

# SRS Tech Note

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## Adding New Gas Mixtures to the Gas Table

The BGA244 Binary Gas Analyzer is used to measure the composition of gas mixtures. The analyzer's Gas Table contains the molar masses and thermodynamic constants for about 500 pure gases and liquids, for which there are tens of thousands of binary mixtures. In addition to measuring binary mixtures of pure gases, the BGA244 can also measure binary mixtures of "pseudo-pure" gases. (Pseudo-pure gases are gas mixtures with a fixed composition, which are defined and listed in the BGA244 Gas Table, and so are treated as a single gas component.)

### An example of a pseudo-pure mixture (Air)

One of the pseudo-pure gases listed in the BGA244's Gas Table is "Dry Air", which is a mixture of about 78% N<sub>2</sub>, 21% O<sub>2</sub> and 1% Ar. This is convenient as it will allow the BGA244 to report the composition of mixtures of Air with other gases.

For example, suppose we want to measure the composition of the gas in a helium recovery system. The principal contaminant is air and so we setup the BGA244 to measure Air in Helium. The BGA244 can do this measurement with better than 0.05% accuracy over the entire range from 0% to 100%.

### Pseudo-pure gas mixtures

There are many situations in which other pseudo-pure gases are useful. For example, Pressure Swing Adsorption (PSA) is a process which is used to separate nitrogen from the other atmospheric gases (oxygen and argon). The BGA244 can be used to monitor purity of the gas streams produced by the PSA process.

In the ideal PSA process, all of the N<sub>2</sub> is separated from air, leaving a mixture of 95.5% O<sub>2</sub> and 4.5% Ar. The BGA244 Gas table lists the pseudo-pure gas, "O<sub>2</sub>-PSA" or "Oxygen;995;Argon;45", which is 95.5% O<sub>2</sub> and 4.5% Ar. This allows the BGA244 to measure and report the composition of the two products of the PSA process: Nominally pure N<sub>2</sub> (polluted by O<sub>2</sub>-Ar) and the nominally pure O<sub>2</sub>-Ar (polluted by N<sub>2</sub>).

In the case where the O<sub>2</sub>-Ar output of the PSA process is used as feedstock to an ozone generator, the BGA244 can measure the conversion of O<sub>2</sub> to O<sub>3</sub>. This case is modeled with two pseudo-pure gases: O<sub>2</sub>-Ar-N<sub>2</sub> and O<sub>3</sub>-Ar-N<sub>2</sub>. The typical ratios would be 93.5/4.5/2.0. The BGA244 can measure and report the ratio of O<sub>3</sub>-Ar-N<sub>2</sub> to O<sub>2</sub>-Ar-N<sub>2</sub> in the ozone generator output and so determine the conversion efficiency of the ozone generator.

### Gas table data

The BGA244's Gas Table has 46 columns of data for each gas. The column entries are shown in the table on the next page. Details for each of the terms in the Gas Table can be found in the Appendix. When creating a new pseudo-pure gas the goal is to occupy as many of the columns with reliable data as can be determined. To do this we use NIST's REFPROP program: We are able to generate reliable parameters for most pseudo-pure gas mixtures composed from the 100+ gases supported by REFPROP.

