# PSYCHROMETRY: FROM PARTIAL PRESSURES TO MOLE FRACTIONS

by

Clifford C.O. Ezeilo
Department of Mechanical Engineering
University of Nigeria, Nsukka.

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## ABSTRACT

This study uses the virial and interaction coefficients of the normal air components in deriving compressibility factors and thereafter a simple iterative formulation for mole fractions. Conversion from partial pressures to mole fractions now becomes tractable by means of determinate multipliers. The results obtained compare most favourably with the widely accepted derivations due to Goff and Gratch. One possible advantage is that the presented formulation permits the evaluation of those multipliers without reference to the virial and interaction coefficients provided that the "dry air" and moist air compressibility's are very accurately measured. A possible simplification is that this partial pressure multiplier is expressed explicitly in a form suggesting acceptable results for air-water gaseous mixtures outside the range of normal air psychometry.

## NOTATION

P pressure (m-bar)
V specific volume ($m^3$/Kg-mole)
$R_O$ universal gas constant = 0.083143 $m^3$ bar/Kg-mole. K
= 8.3143 KJ/Kg-mole. K
T absolute temperature (K)
Z compressibility factor (dimensionless)
B, B′, $A_{11}$, $A_{aa}$, $A_{ww}$ = second virial Coefficients (consistent units)
C, C′ $A_{111}$, $A_{aaa}$, $A_{www}$ = third virial Coefficients (consistent units)
D Fourth virial coefficient (consistent units)
X Mole fraction (dimensionless )
K Boltzmann constant =1.39053 X10-23 (j/k)
N Avogadro number = 6.023 x $10^{26}$/KG- mole
E Maximum negative value of the molecular potential energy (J)
Q Closest approach o two molecules considered as rigid spheres (m)
Å Angstrom unit = 1.0x$10^{-10}$ meter
T* reduced temperature:. T(k/ε). (dimensionless)
B* reduced second virial coefficient = $B/b_o$. (dimensionless)
$b_o$ second viral from the potent malfunction= $2\pi No^3/3$ ($m^3$/Kg-mole)
f pressure multiplier (dimensionless)
w specific humidity (g/kg dry air)

### Subscripts

ss state of air saturated with water vapour
a dry air alone
w water vapour alone
aa molecules of air in pairs also air alone in mixture
ww water molecules in pairs also water alone in mixture
aw air and water molecules also air watersecond virial interaction in the binary mixture
aaa air molecules in threes also the third virial coefficient for air alone
vww water molecules taken in threes also water alone in the third viral coefficient
aww,aaww air-water third virial interactions: one air plus two

water molecules and one water plus two molecule of air

## 1. INTRODUCTION

The earliest studies of psychrometry considered normal air as an ideal gas mixture. Partial pressures then become identical: to mole fractions and sets of psychometric parameters result from rather elementary thermodynamic relations. Search for more accurate data has long led to the realization that neither dry air nor pure water vapour behaves like an ideal gas, despite the fact that the dry air component normally exists at temperatures far inexcess of the critical point temperature while the vapour pressure is much below the critical pressure of steam. This destroys the Gibbs-Dalton law as a basis for standardization.

Modifications of the classical ideal gas equation of state to fit the observed data have been made by many investigators. Most of these efforts take the form of measuring the compressibility factors of dry air, water vapour and their binary mixtures at various mixing ratios and thereafter expressing the P-V-T data as a virial equation of state. Thus from the simple relation

$PV = R_O\ T$ (ideal gas) (1)

we have the equations

$PV/R_OT=Z=1+B/V+C/V^2+D/V^3+$(Volume series) (2)

and

$PV/R_OT = Z = 1+ B^1\ P +C^1P^2 + \ldots\ldots.$ (Pressure series) (3)

The above two expressions are virial equations of state in which the second and third virial coefficients are related in the form

$B^1 = B/(R_OT)$ and $C^1= (C-B^2)/(R_OT)^2$ (4)

Writing

$$PV/R_OT = 1- \left(\frac{A_{11}}{R_OT}\right) - \left(\frac{A_{111}}{R_OT}\right)P^2 \quad (5)$$

it would follow that

$A_{11} = -B$ (6)

and $A_{111} = -(C - B^2)/(R_OT)$ (7)

A11 the virial coefficients: B, C, B 1, C1, A11 and A111 are functions of temperature and some often tabulated for single component gases.

For air as a single component gas

$$Zaa = PV/R_OT = 1 - (P/R_OT)Aaa - \left(\frac{P^2}{R_OT}\right)A_{aaa} \quad (8)$$

Similarly for water vapour,

$$Z_{ww} = (PV/R_OT) = 1 - (P/R_OT)A_{ww} - (p^2/ R_OT)A_{ww} \quad (9)$$

When two or more dissimilar gases form a mixture, interaction force constants complicate the analysis. In the case of binary mixture of dry air and water vapour

$$Z_{aw} = PV/RT_O = 1 - P/R_oT[x_a^2 A_{aa}+ 2x_a x_wA_{aw} +x_w^2A_{ww}] \quad (11)$$

where $A_{aw}$ is the interaction coefficient between the air and vapour molecules considered in pairs. In eqn.10 the series is restricted to the second virial and interaction coefficients only. This restriction has been identified as the "Three Liquid Theory" of binary gas mixtures in statistical thermodynamics.

