A New Definition of the Virtual Temperature, Valid for the Atmosphere and the CO_2-Rich Air of the Vadose Zone

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(Manuscript received 15 April 2010, in final form 24 May 2010)

ABSTRACT

In speleological environments, partial pressures of carbon dioxide (CO_2) are often large enough to affect overall air density. Excluding this gas when defining the gas constant for air, a new definition is proposed for the virtual temperature T_v that remains valid for the atmosphere in general but furthermore serves to examine the buoyancy of CO_2-rich air in caves and other subterranean airspaces.

1. Introduction

In recent years, boundary layer meteorology has broadened to explore surface–atmosphere interactions involving exchanges with caves and other airspaces of the vadose zone (Kowalski et al. 2008; Milanolo and Gabrovšek 2009). The accumulation and subsequent ventilation of large quantities of carbon dioxide (CO_2) in such environments implies a potentially significant yet previously overlooked role for them in the global carbon cycle (Serrano-Ortiz et al. 2010), whose characterization remains a Kyoto-motivated challenge. Gas exchange in the vadose zone can come about via convection (Weisbrod et al. 2009), which is sometimes invoked to suggest a dependence of cave ventilation on the temperature difference with the external atmosphere (Fernandez-Cortes et al. 2009; Kowalczk and Froelich 2010; Liñán et al. 2008).

However, differences in air density at a given pressure level (altitude) are determined not only by temperature but also by air composition. In the troposphere, the only gas whose surface exchange and fluctuating partial pressure appreciably affect air density is water vapor, which varies from near 0% (volumetric) in cold environments to 4% in the tropics, and locally in the presence of evaporation. Thus, meteorologists employ a traditional definition of the virtual temperature (T_v) to account for air density variations associated with the molecular weight of water vapor (Guldberg and Hohn 1876; Wallace and Hobbs 2006). By contrast, in speleological environments volumetric fractions of CO_2 have been often observed to exceed a few percent (Ek and Gewelt 1985), a fact which highlights the need for an expanded definition of T_v for the purpose of studying air buoyancy in such spaces.

We propose a redefinition of T_v to accommodate such CO_2-rich air without compromising its validity for use in the atmosphere in general, including comparison with the traditional definition of T_v.

2. Analyses and approximations

In the following development, subscripts are used to identify individual gases including water vapor (v) and CO_2 (c), as well as gas mixtures defined by the mixture of nitrogen, oxygen, and argon (noa), "dry air" (d), and the overall mixture of moist air including CO_2 (mc).

The fundamental change proposed here is to substitute the mixture of nitrogen, oxygen, and argon for the traditional dry air, both in defining the nonvariable gas constant and also in the denominators defining the mixing ratios for water vapor (r_v) and carbon dioxide (r_c). Such a substitution modifies tropospheric values of r_v and r_c by less than 0.06% relative to the traditional definitions, according to the current mass fraction of CO_2 in such air.

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DOI: 10.1175/2010JAMC2534.1

The gas constant for the mixture mc shows variable behavior according to the mass M contributed by each constituent, weighting that constituent's gas constant:

$$R_{\mathrm{mc}} = \frac{M_{\mathrm{noa}} R_{\mathrm{noa}} + M_v R_v + M_c R_c}{M_{\mathrm{noa}} + M_v + M_c}. \tag{1}$$

This is the constant that must be used when expressing the gas law $p = \rho R_{\mathrm{mc}} T$ for the moist, CO_2-laden air of a subterranean airspace. Dividing both numerator and denominator of Eq. (1) by M_{noa} leaves

$$R_{\mathrm{mc}} = \frac{R_{\mathrm{noa}} + r_v R_v + r_c R_c}{1 + r_v + r_c}. \tag{2}$$

Generally this can be expressed as

$$R_{\mathrm{mc}} = R_{\mathrm{noa}} \left[\frac{1 + \sum_{i=1}^{N} (r_i/\varepsilon_i)}{1 + \sum_{i=1}^{N} r_i} \right], \tag{3}$$

which can be expanded to consider other gases for other applications. Equation (2) can be manipulated by multiplying both numerator and denominator by the factor $(1 - r_v - r_c)$ to yield an expression that is complex but suitable for approximation:

$$R_{\mathrm{mc}} = \frac{R_{\mathrm{noa}} - r_v R_{\mathrm{noa}} - r_c R_{\mathrm{noa}} + r_v R_v - r_v^2 R_v - r_v r_c R_v + r_c R_c - r_v r_c R_c - r_c^2 R_c}{1 - r_v^2 - 2 r_v r_c - r_c^2}. \tag{4}$$

The denominator of Eq. (4) can be approximated as unity when recognizing that every second-order term is several orders of magnitude smaller. Similarly, second-order terms may be safely neglected in the numerator, simplifying to the following approximation:

$$R_{\mathrm{mc}} = R_{\mathrm{noa}} - r_v R_{\mathrm{noa}} - r_c R_{\mathrm{noa}} + r_v R_v + r_c R_c. \tag{5}$$

Substituting the gas constants for the noa mixture (287.0 J K^{-1} kg^{-1}; practically identical to that of dry air), water vapor (461.5 J K^{-1} kg^{-1}), and CO_2 (188.9 J K^{-1} kg^{-1}) into Eq. (5) allows an approximate definition of the (variable) gas constant for the moist, CO_2-laden mixture as

$$R_{\mathrm{mc}} = R_{\mathrm{noa}}(1 + 0.6079 r_v - 0.3419 r_c). \tag{6}$$

Finally, in the context of the gas law, shifting the variability caused by constituent fluctuations from the gas constant to the virtual temperature results in the following new definition:

$$T_v = T(1 + 0.6079 r_v - 0.3419 r_c). \tag{7}$$

This is the temperature that a mixture of nitrogen, oxygen, and argon would need in order to equal the density of the mixture of moist air including CO_2; it allows us to compare the densities of any (cave or atmospheric) air at equal pressures. Furthermore, this version of T_v can be used to compute the density of cave air from pressure using the gas law $p = \rho R_{\mathrm{noa}} T_v$ (with $R_{\mathrm{noa}} = 287.0$ J K^{-1} kg^{-1}) and compared with the traditional T_v for atmospheric air.