Column	Name	Units	N2 Value	Description
1	CAS#	Alpha-numeric	7727-37-9	Chemical Abstract Service number
2	Preferred name	Alpha-numeric	Nitrogen	Preferred name. Often the systematic name if not arcane.
3	Alt 1 name	Alpha-numeric		Alternate name or ASKRAE designation. Example: R-134A
4	Alt 2 name	Alpha-numeric		Alternate name or non-Hill formula. Example: SF6 rather than F6S
5	Formula	Hill form	N2	Chemical formula, carbon(s) first, hydrogen(s) next, alpha thereafter
6	Molar mass	g/mol	28.01348	Molecular weight in grams per mole
7	a0(Cp)	dimensionless	3.4379	Scaled coefficient of polynomial for isobaric heat capacity in units of R
8	a1(Cp)×1E+03	1/K	0.7884	Scaled coefficient of polynomial for isobaric heat capacity in units of R
9	a2(Cp)×1E+05	1/K^2	-0.3505	Scaled coefficient of polynomial for isobaric heat capacity in units of R
10	a3(Cp)×1e+08	1/K^3	0.6090	Scaled coefficient of polynomial for isobaric heat capacity in units of R
11	a4(Cp)×1e+11	1/K^4	-0.2508	Scaled coefficient of polynomial for isobaric heat capacity in units of R
12	Cp(Tnorm)/R	dimensionless	3.5026997	Isobaric heat capacity (in units of R) calculated from polynomial at T=T(norm)
13	Wo(Tnorm, P=0)	m/s	348.963	Ideal gas speed of sound at T_norm. Wo=sqrt( $\gamma RT/M$ )
14	Pc	bar	33.958	Critical pressure (bar)
15	Vc	cc/mol	89.414	Critical volume (cc/mol)
16	Tc	K	126.192	Critical temperature (K)
17	Zc	dimensionless	0.289387	Critical compressibility
18	Acentric factor	dimensionless	0.0	Pitzer acentric factor
19	Dipole moment	D (debye)	0.00	Electric dipole moment
20	Family	Integer	1	Integer (1-6) to describe chemical "family" per table, below. (For CSP methods)
21	a_Tsono	dimensionless	0.00	Tsonopoulos correlation a-parameter for 2nd virial (see PG&L Pg 4.15)
22	b_Tsono	dimensionless	0.00	Tsonopoulos correlation b-parameter for 2nd virial (see PG&L Pg 4.15)
23	av	cc/mol	144.14	Zuckerwar parameter for exponential form of 2nd virial. (See Eq 4.30, pg 94)
24	bv	cc/mol	101.08544	Zuckerwar parameter for exponential form of 2nd virial. (See Eq 4.30, pg 94)
25	cv	K	115.778	Zuckerwar parameter for exponential form of 2nd virial. (See Eq 4.30, pg 94)
26	dv	[cc/mol]^2	16689.36	Zuckerwar parameter for exponential form of 3rd virial. (See Eq 4.35, pg 98)
27	ev	[cc/mol]^2	49.618	Zuckerwar parameter for exponential form of 3rd virial. (See Eq 4.35, pg 98)
28	fv	K	552.72650	Zuckerwar parameter for exponential form of 3rd virial. (See Eq 4.35, pg 98)
29	gv	1/K	0.015	Zuckerwar parameter for exponential form of 3rd virial. (See Eq 4.35, pg 98)
30	C_asymptote	[cc/mol]^2	1188.1	Zuckerwar parameter for exponential form of 3rd virial. (See Eq 4.35, pg 98)
31	a0( $\eta$ )	$\mu Pa \cdot s$	1.66702397	Polynomial coefficient for viscosity, $\eta(T)$
32	a1( $\eta$ )×100	$\mu Pa \cdot s/K$	6.22979799	Polynomial coefficient for viscosity, $\eta(T)$
33	a2( $\eta$ )×10,000	$\mu Pa \cdot s/K^2$	-0.28410365	Polynomial coefficient for viscosity, $\eta(T)$
34	a0(k)	mW/m.K	1.904	Polynomial coefficient for thermal conductivity $\kappa(T)$
35	a1(k)×100	mW/m.K^2	8.706	Polynomial coefficient for thermal conductivity $\kappa(T)$
36	a2(k)×10,000	mW/m.K^3	-0.267	Polynomial coefficient for thermal conductivity $\kappa(T)$
37	Vib Temp	K	3352.00	Characteristic temperature for excitation of vibrational mode
38	a1_r	dimensionless	-3.65	Coefficient for relaxation-time x pressure product (us-atm)
39	a2_r	K^1/3	71.63	Coefficient for relaxation-time x pressure product (us-atm)
40	a3_r	K	0.00	Coefficient for relaxation-time x pressure product (us-atm)
41	A_vp	Result in Pa	0.00	Coefficient for the Antoine Equation for vapor pressure. (PG&L Eq 7-3.1, pg 7.4)
42	B_vp	Result in Pa	0.00000	Coefficient for the Antoine Equation for vapor pressure. (PG&L Eq 7-3.1, pg 7.4)
43	C_vp	Result in Pa	0.00000	Coefficient for the Antoine Equation for vapor pressure. (PG&L Eq 7-3.1, pg 7.4)
44	W_offset	ppm	0.00	Empirical offset for the computed speed of sound
45	W_Pslope	ppm/psi	0.00	Empirical pressure slope for the computed speed of sound
46	W_Tslope	ppm/T	0.00	Empirical temperature slope for the computed speed of sound