If the third viral and interaction coefficients are also known, then, considering the molecules in groups of threes will extend eqn.10 into the longer series relation

$$Z_{aw} = \frac{PV}{RT_o} = 1 - \frac{P}{R_OT}[x_a^2 A_{aa}+ 2x_a x_wA_{aw} +x_w^2A_{ww}] - P^2/R_oT[x_a^3A_{aaa} + 3x_a^2x_wA_{aaw} + 3x_ax_w^2 A_{aww} + x_w^3A_{www}] \quad (11)$$

$A_{aaa}$ and $A_{www}$ are the third virial coefficient while $A_{aaw}$ and $A_{aww}$ are the interaction third virial coefficients. Hilesenrath [1 ] tabulates values of B, C, and D for dry air form 50 k to 1500 k. Goff [2 ] give tables of $A_{aa}$, $A_{ww}$, $A_{www}$ and $A_{aw}$ for air – water mixtures for the temperature range $-90^0$c.

Keyes [3] gives values from which $A_{ww}$ and $A_{www}$ can be deduced for pure water vapoure. Mason and monchick [4] have produced data from which Aww may be evaluated, and they stipulate that only the first, second and third virial coefficients have simple physical interpretations. Goff and Gratch [5] formulation sets

$$x^3_a A_{aaa} = x_a^2 x_w A_{aaw} = x_a x_w^2 A_{aww} = 0.0 \quad (12)$$

and arrive at the generally accepted equation [6]

$$Z_{aw} = 1 - \frac{P}{R_o T}[x_a^2 A_{aa} + 2x_a x_w A_{aw} + x_w^2 A_{ww}] + P/P_o( x_w^3 A_{www} )] \quad (3)$$

Theory and reported experimental deductions do not agree on the interaction second virial coefficient $A_{aw}$ and considerable uncertainties still exist [4] as to the values of the interaction third virial coefficients $A_{aaw}$ and $A_{aww}$ Goff and Gratch [5] give values of Z for dry air at temperature varying from $-100^0$C to $+60^o$Cfor pressures ranging from zero to 1100 mb. Their data for moist air are reported at 25% mixing ratio to degree of saturation intervals from $0^0$C to $60^0$C and at total pressures of 0,300, 700 and 1100 mb. They also tabulate values corresponding to pure water vapour (vapour over ice and vapour over water) at saturation or boiling point temperatures of$-100^0$C to $+60^0$C. Hilsenratch [1] presents values for steam at one and ten atmospheres pressure for absolute temperatures ranging from $380^0$K to $850^0$K. His data for dry air are presented in a deviations form leading of a table of $(Z_{aa}-1) \times 10^5$.

In all the literature quoted above the accuracy level of the data will be inadequate for the theory developed later: a theory that relies on small differences. Practically, if the compressibility factors of dry air ($Z_{aa}$) and air-water mixtures ($Z_{aw}$) are measured to the high degree of accuracy demanded by the analysis, then the precise values of the interaction and virial coefficients become an exercise in statistical thermodynamics. That the available measured data do not satisfy this need of small differences has led to the inverse problem of evaluating Z from the known second virial coefficients and the theoretical predictions of the interaction coefficients.

In this inverse problem, statistical thermodynamics considers water vapour molecules as polar molecules with the force constants (which determine the second virial coefficients) evaluated on the basis of the Stockmayer 12-6-3 Potential Function. Dry air, on the other hand, is of non-polar molecules with the force constants evaluated from the Lenard Jones 12 - 6 Potential. Standard works in this field are contained in books such as by Tieu and Lienhard [7] and by Hirschfelder et al [8]. Extensions to moist air (as a binary mixture) are reported by Hirschfelder et al,[8] Shaddock [9] and Mason and Monchick [4]. Statistical single - value constants such as k, $\varepsilon$ and $\sigma$ exist for dry air (as of non-polar molecules) and pure steam (as of polar molecules). For dry air, the reduced second virial coefficients $B^*(=B/b\ )$ and reduced temperatures $T^*$ are available as one of the Lenard-Jones . gases in a tabular form *[9, 10]* for the range

$$0.30 \le T^* = T(\varepsilon/k) \le 50.$$

Similar relations are presented by Shaddock [9] quoting Rawlinson [11] for a stockmayer Gas like pure steam in the: range $0.80 \leq T^* \leq 100$.

An assumption made by Hirschfelder et. al. is that the effective interaction force constant between a polar and a non-polar molecule is identical in value to that between two non-polar molecules. With this assumption the interaction coefficients of air-water mixtures can be determined for a good rage of temperatures.

In this work the second and third virial coefficients for single-component gases are taken from existing results (Hilsenrath [11] for air and Keyes [3] for steam). The interaction second virial coefficients are computed from statistical data. The differences between these theoretical values and those due to Goff and Gratch are compared. The effect on the moist air compressibility factor is found to be small. On the partial pressure multiplier the difference becomes practically insignificant. This multiplier ($f_{ss}$) is computed for air saturated with water vapour at total pressures varying from 800 mb to 110mb. The nearest relations found in the literature, where f is expressed explicitly in terms of other variables, as in the formula developed, are reported by Harrison [12] using two data sources: the first due to Landsbaum, Dodd's and Stutsman [3] and the second using the data from Webster [14]. Both are of the form

$$f_{ss} = [1 + (P-P_{ss})]\ C(T) \quad (14)$$

(in our present notation)

where C(T) is a suitable function of temperature but with the dimensions of atmosphere.

## 2. THEORY

When moles of dry air alone Occupies volume (V) at temperature (T) under the pressure ($p_a$) then from a eqn.8

$$P_a^1(V/R_OT) = x_a\ [1-\frac{P_a^1A_{aa}}{R_oT} - (P_a^1)^2\frac{A_{aaa}}{R_oT}] \quad (15)$$

Similarly for $x_w$ moles of water vapour alone, using eqn. 9 gives

$$P_w^1(V/R_OT) = x_w\ [1-\frac{P_w^1A_{ww}}{R_oT} - \frac{(P_w^1)^2A_{www}}{R_oT}] \quad (16)$$

If $x + x_w = 1.00$ and the above gases mix under Gibbs-dalton law, then $P_a^1$

$$(P_a^1 + P_w^1)\ V/R_OT = x_a + x_w - x_a^2\frac{PA_{aaa}}{R_oT} - x_a^3\frac{P^2A_{aaa}}{R_oT} - x_w^2\frac{PA_{ww}}{R_oT} - x_w^3\frac{P^2A_{aaa}}{R_oT} \quad (17)$$

where $x_a = \frac{P_a^1}{P}$ and $x_w = \frac{P_w^1}{P}$

$P^1{}_a$ and $p^1{}_w$ are idealized partial pressures to yields the pressure P.

