$\rho = \frac{P\,M}{R\,T\,Z}. \qquad (4)$$

For gases with Z close to 1.0, the ideal gas molar density (i.e. assuming $Z = 1$ in Eq.3) gives a sufficiently accurate calculation of Z and of density. However, if Z is not close to one, an iterative procedure is necessary: 1) calculate B and C, 2) use B, C, and the ideal molar density to calculate Z, 3) use this initial value of Z to calculate a better value of the molar density, 4) use the new value of molar density to recalculate Z, 5) return to step 2 and repeat the process until Z changes by less than some tolerance (we use 10^{-6}). The iterative process is only necessary for carbon dioxide: the other gases are close enough to ideal in behavior that using the ideal molar density gives matching to Refprop values within a few PPM. But the iterative algorithm has been applied to all gases in the example programs for consistency and simplicity.

In the example programs, C^* is calculated by the following equation:

$$C^* = \sqrt{\gamma \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}}} \qquad (5)$$

where $\gamma = {Cp}/{Cv}$. There was some consideration of dividing this formula by $\sqrt{Z}$ as suggested by Arnberg and Seidl.[7] However, it was discovered that this "improvement" actually increased the discrepancy between the previously used correlations for nitrogen and air (based on Johnson) and the present work, at least for the parameter space of the present work. This is verified by figures 2 and 3 of the Arnberg and Seidl paper where the percent error for room temperature and low pressure conditions is less without the $\sqrt{Z}$ term. Without the $\sqrt{Z}$ term, the agreement with our previously used correlations is between -0.005% and +0.012% for nitrogen and between +0.01% and –0.025% for air. A change of this magnitude will have negligible impact on our customers since until the introduction of the 34 L and 677 L PVTt standards, our calibration uncertainties were approximately 0.2%.

The Labview program was used to calculate gas properties for all 5 gases at the same T and P conditions inputted to the Refprop database. The Refprop and correlation outputs

[7] Arnberg, B. T and Seidl, W. F., *A Comparison of Errors in Four Methods for Determining Critical Flow Functions for Sonic Flow Nozzles and Venturis*, FEDSM2000-11343, Proceedings of ASME FEDSM'00 Boston, MA, June 2000.

were compared over the parameter space and the differences were examined. The fit residuals of *Z* and specific heat ratio are less than 2 PPM for all gases except for carbon dioxide for which they are as large as 10 PPM and 32 PPM respectively. Viscosity residuals are less than 4 PPM for all gases except helium which had residuals as large as 28 PPM. One should not assume these values are the uncertainties; these values only represent the quality of the fit to the Refprop data.

Air properties calculated with the Refprop based fits agree with previously used correlations (as documented in NCSL 1998 paper) within 130 PPM for density, within 340 PPM for C*, within 70 PPM for Cp/Cv, and within 1.3% for viscosity. Recall that experimental viscosity measurement uncertainties are quite large and that the old correlation was a function of temperature alone while the newer one is a function of both *T* and *P*.

Table 1. The coefficients used in the gas property correlation equations.

N2	B	-2.0851343E+02	0.0000000E+00	0.0000000E+00	0.0000000E+00
		1.4276670E+00	0.0000000E+00	0.0000000E+00	0.0000000E+00
		-3.3567990E-03	0.0000000E+00	0.0000000E+00	0.0000000E+00
		2.8804750E-06	0.0000000E+00	0.0000000E+00	0.0000000E+00
	C	5.6478290E+03	0.0000000E+00	0.0000000E+00	0.0000000E+00
		-3.3379509E+01	0.0000000E+00	0.0000000E+00	0.0000000E+00
		8.8698095E-02	0.0000000E+00	0.0000000E+00	0.0000000E+00
		-8.1722220E-05	0.0000000E+00	0.0000000E+00	0.0000000E+00
	Cp/Cv	1.4056413E+00	2.2572496E-04	2.5437843E-08	-6.6886724E-12
		-7.2386281E-05	-1.5901777E-06	-2.3195664E-10	6.9680936E-14
		3.0949830E-07	4.0923336E-09	7.1401515E-13	-2.4230399E-16
		-4.5436508E-10	-3.7013989E-12	-7.4254449E-16	2.8058361E-19
	viscosity	-4.1229535E-08	7.1902522E-09	-5.6328086E-13	6.5716697E-16
		7.6905439E-07	-3.7512432E-11	-2.3973570E-15	1.8538554E-18
		-7.0180272E-10	7.8744504E-14	3.8239535E-17	-3.4571908E-20
		4.1865079E-13	-5.4814015E-17	-7.8162575E-20	7.0145901E-23
Air	B	-2.1667059E+02	0.0000000E+00	0.0000000E+00	0.0000000E+00
		1.4668129E+00	0.0000000E+00	0.0000000E+00	0.0000000E+00
		-3.4509886E-03	0.0000000E+00	0.0000000E+00	0.0000000E+00
		2.9626275E-06	0.0000000E+00	0.0000000E+00	0.0000000E+00
	C	5.7671674E+03	0.0000000E+00	0.0000000E+00	0.0000000E+00
		-3.4865483E+01	0.0000000E+00	0.0000000E+00	0.0000000E+00
		9.1331777E-02	0.0000000E+00	0.0000000E+00	0.0000000E+00
		-8.3295000E-05	0.0000000E+00	0.0000000E+00	0.0000000E+00
	Cp/Cv	1.4003554E+00	2.3159479E-04	2.3236102E-08	3.4836950E-13
		-2.5127363E-06	-1.6301861E-06	-2.0177371E-10	-4.0263153E-15
		9.4077636E-08	4.1921369E-09	5.9005669E-13	1.4252647E-17
		-3.0184524E-10	-3.7908650E-12	-5.8155964E-16	-1.6133559E-20
	viscosity	-1.4871190E-06	2.3655058E-08	-4.7472835E-11	3.8095178E-14
		8.0343328E-07	-2.0644769E-10	4.8681938E-13	-3.8744288E-16
		-7.3210884E-10	6.6059876E-13	-1.6567074E-15	1.3101251E-18
		4.4444444E-13	-7.2390572E-16	1.8728956E-18	-1.4730640E-21