## NIST's REFPROP

NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP Version 9.1), also known as NIST Standard Reference Database 23, includes 69 pure fluids and 55 pseudo-pure fluids (refrigerant mixtures and air) which are listed here:

<b>Pure Gases</b>	neon	R114	R409A
acetone	neopentane	R115	R409B
ammonia	nitrogen	R116	R410A
argon	nitrogen trifluoride	R123	R410B
benzene	nitrous oxide	R124	R412A
butane	nonane	R125	R413A
butene	octane	R134a	R414A
carbon dioxide	oxygen	R141b	R414B
carbon monoxide	parahydrogen	R142b	R416A
carbonyl sulfide	pentane	R143a	R417A
cis-butene	perfluorobutane	R152a	R419A
cyclohexane	perfluoropentane	R218	R420A
cyclopropane	propane	R227ea	R421A
decane	propylene	R236ea	R421B
deuterium	propyne	R236fa	R422A
dimethylether	sulfur dioxide	R245ca	R422B
dodecane	sulfur hexafluoride	R245fa	R422C
ethane	toluene	R365mfc	R422D
ethanol	trans-butene	RC318	R423A
ethylene	trifluoroiodomethane		R424A
fluorine	water	<b>Mixtures</b>	R425A
heavy water	xenon	air	R426A
helium		R402A	R427A
heptane	<b>Refrigerants</b>	R402B	R428A
hexane	R11	R403A	R500
hydrogen (normal)	R12	R403B	R501
hydrogen sulfide	R13	R404A	R502
isobutane	R14	R406A	R504
isobutene	R21	R407A	R507A
isohexane	R22	R407B	R508A
isopentane	R23	R407C	R508B
krypton	R32	R407D	R509A
methane	R41	R407E	
methanol	R113	R408A	

The program allows mixtures with up to 20 components and uses the most accurate equations of state and models currently available: A High accuracy Helmholtz energy equations of state, MBWR equations of state, the Bender equation of state, an extended corresponding states model for fluids with limited data, an excess Helmholtz energy model for mixture properties, experimentally based values for mixture parameters, and the American Gas Association equation AGA8 for natural gas properties. Viscosity and thermal conductivity are based on fluid-specific correlations (where available), a modification of the extended corresponding states model, or the friction theory model.

Available properties in REFPROP include: Temperature, pressure, density, energy, enthalpy, Entropy,  $C_v$ ,  $C_p$ , sound speed, compressibility factor, Joule Thomson coefficient, quality, 2nd and 3rd virial coefficients, 2nd and 3rd acoustic virial coefficients, Helmholtz energy, Gibbs energy, heat of vaporization, fugacity, fugacity coefficient, chemical potential, K value, molar mass,  $B_{12}$ , thermal conductivity, viscosity, kinematic viscosity, thermal diffusivity, Prandtl number, surface tension, dielectric constant, gross and net Heating Values, isothermal compressibility, volume expansivity, isentropic coefficient, and adiabatic compressibility.

### Computing Gas Table parameters for new gases

The details for computing the Gas Table entries for a new User Gas are complicated. The good news is that SRS is continuously adding important pseudo-pure gases (such as the O<sub>2</sub>-PSA Gas) to the standard Gas Table so that you won't have to.

SRS has developed a program which links to NIST's REFPROP via a DLL to compute the molar mass, ideal gas speed of sound at 20C, critical pressure, volume, temperature and compressibility, and heat capacities, thermal conductivity, viscosity, vapor pressure, and 2<sup>nd</sup> and 3<sup>rd</sup> virials of specific pseudo-pure gas mixtures. These properties are computed at ten temperatures spanning the BGA244's operating temperature range. The program then fits polynomials (for heat capacity, thermal conductivity and viscosity), or parameters for the Antoine equation (for vapor pressure), or parameters for the exponential forms of 2<sup>nd</sup> and 3<sup>rd</sup> virial coefficients. These computed parameters are then used to populate the Gas Table in the BGA244, allowing the BGA244 to determine the composition of complex gas mixtures.