Thus, on considering the gases as Gibbs-Dalton gases one arrives at the relation.

$$PV/R_OT = 1- \frac{P}{R_oT}[x_a^2 A_{aa} + x_w^2 A_{ww}] - \frac{P^2}{R_oT}[x_a^3A_{aaa} + x_w^3A_{www}] \quad (18)$$

Since $P_a^1 + P_w^1 = P$.

However, for the real mixing process, it is shown by eqn.11 that the interaction coefficients get involved. Thus if $P_a$ and $P_w$ are the actual partial pressures on mixing, then from eqn. 11

$$(Pa + Pw)\ V/R_OT = 1- \frac{P}{R_oT}[x_a^2 A_{aa} + 2x_ax_wA_{aw} + x_w^2 A_{ww}] - \frac{P^2}{R_oT}[x_a^3A_{aaa} + 3x_a^2x_wA_{aaw} + 3x_a x_w^2A_{aww} + x_w^3A_{www}] + \ldots\ldots \quad (19)$$

Dividing eqn.19 with eqn.18 result with series approximation in the mixture partial pressures equation

$$(P_a + P_w)/P = 1- \frac{P}{R_oT}[2x_ax_wA_{aw}] - \frac{P^2}{R_oT}[3x_a^2x_wA_{aaw} + 3x_ax_w^2A_{aww}] + \quad (20)$$

It would be obvious from the above that mixing of the dissimilar gases leads to the inequality

$$p_a + p_w \neq P \quad (21)$$

and that this inequality is due to the interaction force constants which consequently invalidate the Gibbsalton Law.

When the third virial interaction coefficients are neglected eqn.20 reduces to

$p_a + p_w = P- \frac{P}{R_oT}$ $[2x_a x_w A_{aw}]$ (21)

The above equation is quoted by Goff [15] who also gives the following relations between partial pressures and mole fractions:

$Pa = x_a P + \frac{x_w x_a}{R_oT}[-A_{aa} + x_w(A_{aa} -2A_{aw} +A_{ww})] P^2 +$ (22)

It is easily verified that the addition of the last two equations results in eqn.21.

Since

$x_a + x_w = 1.00$ (24)

eqn.23 readily transforms to yield

$Pw/P = x_w-x_a[x_a^2 A_{aa} + 2x_a x_w A_{aw} + x_a^2 A_{ww}]$

$(P/R_OT) + x_a^2 A_{aa}$ $(P/R_OT)$ (25)

$Pw/P=xw-xa(1-z_{aw}) +x_a^2(1-z_{aa})$ (26)

$Zaw=(PV/R_OT)_{aw}=1-$

$[\frac{x_a^2 Aaa + 2xaxwAaw + x_a^2 Aww}{R_oT}]P$ (27)

and

$z_{aa} = (PV/R_OT)_{aa}= 1- (\frac{P}{R_oT})A_{aa}$ (28)

The last two equations follow from eqn.10 but the longer series/equation given in 13 can also be used in eqn.26 for numerical values of z.

A further reduction of eqn.26 when $x_a \neq 0.00$ results in the final expression

$P_w/P=x_w(2z_{aa} - z_{aw})- (z_{aa} - z_{aw})$ (29)

or

$x_w = [P_w/P+(z_{aa}-z_{aw})]/(2z_{aa}-z_{aw})$ (30)

The object of this analysis is the evaluation of the mole fraction ($x_w$) when the vapour pressure ($P_w$) is known. The problem therefore demands that both $z_{aa}$ and $z_{aw}$ be evaluated fairly accurately since small differences are involved.

In order that mole fractions can be determinate from partial pressures we define the partial pressure multiplier ($f_{aw}$) in the form

$x_w =f_{aw}$ $(P_w /P)$ (31)

Hence from eqn. 30, $f_{aw}$ can be written explicitly to give

$f_{aw}=[1+(P/P_w)+(z_{aa}-z_{aw})]/(2z_{aa}-z_{aw})$ (32)

The special case of wet - bulb saturation or dew point temperature would result in the equivalent equations.

$x_{ss}=[P_{ss}/P+(z_{aa}-z_{aw})]/(2z_{aa}-z_{ss})$ (33)

and

$f_{ss}=[1+(P/P_{ss})(z_{aa}-z_{ss})]/(2z_{aa}-z_{ss})$ (34)

Use of relations 30,32,33 or 34 will demand integrative techniques since the Z terms cannot be obtained unless the x terms are found. Thus for a selected saturation temperature and a given barometric pressure, $P_{ss}$ is obtained from tables, $x_{ss} \cong p_{ss} /p$ and use of this in equ, 13 result in a rough estimate of Z since the corresponding virial and interaction coefficients are determinate. Thereafter, use of eqn.33 gives a better value of x which is then inserted back in eqn3 until both relations 13 and 33 are satisfied.

In this article, results are presented only for the wet-bulb saturation or dew point temperatures due to space limitations. However, the analysis applies to other steam-air mixtures since the vapour pressure ($P_w$) isread1ly obtained.

