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How the non-ideality of real gases affects results of the ozone Standard Reference Photometer (SRP)

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Abstract

The equations that describe the operation of the ozone Standard Reference Photometer (SRP) assume that dry air mixed with trace amounts of ozone is an ideal gas. The following report examines this assumption in considerable detail and concludes that it is indeed justified within typical operating conditions of the SRP. This report also answers the related question of whether there is a difference between ozone mole fractions, typically reported as nmol/mol, and the corresponding volume fractions, typically reported as ppbv.

1. Introduction

1.1 How non-ideality of atmospheric gases enters the SRP equations

The number of ozone molecules/unit volume (number concentration), C_{oz}, is measured by a Standard Reference Photometer (SRP) with results interpreted in terms of the Beers-Lambert (B-L) law:

$$C_{\mathrm{oz}} = f\left(\sigma L_{\mathrm{opt}}, \tau\right) \tag{1}$$

where f is the B-L relation, which is a function of σL_{opt} and τ. Here σ is the ozone cross-section (SI coherent unit: m^2), L_{opt} is the optical length (SI coherent unit: m) and τ is the transmittance (dimensionless), all as appropriate to the photometer. The value of C_{oz} determined from (1) is for the sampled air at pressure P and temperature T. The result of (1) is then corrected to air at standard conditions of pressure and temperature (P_{std}, T_{std}) by multiplying both sides of the equation by $C'_{\mathrm{oz}}/C_{\mathrm{oz}}$, where C'_{oz} is the number concentration C_{oz} normalized to the standard conditions. The required correction factor is obtained from the equation of state of the sampled air, $P = CZkT$, where Z is the compressibility factor (or compression factor) of the mixture at T and P and k is the Boltzmann constant. Thus

$$\frac{C'_{\mathrm{oz}}}{C_{\mathrm{oz}}} = \frac{P_{\mathrm{std}}}{P}\frac{T}{T_{\mathrm{std}}}\frac{Z}{Z'} \tag{2}$$

We introduce the compressibility factor Z' of the air/ozone mixture at standard conditions, and the factor Z at the experimental conditions, although the approximation $Z = Z' = 1$ is taken to be exact for the SRP.

From the definition of the mole, the number of moles per unit volume (or amount concentration) of ozone at standard conditions, c'_{oz} is

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$$c'_{\mathrm{oz}} = \frac{C'_{\mathrm{oz}}}{N_{\mathrm{A}}}, \tag{3}$$

where N_{A} is the Avogadro constant.

$$c'_{\mathrm{oz}} = \frac{1}{N_{\mathrm{A}}} \frac{C'_{\mathrm{oz}}}{C_{\mathrm{oz}}} f \tag{4}$$

We now need to find x_{oz}, the mole fraction of ozone in the sampled gas (dry air + ozone) at standard conditions. This is given by

$$x_{\mathrm{oz}} = \frac{c'_{\mathrm{oz}}}{c'_{\mathrm{air}} + c'_{\mathrm{oz}}} \tag{5}$$

Mole fraction is a dimensionless quantity (*i.e.* its unit is equal to 1), but its value is commonly expressed as a fraction of the unit ratio mol/mol to reduce ambiguity.

The SRP measurement range is (0 – 1000) nmol/mol. For $x_{\mathrm{oz}} < 1000$ nmol/mol ($<10^{-6}$) and a requirement to measure x_{oz} to a relative uncertainty no greater than 0.01%, the following approximation should be completely adequate:

$$x_{\mathrm{oz}} = \frac{c'_{\mathrm{oz}}}{c'_{\mathrm{air}}}$$

but in the spirit of this report, we will not make this approximation just yet.