### A few more details

There are no CAS numbers for gas mixtures so we assign the string "MIX" followed by a three digit number from 001 to 999. For example, "MIX001" is air (Nitrogen;7812;Oxygen;2096;Argon;92) and "MIX002" is the refrigerant R402A which is a mixture of R22, R125 and propane. This string can be used to select gases via the instrument's remote interfaces.

The pseudo gas program does not populate parameters which are used to compute the cross virial coefficients of polar gases (the Pitzer acentric factor, the electric dipole moment or the Tsonopoulos a & b factors) which may affect the accuracy of mixture results when polar gases are used as components in pseudo-pure gases. The heat capacity relaxation parameters are all set to zero and so there is no attempt to correct for dispersion. Coefficients for the 3<sup>rd</sup> virial will be set to zero if they deviate from the results computed by other methods. And finally, absent experimental information, the three speed of sound offset parameters (Columns 44-46) are all set to zero.

Contact us at [ThinkSRS.com](http://ThinkSRS.com)

SRS provides support for the expanding list of applications and industries which use the BGA244. If you need a new gas mixture added to the BGA244 Gas Table, please call us to discuss your application.

## Appendix: The Gas Table

The Gas Table is a database of names, formulas and thermodynamic data for about 500 gases and liquids, allowing the BGA244 to measure the composition of tens of thousands of binary gas mixtures. This Appendix provides detailed information on that database.

### Introduction

The BGA244 binary gas analyzer determines gas purity and mixture compositions by measuring the temperature and the speed of sound in the gas. The speed of sound in an ideal gas is given by Eq. 1

$$W_0 = \sqrt{\frac{\gamma_0 R T}{M}} \quad \text{Eq. 1}$$

Where  $W_0$  is the speed of sound in the ideal gas (low pressure) limit,  $\gamma_0$  the ratio of heat capacities,  $M$  the molar mass,  $T$  the absolute temperature, and  $R$  the ideal gas constant. For argon,  $\gamma_0 = C_p/C_v = C_p/(C_p - R) = 5/3$  and  $M = 0.039948 \text{ kg/mol}$ , and so the ideal speed of sound at 20°C (293.15 K) is about 318.89 m/s.

For the BGA244 to determine the purity of an *ideal* gas it needs to know the isobaric heat capacity ( $C_p$ ) and  $M$ . The measurement of *real* gases will be improved if the other thermodynamic and transport properties, and the gas pressure, are also known.

The Gas Table contains information on about 500 gases listed by common names, formulas, and registration numbers. In addition to the molar mass, the Gas Table provides parameters to estimate each of the following (all of which can modify the speed of sound in the gas): The temperature dependence of the heat capacity, the second and third virial coefficients, the viscosity and thermal conductivity as functions of temperature, the translational/vibrational relaxation of the heat capacity, and the saturation vapor pressure.

In addition, the Gas Table provides information on the critical parameters ( $P_c, V_c, T_c, Z_c$ ), the Pitzer acentric factor, the electric dipole moment, and chemical family allowing the computation of cross virial coefficients by the BGA244 firmware.

Finally, to allow for gas specific corrections caused by uncertainties in all the other parameters, there are three offset parameters to repair a fixed offset or offsets which change linearly with pressure or temperature.

There are 46 data fields (columns) associated with each gas. The table shown in the App Note details the column number, name, units, value for nitrogen, and a brief description for each of the column entries. A more complete description is given below.

### CAS Registry number (Column 1)

The CAS registry number is a unique identifier assigned by the Chemical Abstract Service (CAS) to every chemical substance described in reviewed scientific literature. The CAS numbers are used by chemical suppliers, governmental regulators, safety data sheets (MSDS), chemical and thermodynamic databases. Using the CAS number (instead of a chemical name) will assure that correct gas has been selected. The CAS Registry Number is a Registered Trademark of the American Chemical Society.