## 3. DERIVATIONS

### 3.1 VIRIAL COEFFICIENTS FOR DRY Air and Pure Water (Steam)

Table I gives the reported virial coefficients for the single-component gases: dry air and steam from three sources. Agreements are sufficiently close to permit no further reference to theoretical formulations. For substitution in eqn.13, Hilsenrath's data are used for air while those due to Keyes are utilized for steam. It is found that Hilsenrath's table which is given in 10 K intervals can be curve-fitted for the range 240 K <T <370 K with the equation

$$A_{aa} = 205.0067-.3653(T) + 0.003159(T^2)-0.2674\ x10^{-5}\ (T^3) \quad (35)$$

Use of the above relation reduces inter potation errors.

### 3.2 The Interaction Second Virial Coefficients

Theoretical results are obtained in the manner suggested by Shaddock which relies on the intermolecular force constants for dry air, pure water vapour and air-vapour mixtures. These statistical force constants are reported as follows:

(i) Dry Air: (Lennard Jones 12-6 Potential): Non-polar molecules.

$\sigma_{aa}$=3.522Å

$(b_o)_{aa}=1.2615\sigma_{aa}^3=55.11x10^{-3}m^3$/kg-mole

$\varepsilon_{aa}/k$ = 99.2 k

(ii) Pure Water Vapour (Stockmayer 12-6-3 Potential):
Polar molecules.

$\sigma_{ww}$=2.65Å

$(b_o)_{ww}=1.2615\sigma_{aa}^3=2.48x10^{-3}m^3$/kg-mole

$\varepsilon_{ww}/k$ = 380 k

(iii) Steam-Air Mixtures (Lennard Jones 12-6 Potential):
Polar/non-polar molecules in a binary mixture.

$\sigma_{aw}$=3.053Å

$(b_o)_{aw}=35.90x10^{-3}m^3$/kg-mole

$\varepsilon_{aw}/k$ = 220.5 k

For the above force constants to be valid in eqn.13, use of eqn.6 results in the equalities:

$A_{aa} = -B_{aa} = -(b_0)_{aa}B^*_{aa}$
$A_{aw} = -B_{aw} = -(b_0)_{aw}B^*_{aw}$

$A_{ww} = -B_{ww} = -(b_0)_{ww}B^*_{ww}$

where B* is the reduced second virial interaction coefficient in the volume series (eqn.2). Tables exist to relate B* to the reduced temperature (T*) for non-polar substances (Bird and Spotz [10]) and for polar molecules (Rowlinson[11]). Hence, for any selected absolute temperature (T), T.* can be evaluated and hence B*. It follows that $A_{aa}$, $A_{ww}$ and $A_{aw}$ are determinate. The first two of these parameters differ only slightly from the data of Table 1. The third, which is the interaction second virial coefficient, is tabulated in Table 2. These calculated theoretical results differ significantly from the experimental extrapolations due to Goff *[2]*.This difference is of the order 50% above Goff’s data for the temperature range covered. However, when used in eqn. 13 the effect on the compressibility factor is not very significant. This is illustrated in Fig. 1 where both $z_{aa}$ and $z_{ss}$ are plotted for saturation temperature of up to 70 $^0$C at a total pressure of 1100 mb.

Table 1: Virial Coefficients for Dry Air and Pure Water Substance from Three Sources

| $t(^0c)$ | $A_{aa} X 10^3$ ($m^3$/ kg - mole) | | $A_{ww} X 10^3$ ($m^3$/ kg - mole) | | $A_{ww} X 10^3$ ($m^3$/ kg mole Atmos ) | |
|---|---|---|---|---|---|---|
| | Goff[2] | Hilsenrath[1] | Goff[2] | Keyes[3] | Goff[2] | Keyes[3] |
| -30 | 21.6 | 21.360 | - | - | - | - |
| -10 | 15.7 | 15.755 | 2300 | - | - | - |
| 0 | 13.2 | 13.275 | 1830 | 1854.4 | - | 4130.4 |
| 10 | 10.9 | 10.988 | 1510 | 1519.5 | - | 2095.6 |
| 20 | 8.81 | 8.879 | 1260 | 1266.0 | - | 1131.9 |
| 30 | 6.87 | 6.932 | 1074 | 1070.5 | - | 641.3 |
| 40 | 5.09 | 5.130 | 924 | 916.8 | - | 379.0 |
| 50 | 3.44 | 3.457 | 803 | 794.1 | - | 233.2 |
| 60 | 1.91 | 1.897 | 705 | 694.9 | 110 | 146.5 |
| 70 | 0.49 | 0.435 | 625 | 613.3 | 72 | 96.7 |
| 80 | -0.84 | -0.946 | 558 | 545.7 | 48 | 65.44 |
| 90 | -2.07 | -2.261 | 501 | 489.0 | 33 | 45.26 |
| 100 | - | -33.528 | - | 441.0 | - | 32.01 |

Table 2: Interation Second Virial Coefficients for Moist air

| $t(^0c)$ | | -30 | 10 | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $A_{aw}$ x $10^3$ ($m^3$/kg mole) | (a)Goff | 51.8 | 45.0 | 42.0 | 39.3 | 36.8 | 34.5 | 32.3 | 30.4 | 28.5 | 26.8 | 25.2 | 23.7 | |
| | (b)Theoretical | 73.31 | 66.57 | 62.65 | 58.19 | 54.44 | 51.15 | 47.93 | 45.16 | 42.49 | 40.02 | 37..67 | 35.62 | 33.55 |
| | (b/a) | 1.415 | 1.479 | 1.492 | 1.481 | 1.479 | 1.483 | 1.483 | 1.486 | 1.491 | 1.493 | 1.495 | 1.503 | |