Thus we need the value of $c'_{\mathrm{air}} + c'_{\mathrm{oz}}$, the amount concentration (mol m^{-3}) of the sampled gas at standard conditions. We obtain this from the gas laws:

$$c'_{\mathrm{air}} + c'_{\mathrm{oz}} = \frac{P_{\mathrm{std}}}{Z'RT_{\mathrm{std}}} \tag{7}$$

where R is the universal gas constant. Combining equations (1)-(7) we finally arrive at:

$$x_{\mathrm{oz}} = \frac{1}{N_{\mathrm{A}}} \frac{C'_{\mathrm{oz}}}{C_{\mathrm{oz}}} \frac{Z'RT_{\mathrm{std}}}{P_{\mathrm{std}}} f \tag{8}$$

which is the same as Eq. (3) of [1] except for the inclusion of the compressibility factor Z of the sampled gas. In other words, using the above equations, it can readily be shown that (8) reduces to

$$x_{\mathrm{oz}} = Z \frac{R}{N_{\mathrm{A}}} \frac{T}{P} f = Z \frac{kT}{P} f \tag{9}$$

For ideal gases $Z = 1$ and this approximation is made for the SRP.

Note that (9) is independent of P_{std} and T_{std} which demonstrates that we could have progressed from (1) to (9) without all the intermediate steps involving corrections to standard conditions. The mole fraction x_{oz} is independent of changes to the temperature or pressure of a given gas sample. Correction to standard conditions is useful if we are interested in comparing dimensioned concentrations, such as C_{oz} and c_{oz}, which depend on the pressure and temperature of the sampled gas.

A word should be said about the value of σ which appears in (9). The value chosen is essentially that reported in 1961 by Hearn, but with a standard relative uncertainty of 1.06% ($k = 1$) as recalculated in [1]. The authors of [1] point out that the Hearn value is used conventionally by the air-quality monitoring community and it would be unreasonable to propose a change in this practice. Indeed, it is shown in [1] that the Hearn value is quite consistent with a suite of 11 other independent determinations of σ made using a variety of different methods. However, in the context of this report we point out that determinations of σ have treated oxygen/ozone mixtures as an ideal gas. The assumption of ideality does not figure in the modern re-analysis of Hearn's data [1], an indication that non-ideality contributes negligibly to the combined uncertainty.

1.2 The difference between mole fraction in nmol/mol and the volume fraction in ppbv for results obtained with the SRP

The mole fraction of ozone in dry air is often equated to a quantity known as the "volume fraction" or "volume mixing ratio" which, like mole fraction, is dimensionless. Volume ratio has traditionally been expressed in ppbv.[1] As can be inferred from [2], for the mole fraction in nmol/mol and the volume fraction in ppbv will be identical for SRP measurements it is sufficient that the use of the ideal gas approximation be valid to the required accuracy. Another way of saying this is that the volume fraction takes no account of compressibility factors involved in the measurement, assuming that these factors can be taken to be exactly 1 without significant effect on the end results. By contrast, the mole fraction takes account of the compressibility factors.[2]

Although often taken to be identical, the mole fraction determined from (9) is conceptually different from the volume fraction. However, it will be shown quantitatively in the following that Z in (9) is closely approximated by 1. Based on our calculations and the compressibility factors shown below in Table 1, at typical laboratory conditions the mole fraction x_{oz} (expressed in nmol/mol), is only 0.04% smaller than the corresponding volume fraction (expressed in ppbv). At present, therefore, the distinction between mole fraction and volume fraction is without any practical difference for SRP measurements.

The general conclusions of Schwartz and Warneck dating from 1995 [2], still apply to the SRP:

> "Because air at atmospheric pressure is essentially an ideal gas, the volume fraction is essentially equal to the mole fraction, and for all practical purposes the two quantities can be used interchangeably and without distinction. Mole fraction is preferable, however, because it does not require an implicit assumption of ideality of the gases…"

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[1] ppbv stands for parts per billion by volume. Use of the symbol ppbv is discouraged by IUPAC [2] but nevertheless remains widespread.

[2] The effect of non-ideality in determinations of the conventional value of ozone cross-section, which appears as a parameter in *f* has not been considered (see last paragraph of section 1.1).

Nevertheless, it may be useful to see at what conditions one might expect gas non-ideality to be a problem should accuracy requirements increase. This estimate is carried out in the next section.