### Preferred name (Column 2)

Except for a few arcane cases (for example, “carbon dioxide” is used instead of “methanedione” and “ozone” is used instead of “2-trioxiden-2-ium-1-ide”) the preferred name is usually the IUPAC name (International Union of Pure and Applied Chemistry).

### First and second alternate names (Column 3 & 4)

Many compounds are commonly called by more than one name. For example, difluoromethane ( $\text{CH}_2\text{F}_2$ ) is also called methylene fluoride and is an ASHRAE registered refrigerant designated as R-32. The alternate name columns accommodate these other names and industry designations.

### Formula (Columns 5)

Formulas for compounds may be written in several ways. The BGA244 uses a simple, non-structural form called Hill notation. The rules are simple: For molecules containing carbon, the carbons are listed first, followed by the hydrogens, followed by everything else in alphabetical order of the element symbols. If the compound contains no carbons everything is listed in alphabetical order of the element symbols, including hydrogen. This system yields sensible results in most cases, for example, methane is  $\text{CH}_4$ . There are a few exceptions however:  $\text{SF}_6$  is written  $\text{F}_6\text{S}$  in Hill notation. In such cases the formula  $\text{SF}_6$  is included as one of the alternate names so that a user looking for  $\text{SF}_6$  will indeed find sulfur hexafluoride.

### Selecting a gas

From the GUI, the user enters a string which simultaneously searches CAS #, preferred and alternate names and formulas. As the string is entered the number of potential matches are displayed allowing the user to select a gas from an ever-shortening list. Via the computer interface, the only way to select a gas is to use a CAS number (which are easily found via Google or Wikipedia).

### Source of data

Many references (listed at the end of this section) were used to compile (or calculate) the data used in the Gas Table. Data from those references was critically evaluated, primarily by comparison between the various references but also taking into consideration the sources used by those references.

Not all references had all of the data required for the Gas Table. Different references also used different correlation functions and applied those functions to different temperature ranges. As an example, consider the parameterization of the isobaric heat capacity vs. temperature. The BGA244 uses a 4<sup>th</sup> order polynomial for this task. This polynomial is well behaved and offers more than enough flexibility to accurately follow the heat capacity over the BGA244's operating temperature range. This is the same

polynomial as used in one of the references, however, the accuracy of the coefficients presented in that reference were found to be less accurate than could be found by fitting a polynomial over the operating temperature range to data extracted from the correlation functions of other references, or to data extracted from NIST's REFPROP.

The same methodology was applied to other gas parameters and parameters for correlation functions to estimate the second and third virial coefficients, the viscosity and thermal conductivity as functions of temperature, the translational/vibrational relaxation of the heat capacity, and the saturation vapor pressure. The distillation of all of these estimates and the parameters for new correlation functions are presented in the Gas Table.

### Corresponding States Principle (CSP)

CSP methods allow the estimation of fluid properties which depend on intermolecular forces by correlation functions scaled with the critical constants of the fluid. For example, the departure from ideal gas compressibility can be described with a virial equation of state (EOS). The first two coefficients of that EOS, called the 2<sup>nd</sup> and 3<sup>rd</sup> virial coefficients, can be measured directly or estimated using CSP methods.

CSP methods were used to estimate the gases' 2<sup>nd</sup> and 3<sup>rd</sup> virial coefficients, thermal conductivity and viscosity. These results would be used in the Gas Table if experimental results (or correlation functions derived from those results) were not available.

### Molar mass (Column 6)

The molar mass is in units of grams per mole. Note that these are not SI units, for which the molar mass is in kg/mole. An accurate molar mass is critically important as a 200 ppm error in the molar mass results in a 100 ppm error in the speed of sound. The molar mass is often rounded to two or three digits in published tables which is insufficient for the lighter gases.