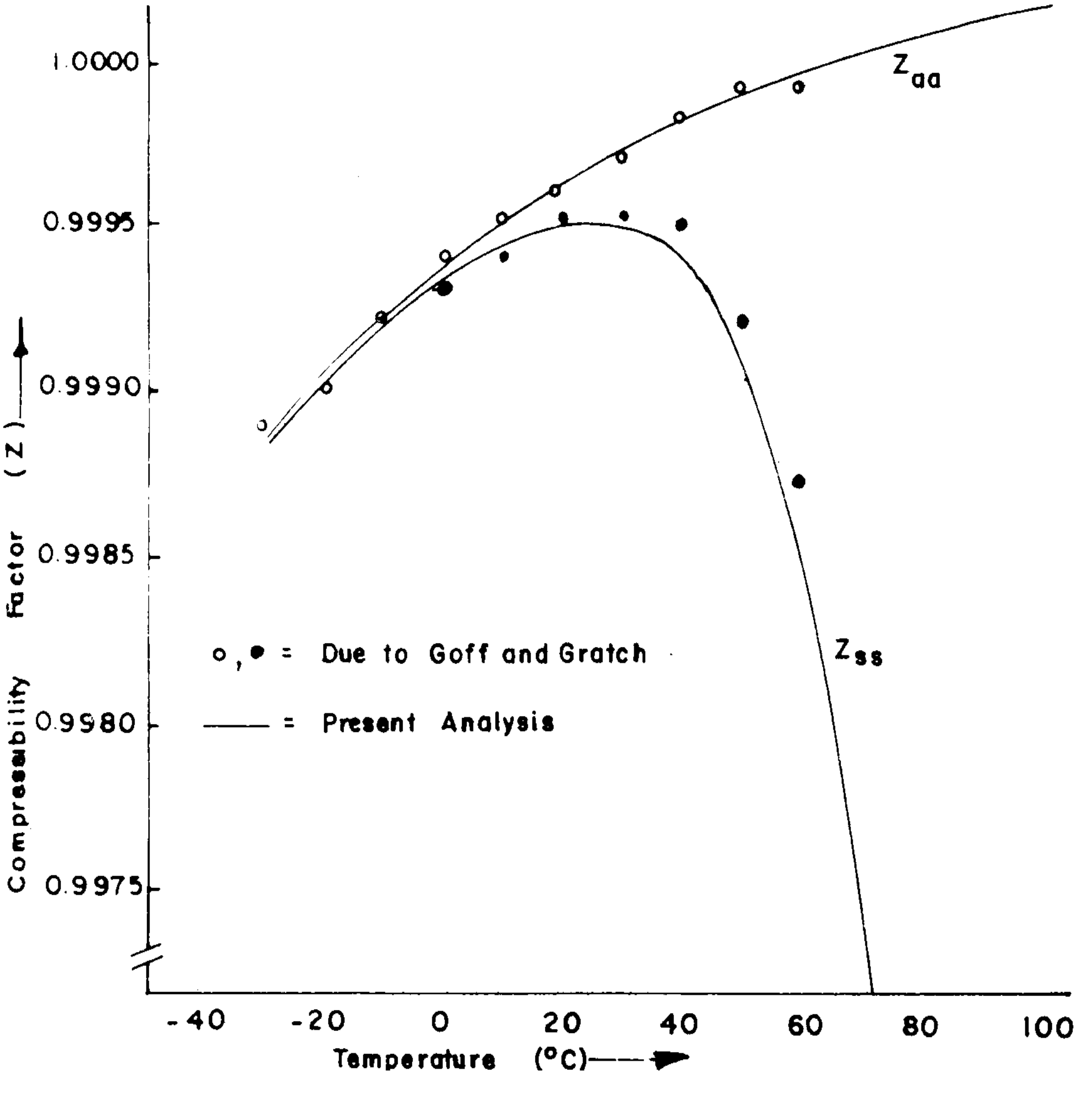

Fig.1 compressibility factors of dry air ($Z_{aa}$) and saturated air ($Z_{aa}$) at 1100mb total pressure