2. Secondary questions

2.1 Under what conditions must we abandon the approximation Z = 1 in (9), even if we can assume that the ozone concentration is so small that Z is essentially the value for dry air alone?

In this case, we can easily calculate Z from the second and third virial coefficients of dry air at the conditions of measurement as published by Hyland and Wexler [3]. Recall that the virial expansion is usually written as

$$\frac{PV_{\mathrm{m}}}{RT} = Z = 1 + B(T)V_{\mathrm{m}}^{-1} + C(T)V_{\mathrm{m}}^{-2} + \cdots$$

where $B(T)$ and $C(T)$ are the second and third virial coefficients respectively, and V_{m} is the molar volume of the gas. If we truncate the expansion after the third virial coefficient, the expansion rewritten in powers of pressure becomes:

$$\frac{PV_{\mathrm{m}}}{RT} = Z = 1 + \frac{B(T)}{RT}P + \frac{C(T) - B(T)^2}{(RT)^2}P^2 .$$

In fact, terms in V_{m}^{-2} or P^2 can be safely neglected in the following discussion. Note that the second virial coefficient B has the SI coherent unit m^3/mol. Hyland and Wexler fitted B by a third-order polynomial expanded in powers of $1/T$ in order to describe the experimental data available to them. The compressibility of air is then well approximated by

$$Z_{\mathrm{air}} = 1 + \frac{B_{\mathrm{air}}(T)}{RT}P \tag{10}$$

over normal laboratory conditions and, indeed, over conditions of temperature and pressure encountered on the Earth's surface. Values of Z_{air} for dry air over a range of temperatures and pressures are summarized in Table 1. In generating the table we have used both the second and third virial coefficients of [3] although we observe that simply using (10) does not change any of the compressibility factors shown in the table.

2.2 Does Z for mixtures of ozone and dry air, where $x_{oz} < 10^{-6}$, differ from Z for dry air alone?

Before answering this question, it will be instructive first to estimate Z_{oz} for pure ozone. We will then estimate Z_{mix} for the mixture of trace amounts of ozone in dry air under experimental conditions. We add the subscript "mix" to Z in this section whenever needed for clarity; the subscript "mix" refers to a mixture of ozone in dry air.

Pure ozone

Experimental data for ozone are relatively scarce. Therefore compressibility data in the literature are based on the critical values (T_{c}, P_{c}) of ozone, which are then incorporated into an empirical equation based on the principle of corresponding states. In its simplest formulation, the principle holds that all gases at the same the reduced temperature $T_{\mathrm{r}} = T/T_{\mathrm{c}}$ and reduced pressure $P_r = P/P_c$ have the same compressibility factor. In the absence of experimental determinations or *ab initio* calculations of the second virial coefficient for ozone, B_{oz}, we infer this datum from the reduced temperature and pressure using the empirical formulas for corresponding states proposed by Tsonopoulos [4]:

	***P* / kPa**				
***t* / °C**	**120**	**110**	**100**	**90**	**80**
50	0.9999	0.9999	0.9999	0.9999	0.9999
40	0.9998	0.9998	0.9998	0.9998	0.9999
30	0.9997	0.9997	0.9997	0.9998	0.9998
20	0.9996	0.9996	**0.9996**	0.9997	0.9997
10	0.9995	0.9995	0.9995	0.9996	0.9996
0	0.9993	0.9994	0.9994	0.9995	0.9995
-10	0.9991	0.9992	0.9993	0.9994	0.9994
-20	0.9989	0.9990	0.9991	0.9992	0.9993
-30	0.9987	0.9988	0.9989	0.9990	0.9991
-40	0.9985	0.9986	0.9987	0.9988	0.9990
-50	0.9981	0.9983	0.9984	0.9986	0.9988

Table 1. Values of Z_{air} for dry air over a range of temperature and pressure, from Hyland and Wexler [3].

$$\frac{BP_c}{RT_c} = F_0\left(T_r\right) + \omega F_1\left(T_r\right) \tag{11}$$

where F_0 and F_1 are universal functions that depends only on reduced temperature. The parameter ω is the acentric factor introduced by Pritzer and Curl [5] to account for the effects of the non-sphericity of molecules such as water (and ozone).

