

# Water in the Atmosphere

Joel M. Kauffman

Department of Chemistry & Biochemistry, University of the Sciences in Philadelphia, Philadelphia, PA 19104; kauffman@hslc.org

## Concentration of Water in the Atmosphere

Omission of the concentration of the third greatest constituent of the Earth's atmosphere in texts is misleading for students, and unjustified by scientific ethics. Nevertheless, examination of eight college-level general chemistry texts (1–8) reveals that none gave a mean value for the concentration of water. This omission is all the more inexplicable because the concentrations are given of minor constituents such as xenon and hydrogen sulfide down to < 1 part per billion. The reason usually given for presenting the composition of *dry* air is that water content can vary greatly in concentration both in space and time, which is true, but that is not an adequate reason to omit its mean concentration.

Masterton et al. gave a range of the mole fraction of water vapor as 0.0005 in polar regions to 0.06 in the tropics, but no mean value (5). Oxtoby et al. gave a fraction by volume of 0–0.07, but no mean value (4). Timberlake gives the partial pressure of the four most prevalent gases in air on a typical day, presumably at sea level, giving (in his Table 8.7) 5.7 mm Hg for water vapor and 0.3 for carbon dioxide; but the sum of the two is said to be 1% (6). This is misleading because the partial pressure of carbon dioxide does not change inversely with that of water vapor.

Besides being of scientific interest, “The amount of water vapor in the air varies seasonally and geographically and is a factor of large importance where air in stoichiometric quantities is required for reaction processes [including combustion], or where water vapor must be removed in [chemical processing,] air-conditioning and compressed-air systems” (9). The mean water vapor content of the troposphere in the populous latitudes of the Earth is about 1.5% (9). This corresponds to a relative humidity of ~60% at 20 °C. Adding liquid and solid water in the atmosphere probably brings the total water content to about 2%.

## Water as a Greenhouse Gas

Perhaps because omission of water as an important component of the atmosphere led to self-deception, the authors of five of the texts omit or marginalize the importance of water as a greenhouse gas (2–4, 6, 7). However, Brown et al. correctly described the effect of water vapor on diurnal atmospheric temperatures and gave an excellent example explaining desert temperature ranges (1). Masterton et al. gave an excellent description of water vapor as the dominant greenhouse gas, used desert temperature ranges as an example also, but credits clouds alone for maintaining higher temperatures at night (5). McMurry et al. correctly cited water vapor, carbon dioxide, and methane, in that order, as the important greenhouse gases (8).

To resolve the discrepancies, the infrared spectrum of air was measured by the author on June 28, 1999, near sea level at 40° N lat. An aluminum gas cell of 7-cm path length

equipped with *new* potassium bromide windows was flushed with argon and placed in a Perkin-Elmer Spectrum 1000 FT-IR, which was operated in absorbance mode. The automatic baseline program was actuated to give a baseline flat to within  $\pm 0.002$  absorbance units. Outdoor air at 28 °C and 76% relative humidity (RH) was sucked into the cell, and its spectrum was determined (Figure 1). The peaks due to each component were identified by comparison with Sadtler Standard Spectra. The areas of the peaks for water vapor and for carbon dioxide were determined repeatedly with a planimeter until reproducible values were obtained. The water vapor was responsible for 92% of the absorption and carbon dioxide for the remaining 8%; no methane was detected.

Therefore, the pie chart given by Chang of the contribution made by the common greenhouse gases in which water does not appear at all seems to ignore the facts (5). Oxtoby et al. wrote, “[of]...water *vapor* in the clouds...absorbing outgoing radiation with wavelengths near 20,000 nm...” (4). One would think that the effect of clouds is due to their liquid or solid water content, and that water vapor outside of clouds would absorb the most radiation. Also, while the spectrum (Figure 1) shows more intense absorptions at 6000 nm (1700  $\text{cm}^{-1}$ ) and 2700 nm (3700  $\text{cm}^{-1}$ ) than at 20,000 nm (500  $\text{cm}^{-1}$ ), the thermal emission from the Earth's surface peaks at 20,000 nm, possibly making this wavelength more important. Further on clouds, Silberberg's Figure 6A, Timberlake's Note on p 160, and Zumdahl's Figure 6.13 all showed an Earth with no clouds, and therefore no direct reflection of solar radiation from the tops of clouds, while McMurry et al. showed a picture of the Earth with typical 40% cloud cover (p 368). None of the authors mentioned direct reflection of sunlight from the tops of clouds even though common diagrams of Earth's radiation energy balance show it, and some atmospheric scientists think that the global climate models commonly used overestimate the quantity of greenhouse warming by up to

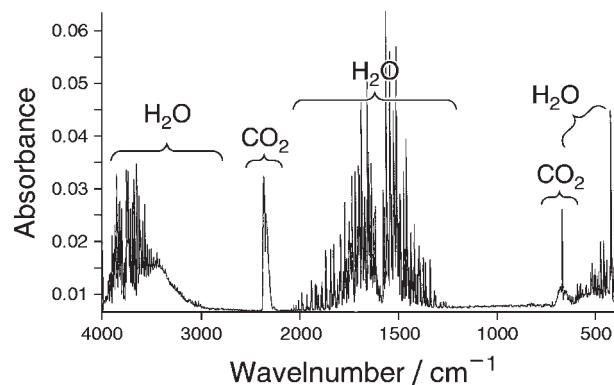


Figure 1. Infrared spectrum of air at 760 torr, 76% RH, 28 °C, with the absorption bands due to carbon dioxide and water identified. See text for experimental details.