### Isobaric heat capacity, $C_p/R$ (Columns 7-12)

The isobaric heat capacity in the ideal gas limit, in units of the ideal gas constant, is computed from the scaled coefficients to the 4<sup>th</sup> order polynomial given in Columns 7-11. (The coefficients are scaled to keep their magnitude on order 1.)  $C_p/R$  is computed from Eq. 2 (where T is the temperature in K):

$$\frac{C_p}{R} = a_0 + \frac{a_1 \cdot T}{1000} + \frac{a_2 \cdot T^2}{100,000} + \frac{a_3 \cdot T^3}{100,000,000} + \frac{a_4 \cdot T^4}{100,000,000,000} \quad \text{Eq. 2}$$

And the ratio of heat capacities,  $\gamma_0$ , is computed from Eq. 3:

$$\gamma_0 = \frac{C_p}{C_v} = \frac{C_p}{C_p - R} = \frac{C_p/R}{C_p/R - 1} \quad \text{Eq. 3}$$

Column 12 of the Gas Table holds the value of  $C_p(T_{norm})/R$  where  $T_{norm} = 293.15 \text{ K}$ . This value serves as a computational check point, allowing the BGA244 firmware to validate the table contents and its method for computing heat capacity.



### Speed of sound at normal temperature (Column 13)

The speed of sound at normal temperature (293.15 K), and in the zero pressure limit, is given in Column 13 in units of meters/second. This value can serve as a computational check of other table values and firmware algorithms, and is useful for sorting the Gas Table by the speed of sound. Such a sort provides prospective on the ability of the BGA244 to measure the composition of a gas mixture: It is difficult to measure the composition of a mixture of two gases which have nearly the same speed of sound.

### Tsonopoulos correlation

The Tsonopoulos correlation is a CSP method which is used to estimate the 2<sup>nd</sup> virial. Absent experimental measurements, this method was used to estimate the 2<sup>nd</sup> and 3<sup>rd</sup> virial coefficients of pure gases in the Gas Table.

The method is also used by the BGA244 firmware to estimate the 2<sup>nd</sup> cross-virials of a gas mixture. This computation is done in firmware (instead of listed in the Gas Table) due to the large number (125,000) possible mixtures for 500 different gases.

To compute the 2<sup>nd</sup> cross-virial via the Tsonopoulos correlation the firmware will require the critical constants ( $P_c$ ,  $V_c$ ,  $T_c$ , and  $Z_c$ ), acentric factor, dipole moment, and categorization into one of six chemical families. The Gas Table details for those values is detailed below.

### Critical constants (Columns 13-17)

The critical constants for each substance,  $P_c$ ,  $V_c$ ,  $T_c$ , and  $Z_c$ , are listed in Columns 13-17. The critical pressure is in units of bar. (1 bar = 100,000 Pa). The critical volume is in units of cc/mole. The critical temperature is in units of kelvin and the critical compressibility is dimensionless.

### Acentric Factor (Column 18)

The Pitzer acentric factor is used to characterize the departure of thermodynamic properties of a substance from those predicted by two-parameter corresponding states principles (CSP). As CSP applies strictly only to spherical molecules, the acentric factor is considered to be a measure of the acentricity of the molecule. The acentric factor is dimensionless, and is determined from the departure of vapor pressures from those predicted for spherical molecules (such as noble gases.)

### Dipole moment (Column 19)

The electric dipole moment of the substance in the gas phase is given in Column 19 in units of D (debye). Debye are not SI units, but provide a dipole value which is on order 1 for molecules.  $1 D \approx 3.33564 \times 10^{-30} C \cdot m = 0.208194 e \cdot \text{\AA}$ .

### Chemical Family (Column 19)

The Tsonopoulos correlation uses different correlation terms depending on the nature of the species, which are categorized into one of six chemical “families” as shown in Table 1.

Table 1.

Family	Description
1	Simple, Normal gases
2	Keytones, Aldehydes, Alkyl Nitriles, Ethers, Carboxylic Acid Esters
3	1-Alkanols except methanol
4	Methanol
5	Water

### Tsonopoulos a,b parameters (Column 20-21)

These parameters, which are detailed in Table 4-5 on page 4.15 in PG&L are used in the Tsonopoulos correlation to compute the 2<sup>nd</sup> virial coefficients and 2<sup>nd</sup> cross-virial coefficients via a CSP method. (Note there is an error in the table in PG&L for the exponent for the a-parameter for Alkyl Halides, Mercaptans, Sulfides, and Disulfides:  $-2.188 \times 10^{-4}$  should read  $-2.188 \times 10^{-11}$  per original published papers.)