We have taken T_c and P_c for ozone from the tabulated values of *Kaye and Laby* [6]. These are essentially the same as the experimental values determined by Jenkins and Birdsall [7]. Reference [7] also contains sufficient empirical information to estimate the acentric factor of ozone to be approximately 0.2, in agreement with handbook values [8][3]. At standard conditions, the acentric factor does not significantly alter the value of B for ozone that would be calculated from F_0 alone.

It should also be mentioned that [4] introduces a term F_2 to be added to the right-hand side of (11) in order to account for the finite electric dipole moment of molecules such as water (and ozone). It is suggested that the correction depends in part on a dimensionless parameter called the reduced electric dipole moment [4]. Based on the work of Mack and Muenter [9], this parameter is approximately 22.5 for ozone (173 for water [4]). Tsonopoulos observes that the analytic form of the added term depends on the chemical family of the gas (e.g. different terms are proposed for ethers, ketones, water etc. to account for their finite dipole moments) [4]. No specific information is given for ozone but insertion of its reduced dipole moment into

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[3] By contrast, the acentric factor for water is listed in [4] as 0.344.

the proposed empirical functions for other chemical families would leave the calculated compressibility unchanged at any of the experimental pressures and temperatures of interest to us.

Finally, then, we use (11) to determine the second virial coefficient for ozone based on the following input data:

$$T_{\mathrm{c\_oz}} = 261.1 \text{ K [6]}$$

$$P_{\mathrm{c\_oz}} = 5.57 \text{ MPa [6]}$$

$$\omega_{\mathrm{oz}} = 0.2 \text{ [7,8]}$$

from which the compressibility factor of ozone is then estimated to be

$$Z = 1 + \frac{P_{\mathrm{r}}}{T_{\mathrm{r}}}\left(F_0 + \omega F_1\right) \qquad (12)$$

where all parameters are appropriate to pure ozone.

We find that the term in ω which corrects for acentricity makes only a small contribution at normal laboratory conditions of pressure and temperature. We do not have sufficient information to add a term to account for the electric dipole-moment of ozone, but we suspect that this term is also small for the P-T range of Table 1. For pure ozone at temperature 20 °C and pressure 101.325 kPa, we estimate that $Z_{\mathrm{oz}} = 0.9957$ whether or not the acentric term is included. At the extreme conditions of low temperature and high pressure given in Table 1, the compressibility of ozone is calculated to be about 0.985, where the acentric term has been included. These calculations may be compared with those presented in [10] using an earlier equation of corresponding states which estimates the second through the fourth virial coefficients but does not consider acentricity or dipole terms. Figure 1 of [10] shows the authors' estimate of the compressibility factor for pure ozone as a function of temperature and pressure. The graph also includes the ozone saturation curve and the critical point.

Mixtures of ozone in dry air

We do not expect that mixtures of trace amounts of ozone in dry air will significantly affect the compressibility factor of the pure air. However, we wish to justify this assertion quantitatively. A simple approach will be sufficient for our purpose. Reid and Leland [11] examine under what circumstances elaborate rules that have been proposed in the literature for determining the equation-of-state for gas mixtures reduce to "Kay's rule", which is indeed very simple, for obtaining pseudo-critical values for the mixture. They conclude that "all mixing equations reduce to Kay's rule in certain limiting cases." A mixture of ozone in air is one of those limiting cases, based on guidance given in this reference.

Kay's rule asserts that the critical temperature and pressure of a gas mixture can be found by weighting the critical values of each component by its mole fraction in the mixture. For a two-component system involving gases **a** and **b**, with **b** having mole fraction x_{b}, the rule becomes:

$$T_{\mathrm{c\_mix}} = (1 - x_{\mathrm{b}})T_{\mathrm{ca}} + x_{\mathrm{b}}T_{\mathrm{cb}} \qquad (13)$$

and

$$P_{\mathrm{c\_mix}} = (1 - x_{\mathrm{b}})P_{\mathrm{ca}} + x_{\mathrm{b}} P_{cb} \quad . \tag{14}$$

(A similar rule applies to the acentricity factors of the two components but, for the purposes of this rough calculation we ignore acentricity.)