3. Implications and validity

The ramifications of the proposed change in definition depend directly on the CO_2 mixing ratio. In the troposphere, this is currently around 0.587 g kg^{-1}, equivalent to 387 ppm, or 0.0387% volumetric (fractional CO_2 content is expressed hereinafter in volumetric terms to correspond to the data typically reported in both speleological and atmospheric literature). For such low atmospheric CO_2 fractions the difference between the traditional definition of T_v and that defined in Eq. (7) is generally less than 0.1°C. However, high levels of CO_2 in cave atmospheres can lead to situations where using the inappropriate definition of T_v (or simply the temperature) can lead to erroneous conclusions regarding buoyancy and the onset of convective processes.

A preliminary climatology of vadose-zone CO_2 volumetric fractions (Ek and Gewelt 1985) indicated that while caves in subpolar and cold-temperate boreal zones rarely exceed double the atmospheric concentration (well below 0.1%), much larger values can be found in cool–temperate zones inside caves (approaching 1%), and particularly in fissures, sometimes exceeding 6% (Denis et al. 2005). More modest values have been reported in continental and subcontinental caves, but indications from warmer climates suggest that CO_2 volumetric fractions in excess of 5% can be reached, particularly in poorly ventilated fissures (Benavente et al. 2010). For such extreme cases the virtual temperature can differ from the air temperature by many degrees, and the former must be used to draw accurate conclusions about comparative density.

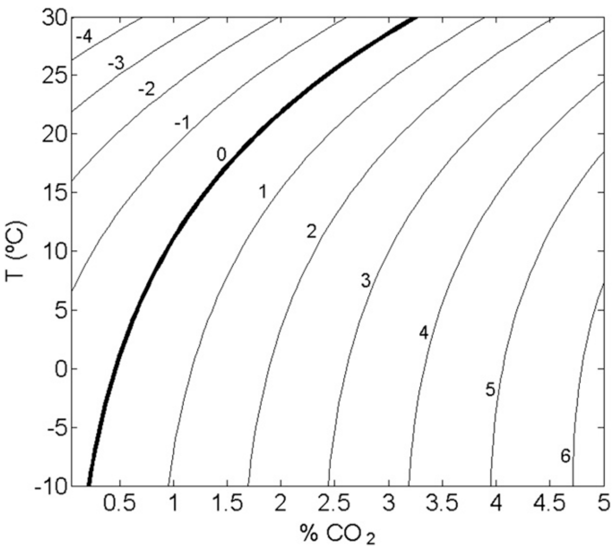

FIG. 1. The virtual temperature depression ($T - T_v$) as a function of both the volumetric CO_2 concentration (1% is equivalent to 10 000 ppm) and the temperature (T) for a subterranean environment with 100% relative humidity.

Figure 1 shows T_v, determined exactly from the gas law and Eq. (2), for a typical range of conditions in the terrestrial vadose zone, always assuming saturated humidity as is typical for cave atmospheres. The errors committed when approximating T_v using Eq. (7) have been evaluated explicitly for the range of gas concentrations typically found in terrestrial caves and found to be less than 0.1% (~0.3 K) over the full scale of Fig. 1. At larger CO_2 fractions, however, the inadequacy of Eq. (5) increases rapidly, leading to errors exceeding 1 K not far above 6% CO_2, such that Eq. (2) must be used for the estimation of air density in fissures very rich in CO_2. To cite one example, for the Shaft of the Dead Man in the French Lascaux cave in late January 2001 with 6% CO_2 (Denis et al. 2005), T_v is 6.9°C lower than the cave air temperature (14°C), explaining the stagnancy of this airspace exceeding the CO_2 limits for human safety (Hoyos et al. 1998).

We propose defining T_v as in Eq. (7) for caves and other situations with volumetric CO_2 fractions ranging from a few tenths of a percent, up to 5%.

Acknowledgments. This work was supported by the Andalusian regional government project GEOCARBO (P08-RNM-3721), by the Spanish National Institute for Agronomic Research (INIA, SUM2006-00010), and also by the European Commission project GHG Europe (FP7-ENV-2009-1).

APPENDIX

List of Symbols

Variables (units)

M_i	Mass of constituent i (kg)
p	Pressure (Pa)
ρ	Density (kg m^{-3})
R_i	Particular gas constant for constituent i (J K^{-1} kg^{-3})
r_i	Mixing ratio for constituent i (dimensionless)
T	Temperature (K)
T_v	Virtual temperature (K)
ε_i	Ratio of the molecular mass of constituent i to that of the gas mixture

Subscripts/gases

c	Carbon dioxide (CO_2)
d	Dry air
mc	Mixture of moist air including CO_2
noa	Mixture of nitrogen (N_2), oxygen (O_2), and argon (Ar)
v	Water vapor (H_2O)

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