### Second virial coefficient parameters (Column 23-25)

The second virial coefficient,  $B(T)$ , is parameterized as a function of temperature as shown in Eq. 4. (See Zuckerwar 4.30-4.32b):

$$B(T) = a_v - b_v e^{(c_v/T)} \quad \text{Eq. 4}$$

The coefficients,  $a_v$ ,  $b_v$  and  $c_v$  (with units of cc/mol, cc/mol and K) are found in columns 23-25 of the Gas Table. Several sources were used for these parameters including: Fitting the above equation to values for the 2<sup>nd</sup> virial computed over the operating temperature range from REFPROP, or by using coefficients directly from Zuckerwar or from Kaye & Laby, or (lastly) fitting the above equation to values for the 2<sup>nd</sup> virial computed from the Tsonopoulos correlation.

The 2<sup>nd</sup> virial and its first and second temperature derivatives alter the speed of sound in a manner which increases linearly with gas density. For many gases the virial correction for the speed of sound will be a small correction. For example, in methane at 1.6 atm and 300K, virial effects reduce the speed of sound by only 0.12%. However, even this small factor may be important in determining relative concentrations of species which are close in molecular weight.

### Third virial coefficient parameters (Column 26-30)

The 3<sup>rd</sup> virial as a function of temperature is represented Eq. 5 (See Zuckerwar's Eq 4.35).

$$C(T) = \left[ d_v - e_v \cdot \exp\left(\frac{f_v}{T}\right) \right] \cdot \exp(-g_v \cdot T) + C_{asymptote} \quad \text{Eq. 5}$$

The parameters of this equation,  $d_v$ ,  $e_v$ ,  $f_v$ ,  $g_v$  and  $C_{asymptote}$  are given in columns 26-30 of the Gas Table. The units for these parameters are  $cc/mol^2$ ,  $cc/mol^2$ ,  $K$ ,  $K^{-1}$  and  $cc/mol^2$ .

Coefficients for the 3<sup>rd</sup> virial were sourced from Zuckerwar, computed from a CSP method by Orbey, or extracted from NIST's REFPROP program. All three methods provided reasonable agreement for common gases, but very disparate results for less common gases. There is a scarcity of reliable experimental results for the 3<sup>rd</sup> virial, and the method of Orbey does not address polar compounds, hence coefficients for the 3<sup>rd</sup> virial are missing for many substances.

The 3<sup>rd</sup> virial and its first and second temperature derivatives alter the speed of sound in a manner which increases quadratically with gas density. The impact is vanishingly small below a few atmospheres for most gases, but impacts the speed of sound by about 0.3% in SF<sub>6</sub> at ten atmospheres at 25C.

Finally, we suspect that literature reports of 2<sup>nd</sup> virial measurements have often conjoined 3<sup>rd</sup> virial effects into their fits. (We have seen cases where explicitly adding in the 3<sup>rd</sup> virial overcorrects.)

### Viscosity (Columns 31-33)

The viscous boundary layer (typically a few 0.001") impacts the cavity resonance frequency by a fraction of a percent. The effect can be compensated for if we know the gas viscosity. The viscosity of a gas is approximated by the polynomial as shown in Eq. 6.

$$\eta = A_{\eta} + B_{\eta} \cdot T + C_{\eta} \cdot T^2 \quad \text{Eq. 6}$$

Here, T is the absolute temperature in K. Coefficients for the polynomial,  $A_{\eta}$ ,  $B_{\eta}$  and  $C_{\eta}$ , are tabulated for each gas and scaled so that the result has units of  $\mu\text{Pa}\cdot\text{s}$ .

Polynomial coefficients were determined by least squares fitting to viscosity data points over the operating temperature range. Data points were extracted from NIST's REFPROP, computed from correlation functions provided by Perry or PG&L, or computed from the CSP method of Lucas (see PG&L 9.9).