Argon	B	-2.3003581E+02	0.0000000E+00	0.0000000E+00	0.0000000E+00
		1.5069940E+00	0.0000000E+00	0.0000000E+00	0.0000000E+00
		-3.5532220E-03	0.0000000E+00	0.0000000E+00	0.0000000E+00
		3.0573390E-06	0.0000000E+00	0.0000000E+00	0.0000000E+00
	C	5.5770000E+03	0.0000000E+00	0.0000000E+00	0.0000000E+00
		-3.4713704E+01	0.0000000E+00	0.0000000E+00	0.0000000E+00
		8.9865357E-02	0.0000000E+00	0.0000000E+00	0.0000000E+00
		-8.1273320E-05	0.0000000E+00	0.0000000E+00	0.0000000E+00
	Cp/Cv	1.6666661E+00	3.6167242E-04	4.2323202E-08	1.8582604E-12
		7.6010030E-09	-2.5330777E-06	-3.6235590E-10	-1.7778072E-14
		-3.0212821E-11	6.4987973E-09	1.0506575E-12	5.6119831E-17
		3.7698613E-14	-5.8666353E-12	-1.0297709E-15	-5.8782269E-20
	viscosity	-9.0576309E-06	1.2322123E-08	-4.7851962E-12	2.2792207E-15
		9.7918166E-07	-8.3300833E-11	4.9690312E-14	-2.1785313E-17
		-7.7568877E-10	2.3012051E-13	-1.6447639E-16	6.8241940E-20
		4.3253968E-13	-2.2627064E-16	1.7736892E-19	-7.0145900E-23
Helium	B	1.3299698E+01	0.0000000E+00	0.0000000E+00	0.0000000E+00
		-7.3293620E-03	0.0000000E+00	0.0000000E+00	0.0000000E+00
		2.2620110E-06	0.0000000E+00	0.0000000E+00	0.0000000E+00
		3.0997220E-09	0.0000000E+00	0.0000000E+00	0.0000000E+00
	C	1.0547753E+02	0.0000000E+00	0.0000000E+00	0.0000000E+00
		3.6392529E-01	0.0000000E+00	0.0000000E+00	0.0000000E+00
		-8.6728620E-04	0.0000000E+00	0.0000000E+00	0.0000000E+00
		7.7475000E-07	0.0000000E+00	0.0000000E+00	0.0000000E+00
	Cp/Cv	1.6666672E+00	-2.7704493E-06	1.5943237E-10	-1.3644959E-14
		-5.6447926E-09	6.6161641E-09	-1.1233719E-12	1.2156194E-16
		1.8367376E-11	-3.8585113E-12	2.8546180E-15	-3.5894691E-19
		-1.9841307E-14	-2.8170593E-15	-2.5402842E-18	3.5072985E-22
	viscosity	3.6781871E-05	-5.4114694E-09	2.6091875E-11	-2.0031806E-14
		6.5320629E-07	7.2736881E-11	-2.5684597E-13	1.9711901E-16
		-4.5416666E-10	-2.8373016E-13	8.4027778E-16	-6.4484127E-19
		2.7380952E-13	3.5133077E-16	-9.1390091E-19	7.0145903E-22
CO2	B	-1.5328130E+03	0.0000000E+00	0.0000000E+00	0.0000000E+00
		1.0764513E+01	0.0000000E+00	0.0000000E+00	0.0000000E+00
		-2.7812776E-02	0.0000000E+00	0.0000000E+00	0.0000000E+00
		2.5383290E-05	0.0000000E+00	0.0000000E+00	0.0000000E+00
	C	-5.8844940E+03	0.0000000E+00	0.0000000E+00	0.0000000E+00
		1.4674289E+02	0.0000000E+00	0.0000000E+00	0.0000000E+00
		-5.6430823E-01	0.0000000E+00	0.0000000E+00	0.0000000E+00
		6.4308450E-04	0.0000000E+00	0.0000000E+00	0.0000000E+00
	Cp/Cv	1.5790217E+00	1.4561117E-03	6.2723895E-07	7.4575157E-10
		-1.6565032E-03	-1.1452152E-05	-5.3143079E-09	-6.9368031E-12
		2.8440285E-06	3.1573617E-08	1.5275267E-11	2.1587332E-14
		-1.8683631E-09	-2.9930443E-11	-1.4836649E-14	-2.2458474E-17
	viscosity	-3.4035714E-06	2.3350293E-09	1.7372733E-12	4.0489418E-15
		5.1982908E-07	-6.8418898E-12	-1.3145872E-14	-3.2247074E-17
		3.7551022E-11	3.1694542E-16	4.3586375E-17	8.3874458E-20
		-2.1428572E-13	1.5131473E-17	-5.4112555E-20	-7.0145902E-23