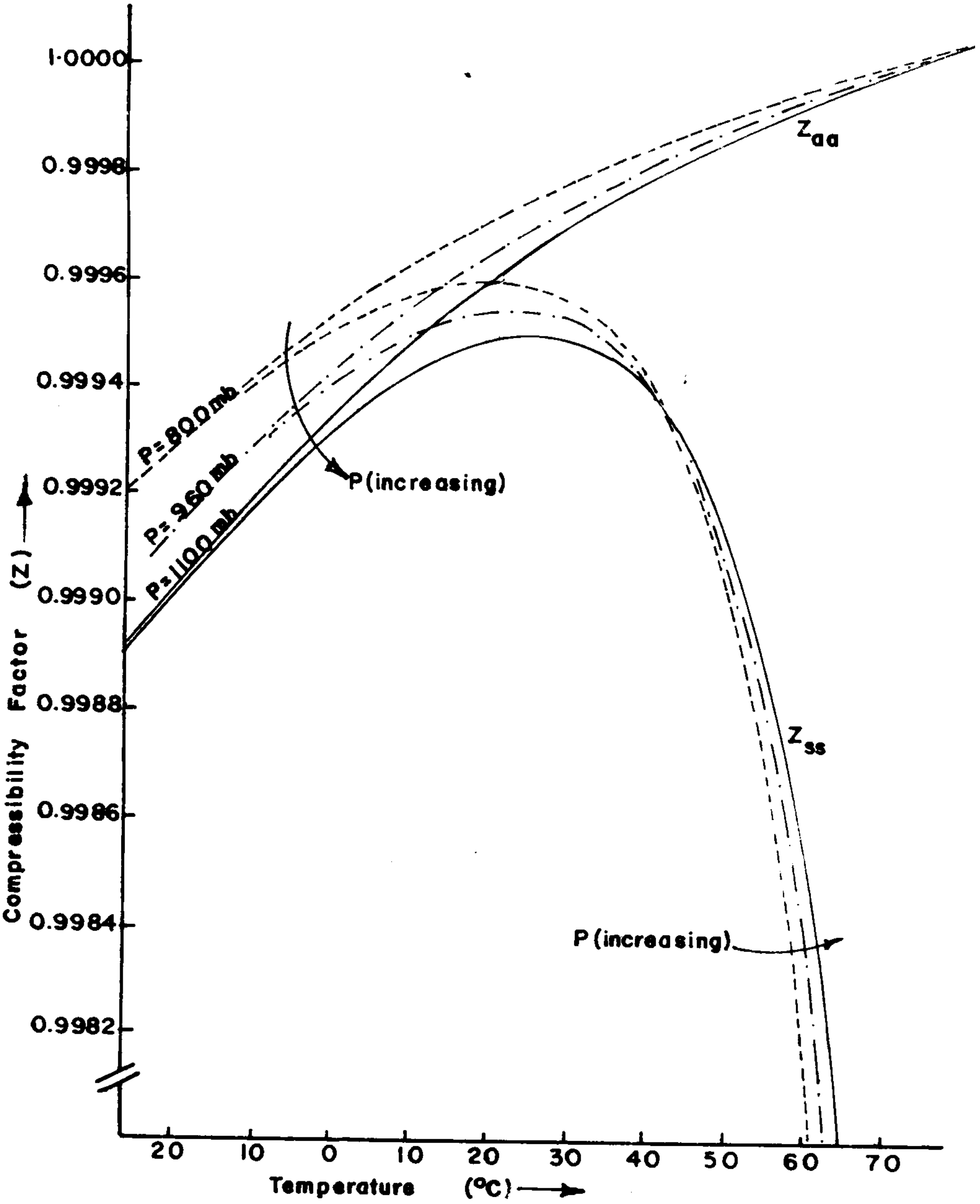

Fig 2. Compressibility factors for dry air ($z_{aa}$) and for normal air at saturation ($Z_{ss}$)

### 3.3 Compressibility Factors

Indications so far are that the derived compressibility factors will not differ significantly (in the case of dry air alone) from other reported data. This is illustrated in Table 3 for dry air at one atmosphere pressure. The same trend was shown in Fig.1 for 1100 mb pressure. Table 4 gives derived results for changing barometric pressures while fig.2 gives a general trend within the temperature and pressure limits of normal air psychromery. When Table 4 is compared with Goff and Gratch's tabulation [16] for Z ,it would be observed that some minor differences occur at the fourth decimal point. These are due to the idealized interaction coefficients adapted in the current analysis.

However, the vital significance of the present study is that both $Z_{aa}$ and $Z_{ss}$ are calculated to an order of magnitude that gives meaning to their differences and thus permits use of eqns.25-29.

### 3.4 The Partial Pressure Multiplier ($f_{SS}$)

The values of $z_{aa}$ (dry air) and $z_{ss}$ (vapour-saturated air) derived are now utilized in eqns.33 and 34 to obtain both the saturation mole-fraction $X_{ss}$ and the multiplier $f_{ss}$ also at saturation. The results are presented graphically in figs. 3 and 4.

In fig.3, a comparison is made between the derived results at 1100 mb total pressure and the tabulations of Webster [14], Harrison *[12]* and Goff and Gratch *[5]* at the same pressure. Variation X is obtained using the theoretical interaction force constants with coefficients as tabulated in Table 2(b). Curve Y is a result of using Goff's interaction coefficients (Table 2(a) in the establishment of Z.

Differences exhibited in these drawings are not nearly as significant as they look. Within the range of normal air psychometric (-10$^0$C to 60°C) the factor $f_{ss}$ has reported values between 1.0025 and 1.0065. The effect on the specific humidity (Table 5) can be shown to cause differences of less than 0.570. In particular, Goff and Gratch values and the theoretical values lead to specific humidity differences less than 0.1070 at saturation.

Table 3: Comparison of Z values obtained from the present work to those Tabulated by Hilsenrath[1] at one atmosphere pressure

| T (k) | $Z_{aa}$ (Hilesenrath) | $Z_{aa}$ (present) | t $^0$c |
|---|---|---|---|
| 260 | 0.99923 | 0.999254 | |
| 270 | 0.99937 | 0.999411 | -10 |
| 280 | 0.99949 | 0.999531 | 0 |
| 290 | 0.99960 | 0.999634 | 10 |
| 300 | 0.99970 | 0.999724 | 20 |
| 310 | 0.99978 | 0.999802 | 30 |
| 320 | 0.99985 | 0.999870 | 40 |
| 330 | 0.99991 | 0.999930 | 50 |
| 340 | 0.99997 | | 60s |

Table 4. Derived Compressibility Factors of Water-Saturated Air and Dry Air at Dew Point Temperature

| $T_{dp}$ $^0$C | P = 800 mb | | P - 840 mb | |
|---|---|---|---|---|
| | $Z_{ss}$ | $Z_{aa}$ | $Z_{ss}$ | $Z_{aa}$ |
| -10 | 0.999413 | 0.999426 | 0.999384 | 0.999397 |
| 0 | 0.999505 | 0.999535 | 0.999482 | 0.999512 |
| 10 | 0.999569 | 0.999630 | 0.999551 | 0.999611 |
| 20 | 0.999590 | 0.999711 | 0.999551 | 0.999696 |
| 30 | 0.999542 | 0.999782 | 0.999535 | 0.999771 |
| 40 | 0.999373 | 0.999844 | 0.999376 | 0.999836 |
| 50 | 0.998980 | 0.999898 | 0.999000 | 0.999893 |
| 60 | 0.998180 | 0.999945 | 0.998228 | 0.999942 |
| | P = 880 mb | | P = 920 mb | |
| -10 | 0.999356 | 0.999368 | 0.999327 | 0.999340 |
| 0 | 0.999459 | 0.999489 | 0.999435 | 0.999465 |
| 10 | 0.999533 | 0.999593 | 0.999515 | 0.999574 |
| 20 | 0.999564 | 0.999682 | 0.999550 | 0.999668 |
| 30 | 0.999528 | 0.999.760 | 0.999521 | 0.999749 |
| 40 | 0.999377 | 0.999828 | 0.999382 | 0.999820 |
| 50 | 0.999017 | 0.999887 | 0.999023 | 0.999882 |
| 60 | 0.99)8276 | 0.999939 | 0.999320 | 0.999937 |