50% because of the inadequate treatment of the optical properties of clouds (10, 11). The cooling effect of clouds is produced by direct reflection of sunlight. This opposition to the warming effect of water vapor is not mentioned by most of the authors, but attempts to quantify both are in the literature, along with the realization that the cooling effects almost nullify the warming effects, depending on location (11).

Zumdahl (3) and Chang (7) wrote that the concentration of water vapor has not changed. Actually there is evidence to the contrary from the observation that nearly all of the slight warming observed in the 20th century occurred at night in winter at higher latitudes in the northern hemisphere. This could be a result of higher levels of water vapor stemming from irrigation of desert farming areas, as well as the combustion of methane and petroleum, which produce more molecules of water vapor than of carbon dioxide (10, 12). All eight texts promoted the use of hydrogen as a fuel, ignoring the fact that the water vapor formed is an important greenhouse gas, as well as the fact that most current sources of hydrogen production, being from fossil fuels, involve carbon dioxide emissions as well.

None of the authors acknowledged that the best correlation of global temperatures is with variations in solar output, not with atmospheric composition. When urban heat island effects are ignored, the slight warming of about 0.8 °C observed mostly in the first half of the 20th century is not correlated with the great increase in carbon dioxide concentration in the second half of the century (10, 12, 13).

## Recommendations

The inconsistencies alone between the texts indicate that there are errors of omission and of fact on the water content of the atmosphere and on the effects of variations in it. As a minimum the mean water content of the atmosphere should be given, along with its role as the dominant greenhouse gas. The cooling effects of clouds should be incorporated into all texts in the excellent fashion of Brown et al. (1) and of Masterton and Hurley (5) along with other effects on the Earth's albedo (14).

## Acknowledgments

Editorial aid and key source materials were provided by Leslie Ann Bowman, Charles Jerry Thoman, and Catherine

Bentzley. The infrared cell was constructed and loaned by Lewis Smith, Senior Forensic Scientist, NJ State Police. The infrared spectrum was determined by Farzad Kobarfard.

## Literature Cited

1. Brown, T. L.; LeMay, H. E., Jr.; Bursten, B. E. *Chemistry: The Central Science*, 8th ed.; Prentice-Hall: Saddle River, NJ, 2000; pp 353–354, 685, 691–693, 697–698.
2. Silberberg, M. *Chemistry: The Molecular Nature of Matter and Change*; Mosby: St. Louis, MO, 1996; pp 205–206, 245–247, 949–956.
3. Zumdahl, S. S. *Chemistry*, 4th ed.; Houghton Mifflin: Boston, MA, 1997; pp 224, 268, 271–273.
4. Oxtoby, D. W.; Gillis, H. P.; Nachtrieb, N. H. *Principles of Modern Chemistry*, 4th ed.; Brooks/Cole: Florence, KY, 2002; pp 99–100, 624–626.
5. Masterton, W. L.; Hurley, C. N. *Chemistry: Principles & Reactions*; Saunders: Philadelphia, PA, 1989; pp 655–656, 663–666.
6. Timberlake, K. T. *General, Organic, and Biological Chemistry: Structures of Life*; Benjamin Cummings: San Francisco, CA, 2002; pp 160, 269.
7. Chang, R. *Chemistry*, 6th ed.; McGraw-Hill: Boston, MA, 1998; pp 694, 707–710.
8. McMurry, J.; Fay, R. C. *Chemistry*, 3rd ed.; Prentice Hall: Upper Saddle River, NJ, 2001; pp 346, 368–370, 598–599.
9. *Van Nostrand's Scientific Encyclopedia*, 8th ed.; Considine, D. M., Ed.; Van Nostrand Reinhold: New York, 1995; pp 64, 270.
10. Singer, S. F. *Hot Talk, Cold Science: Global Warming's Unfinished Debate*, Rev. 2nd ed.; The Independent Press: Oakland, CA, 1999; pp 7, 19, 28.
11. Lindzen, R. S.; Chou, M.-D.; Hou, A. Y. *Bull. Am. Meteorological Soc.* **2001**, *82*, 417–432; <http://ams.allenpress.com> (accessed May 2004).
12. Lomborg, B. *The Skeptical Environmentalist*; Cambridge University Press: Cambridge, United Kingdom, 2001; pp 277, 299.
13. Essex, C.; McKittrick, R. *Taken by Storm: The Troubled Science, Policy and Politics of Global Warming*; Key Porter Books: Toronto, Ontario, Canada, 2002; pp 55, 117191–117192.
14. Goode, P. R.; Qui, V.; Yurchyshyn, J.; Hickey, J.; Chu, M. C.; Kolbe, E.; Brown, C. T.; Koonin, S. E. *Geophys. Res. Lett.* **2001**, *28*, 1, 671–674.