Figure 1. Listing of a Mathcad program that implements the gas property equations.

$M := \text{READPRN}(\text{"gasproperties.prn"})$ $\quad Ru := 8314.471$

Air: $r1 := 16 \quad MW := 28.9646431$

Argon: $r1 := 32 \quad MW := 39.948$

He: $r1 := 48 \quad MW := 4.0026$

CO2: $r1 := 64 \quad MW := 44.0098$

N2: $r1 := 0 \quad MW := 28.01348$

$Bcoeff := \text{submatrix}(M, r1, r1 + 3, 0, 3)^T \quad \gamma coeff := \text{submatrix}(M, r1 + 8, r1 + 11, 0, 3)^T$

$Ccoeff := \text{submatrix}(M, r1 + 4, r1 + 7, 0, 3)^T \quad \mu coeff := \text{submatrix}(M, r1 + 12, r1 + 15, 0, 3)^T$

$$Poly(a, x) := a_0 + a_1 \cdot x + a_2 \cdot x^2 + a_3 \cdot x^3$$

$$Fit(b, Pres, Temp) := Poly(\text{submatrix}(b, 0, 3, 0, 0), Pres) + Poly(\text{submatrix}(b, 0, 3, 1, 1), Pres) \cdot Temp \ldots + Poly(\text{submatrix}(b, 0, 3, 2, 2), Pres) \cdot Temp^2 + Poly(\text{submatrix}(b, 0, 3, 3, 3), Pres) \cdot Temp^3$$

$$Z(Pres, Temp) := \left| \begin{array}{l} ZZ \leftarrow 1 + Fit(Bcoeff, Pres, Temp) \cdot \frac{Pres}{Ru \cdot Temp \cdot 1} + Fit(Ccoeff, Pres, Temp) \cdot \left(\frac{Pres}{Ru \cdot Temp \cdot 1} \right)^2 \\ Z \leftarrow 1 \\ \text{while } |ZZ - Z| > 10^{-6} \\ \quad \left| \begin{array}{l} Z \leftarrow ZZ \\ ZZ \leftarrow 1 + Fit(Bcoeff, Pres, Temp) \cdot \frac{Pres}{Ru \cdot Temp \cdot Z} + Fit(Ccoeff, Pres, Temp) \cdot \left(\frac{Pres}{Ru \cdot Temp \cdot Z} \right)^2 \end{array} \right. \\ ZZ \end{array} \right.$$

$$\rho(Pres, Temp) := \frac{Pres \cdot MW}{Ru \cdot Temp \cdot Z(Pres, Temp)}$$

$$\mu(Pres, Temp) := Fit(\mu coeff, Pres, Temp)$$

$$C1(Pres, Temp) := \sqrt{Fit(\gamma coeff, Pres, Temp) \cdot \left(\frac{2}{Fit(\gamma coeff, Pres, Temp) + 1} \right)^{\frac{Fit(\gamma coeff, Pres, Temp)+1}{Fit(\gamma coeff, Pres, Temp)-1}}}$$

$P := 101.325 \quad T := 290$

$C1(P, T) = 0.684979382 \quad Z(P, T) = 0.999727425$

$\rho(P, T) = 1.177523135 \times 10^{-3}$ gm/cm^3

$\mu(P, T) = 1.743357682 \times 10^{-4}$ gm/(cm s)