Table 4 (contd.)

| $T_{dp}{}^0C$ | P = 960 mb | | P =1000 mb | |
|---|---|---|---|---|
| | $z_{ss}$ | $z_{aa}$ | $z_{ss}$ | $z_{aa}$ |
| 10 | 0.9992 | 0.99311 | 0.999270 | 0.999283 |
| 0 | 0.999412 | 0.999442 | 0.999389 | 0.999419 |
| 10 | 0.999496 | 0.999556 | 0.999478 | 0.999537 |
| 20 | 0.999537 | 0.999653 | 0.999524 | 0.999639 |
| 30 | 0.999513 | 0.999738 | 0.999505 | 0.999728 |
| 40 | 0.999379 | 0.999812 | 0.999379 | 0.999805 |
| 50 | 0.999047 | 0.999877 | 0.999059 | 0.999872 |
| 60 | 0.999934 | 0.999934 | 0.999396 | 0.999931 |
| | P = 1013. 25 mb | | P =1040 mb | |
| -10 | 0.999260 | 0.999254 | 0.999241 | 0.999254 |
| 0 | 0.999382 | 0.999411 | 0.999366 | 0.999396 |
| 10 | 0.999472 | 0.999531 | 0.999460 | 0.999519 |
| 20 | 0.999519 | 0.999634 | 0.999510 | 0.999624 |
| 30 | 0.999502 | 0.999724 | 0.999498 | 0.999717 |
| 40 | 0.999378 | 0.999802 | 0.999378 | 0.999797 |
| 50 | 0.999063 | 0.999870 | 0.999070 | 0.999867 |
| 60 | 0.998408 | 0.999930 | 0.999430 | 0.999928 |

| $t_{dp}$ | P = 1100 mb | |
|---|---|---|
| | $Z_{aw}$ | $Z_{aa}$ |
| -30 | 0.998836 | 0.998838 |
| -10 | 0.999196 | 0.999208 |
| 0 | 0.999328 | 0.999357 |
| 10 | 0.999429 | 0.999487 |
| 20 | 0.999487 | 0.999599 |
| 30 | 0.999482 | 0.999698 |
| 40 | 0.999380 | 0.999783 |
| 50 | 0.999090 | 0.999859 |
| 60 | 0.998486 | 0.999925 |
| 70 | 0.999346 | 0.999983 |
| 80 | 0.995265 | 1.000035 |
| 90 | 0.991639 | 1.000082 |
| 100 | 0.985568 | 1.000125 |

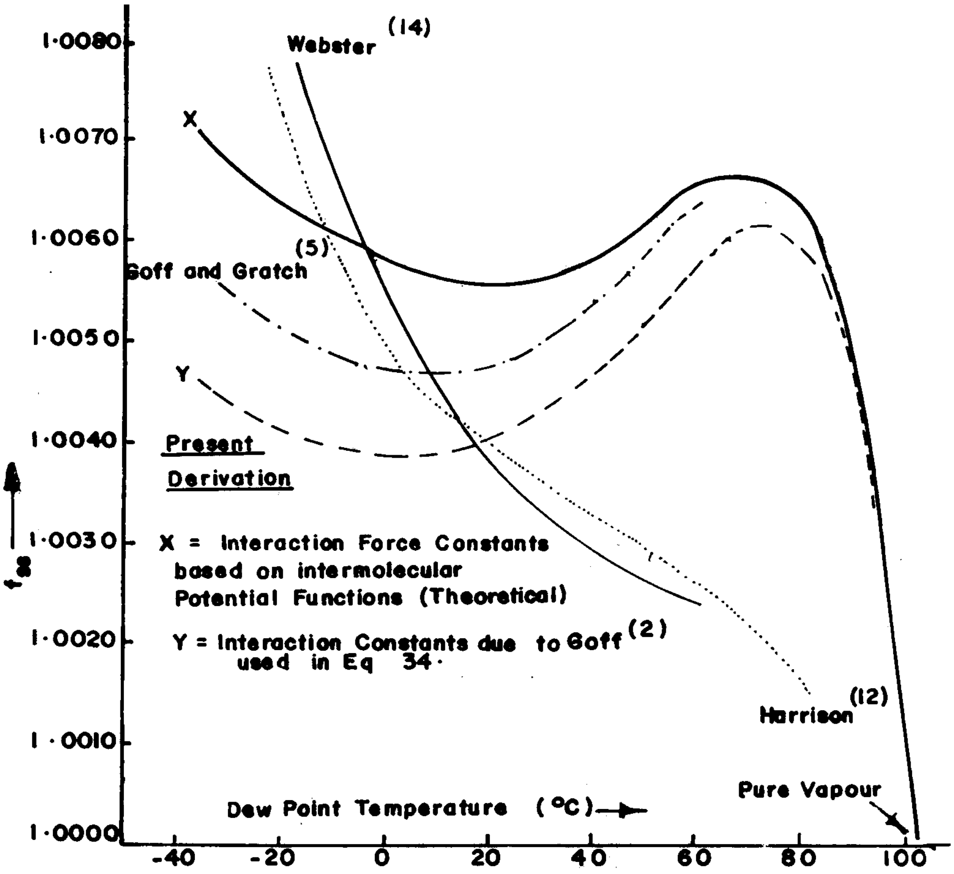

Fig. 3: comparisons of the reported values of the functions $f_{ss}$ with theoretical derivations at 110mb total pressure