### Thermal conductivity (Columns 34-36)

The thermal boundary layer (typically a few 0.001") impacts the cavity resonance frequency by a fraction of a percent. The effect can be compensated for if we know the thermal conductivity of the gas. The thermal conductivity of a gas is approximated by the polynomial in Eq. 7.

$$\eta = A_{\kappa} + B_{\kappa} \cdot T + C_{\kappa} \cdot T^2 \quad \text{Eq. 7}$$

Here, T is the absolute temperature in K. Coefficients for the polynomial,  $A_{\kappa}$ ,  $B_{\kappa}$  and  $C_{\kappa}$ , are tabulated for each gas and scaled so that the result has units of  $\text{mW}/\text{m}\cdot\text{K}$  (1000x larger than SI value with units of  $\text{W}/\text{m}\cdot\text{K}$ ).

Polynomial coefficients were determined by least squares fitting to thermal conductivity data points over the operating temperature range. Data points were extracted from NIST's REFPROP, computed from correlation functions provided by Perry or PPL&G, or computed from the CSP method of Chung (1984, 1988) following PG&L Eq. 10-3.14

### Heat capacity relaxation parameters (Columns 37-40)

There are a few gases for which vibrational energy levels (which contribute to the heat capacity) do not have time to equilibrate with the translational energy during the period of an acoustic cycle. The relaxation correction may be thought of as a correction to the heat capacity of the gas: If the relaxation time,  $\tau_d$ , is longer than the acoustic cycle then vibrational degrees of freedom are partially frozen out, the heat capacity is lower, and so  $\gamma$  and the speed of sound will be higher. Without a correction for this effect, the computed speeds of sound (as is reported by NIST's REFPROP program, for example, which computes the speed of sound at zero frequency) are lower than the actual speed of sound.

We follow Zuckerwar's approach for the relaxation correction to the square of the speed of sound  $W^2$  as shown in Eq. 8:

$$W^2 = W_\theta^2 \left[ 1 + \frac{\varepsilon}{1 - \varepsilon} \cdot \frac{(\omega\tau_d)^2}{1 + (\omega\tau_d)^2} \right] \quad \text{Eq. 8}$$

Here  $W_\theta^2$  is the speed of sound (squared) corrected for the static heat capacity and virial effects (but not relaxation effects),  $\varepsilon$  is the relaxation strength,  $\tau_d$  is the relaxation time and  $\omega = 2\pi \cdot f_{101}$ . The vibrational temperature (in K) in column 37 allows the firmware to compute  $\varepsilon$  and the coefficients in columns 38-40 allow the computation of  $\tau_d$ . Computationally, we cast Zuckerwar's correction as a frequency dependence of the heat capacity.

### Vapor pressure (Columns 41-43)

The saturation vapor pressure of the gas is computed to warn that the system may be close to condensation (which can impact the speed of sound or fill the chamber with liquid) and to limit the range of composition computational results.

The Antoine equation, Eq. 9, is used to model the saturation vapor pressure over the operating temperature range.

$$P_{vp}^{sat}(\text{bar}) = 10^{\left[A - \frac{B}{T+C}\right]} \quad \text{Eq. 9}$$

Values for  $A$ ,  $B$  and  $C$  are given in columns 41-43 of the Gas Table. These values were found by fitting the Antoine equation to vapor pressure data points over the operating temperature range. Vapor pressure data points were generated from multiple sources, including, NIST's REFPROP and correlation functions and parameters found in Perry, PG&L, PPL&G.

Vapor pressure data is omitted for fluids with critical temperatures below 265 K (as these fluids cannot be liquids at the BGA244 operating temperatures). In cases where no vapor pressure data is available, the BGA244 will not provide condensation warnings and will not limit composition results to below the saturation vapor pressure.

### Speed of sound offsets (Columns 44-46)

The BGA244 computes the theoretical speed of sound using accurate molar masses, temperature corrected heat capacities, virial corrections, and translational-vibrational relaxation corrections. The speed of sound is measured using the thermo-viscous corrected resonance frequency and a cavity factor which has been corrected for perturbations and transducer resonances. Uncertainties in all of these corrections can lead to discrepancies between the measured and the computed speed of sound on order of +/- 100 ppm. An empirical speed of sound offset  $W_{offset}(ppm)$ , pressure correction  $W_{p-slope}(ppm/psi)$  and temperature correction  $W_{T-slope}(ppm/K)$  for each gas are used to repair these discrepancies. Values for those corrections are given in columns 44-46 of the Gas Table (and are initially set to zero except for hydrogen).

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