The pseudo-critical values for the mixture can then be used in a formula for corresponding states. Thus we will use (15) to obtain the compressibility factors for the mixtures[4]:

$$Z_{\mathrm{mix}} = 1 + \frac{P_{\mathrm{r\_mix}}}{T_{\mathrm{r\_mix}}} F_0\left(T_{\mathrm{r\_mix}}\right) \quad . \tag{15}$$

To proceed with this calculation we treat dry air as the species **a** and ozone as species **b**. Critical values for dry air are taken from Lemmon *et al.* [12][5]:

$$T_{\mathrm{c\_air}} = 132.53\ \mathrm{K}$$

$$P_{\mathrm{c\_air}} = 3.786\ \mathrm{MPa}$$

It can be shown that, when inserted into (12) these critical values faithfully reproduce the compressibility factors of Table 1, occasionally with a change of 1 in the last digit. The critical constants for pure ozone [6] have already been noted above.

It follows from Kay's rule that

$$T_{\mathrm{c\_mix}} = (1 - x_{\mathrm{oz}})T_{\mathrm{c\_air}} + x_{\mathrm{oz}}T_{\mathrm{c\_oz}} \cong T_{\mathrm{c\_air}}(1 + 2.0x_{\mathrm{oz}}) \tag{16}$$

$$P_{\mathrm{c\_mix}} = (1 - x_{\mathrm{oz}})P_{\mathrm{c\_air}} + x_{\mathrm{oz}}P_{\mathrm{c\_oz}} \cong P_{\mathrm{c\_air}}(1 + 1.5x_{\mathrm{oz}}) \tag{17}$$

where the final approximations are : $x_{\mathrm{oz}} << 1$, $T_{\mathrm{c\_oz}}/T_{\mathrm{c\_air}} \cong 2.0$ and $P_{\mathrm{c\_oz}}/P_{\mathrm{c\_air}} \cong 1.5$.

Thus for all practical purposes, the pseudo-critical values for the ozone/air mixtures encountered by an SRP are identical to the critical values for dry air. It follows that $Z_{\mathrm{mix}} = Z_{\mathrm{air}}$ can be safely assumed[6] when the compressibility factor of the mixture is derived from the principle of corresponding states.

3. Conclusion

Neither Kay's rule for estimating pseudo-critical values for a mixture of ozone and dry air nor empirical formulas of corresponding states for estimating the compressibility factor of

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[4] Note, however, that many authors, including those of [4] and [9], have propose more refined mixing rules based on theoretical considerations. Reference [9] computes compressibility factors for binary mixtures of ozone and oxygen which can be compared with what would be obtained from using pseudo-critical values.

[5] As a point of interest, these critical constants are reasonably well approximated by applying Kay's rule to the mole fractions adopted in [12] for the components of dry air.

[6] For example, this procedure estimates that $Z_{\mathrm{mix}} = 0.9990$ would require $x_{\mathrm{oz}} \approx 2\%$ or 2×10^7 nmol/mol.

ozone/air mixtures are validated by experiment. However, there is no reason to suspect that the calculations proposed above lead to errors gross enough to affect the interpretation of SRP results.

Thus the presence of ozone in dry air at mole fractions less than 1000 nmol/mol cannot significantly change the compressibility factor of pure dry air, Z_{air}. It follows that either the compressibility values for dry air derived from Hyland and Wexler [3] (see Table 1) or factors consistent with the formalism of [12] are suitable for (9). Alternatively, $Z_{\mathrm{air}} = 1$ can be assumed if an error of order 0.05% at usual laboratory conditions is considered negligible, in which case the mole fraction x_{oz} expressed in nmol/mol can be taken to be identical to the volume fraction, expressed in ppbv [2].

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