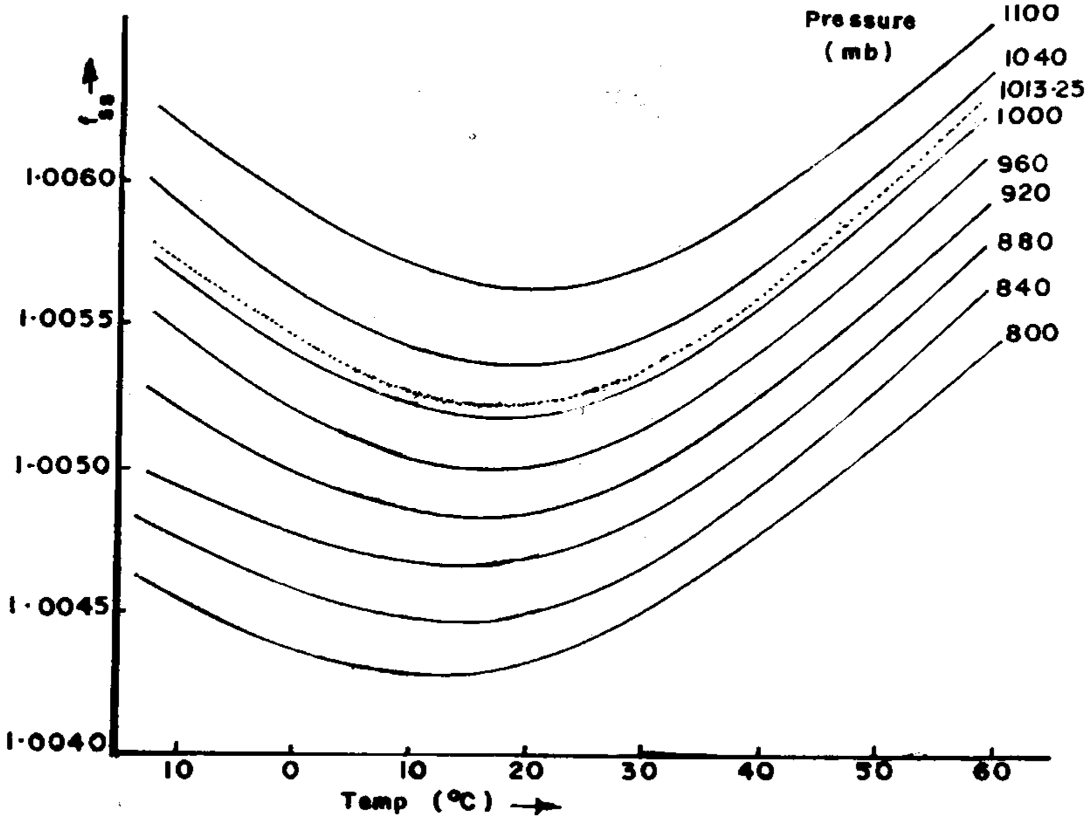

Fig. 4 .the factor $f_{ss}$ as function of P and T

We note also that the data due to Goff and Gratch cannot be extrapolated without grave loss of accuracy. It would be obvious that as the vapour pressure approaches the total pressure, $f_{ss}$ would tend to unity. This is represented by eqn.26 when $x_a$ tends to zero. At a saturation temperature corresponding to the total pressure, steam would exist as a single-component mixture and $f_{ss}$=1.0000. For the 1100 mb total pressure, fg.3 gives the corresponding temperature as 102$^0$C which is a graphical approximation of 102.32$^0$C reported in the 1970 UK Steam Tables.

Table 5 also indicates that an assumption of the _Gibbs-Dalton Law ($f_{ss}$ = 1.0000) under-estimates the mole fraction and thus the specific humidity at all temperatures with the inherent differences increasing with temperature. The same trend is obtained with decreasing total pressures for a fixed temperature.

## 4. CONCLUDING REMARKS

This paper suggests a new formulation for partial pressure multipliers in air-water mixtures of the atmosphere. This multiplier is derived in a form that is explicit in terms of such measurable parameters, as partial pressures and compressibility factors of dry air and of moist air. The simplicity lies in the fact that virial and interaction coefficients need not be known if these compressibility factors can be measured to a high degree of accuracy. The theoretical approach adapted for the second virial interaction coefficients can be seen as an idealized technique in the absence of highly accurate experimental data.

The final results do not differ significantly from those derived with the complicated formulations of Goff and Gratch. These results indicate that equally acceptable values can follow from a simpler analysis.

Table 5:Specific Humidity at Saturation Using Partial Pressure Multipliers from 4 sources (1100 mb Total Pressure)

| t(°C) | $W_{ss} = (621.97)\ f_{ss}P_{ss} / (p - f_{ss}\,p_{ss})$ g/kg air | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | -10 | 0 | 10 | 20 | 30 | 40 | 50 | 60 |
| Webster's | 1.482 | 3.492 | 7.048 | 13.55 | 25.03 | 44.84 | 78.79 | 138.0 |
| Harrison | 1.481 | 3.490 | 7.047 | 13.55 | 25.04 | 44.86 | 78.82 | 138.0 |
| Goff and Gratch | 1.479 | 3.489 | 7.049 | 13.57 | 25.08 | 44.96 | 79.04 | 138.6 |
| Theoretical (Present) | 1.481 | 3.493 | 7.056 | 13.58 | 25.09 | 44.98 | 79.10 | 138.6 |
| Ideal Gases (f =1.000) | 1.472 | 3.472 | 7.016 | 13.50 | 24.94 | 44.70 | 78.55 | 137.5 |

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