

Supplemental Information #1

acpd-2006-0113

“Possible soluble gas losses”

There is a concern that a significant amount of some gases such as ammonia, and other soluble gases, are lost in the experimental set-up presented in this work. A valve was used to control and stabilize the pressure within the cell, where small amounts of water were condensed. It has been noted that only 10% or less of the water present in the sample gas is being trapped at this point. The possibility of having losses within this condensate has been eliminated in the present configuration in which the sample is always kept in the gas phase through heated gas-lines and by the replacement of this valve. Unfortunately, no chemical characterization of the condensate was done in order to quantify the losses for the results presented here. However, the following calculations suggest that the losses were minimal under the given operating conditions:

Duration of experiment (MCMA driving sequence + 2 FTPs) =	4883 s (81 min)
Distance traveled =	27.8 km
Amount of water analyzed by the FTIR spectrometer =	144.6 mg (144.6 mL)
Water trapped in the valve =	12 mL
Temperature at the valve ≈	62 °C
Amount of NH ₃ analyzed by the FTIR spectrometer =	0.1802 g

If we consider that the sample passing through the valve is in equilibrium, then the total amount of moles passing through the valve in one minute could be estimated by

$$PV = n_T RT ,$$

where:

$$\begin{aligned} P_{tot} &= 300 \text{ torr (0.4 atm)} \\ V &= 26 \text{ L} \\ R &= 0.082 \text{ L atm / mol K} \\ T &= 62 \text{ °C (335.15 K)} \end{aligned}$$

and thus

$$n_{Tot} = \frac{PV}{RT} = \frac{0.4 \text{ atm} * 26 \text{ l}}{0.082 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} * 335.15 \text{ K}} = 378.4 \text{ mmol} .$$

The solubility of ammonia can be estimated from its Henry's Law constant at 62 °C, which can be derived from the following equation (Shi et al., 1999):

$$\log H_{NH_3} = -3.22 + \frac{1396}{T}$$

$$\log H_{NH_3} = -3.22 + \frac{1396}{335.15} = 0.9452$$

$$H_{NH_3} = 8.82 \frac{L \cdot atm}{mol}$$

The inverse of the Henry's law constant, multiplied by the partial pressure of the gas above the solution is the molar solubility of the gas (Plambeck, 1995). We have no way of knowing what the partial pressure of ammonia is at this point, although we know its concentration after the valve (measured by the FTIR). Nevertheless, we can set upper limits from what is known in other studies.

For example, if we consider an emission of 34 mg/km of NH₃ as reported by Durbin, 2001, we could calculate the number of moles passing through the valve every minute and relate it to the total to get a partial pressure:

$$n_{NH_3} = \frac{0.034g}{km} \cdot \frac{27.8km}{81min} \cdot \frac{mol}{27g} = 0.686 \frac{mmol}{min}$$

$$P_{NH_3} = \frac{n_{NH_3}}{n_{Tot}} \cdot P_{tot} = 7.25 * 10^{-4} atm$$

$$SOLUBILITY = \frac{P_{NH_3}}{H_{NH_3}} = \frac{7.25 * 10^{-4} atm \cdot mol}{8.82 \cdot L \cdot atm} 0.0822 \frac{mmol}{L} = 1.40 \frac{mg}{L}$$

The amount of NH₃ trapped in 12 mL of condensate from the solubility calculated above, would be 0.02 mg which is really insignificant compared with the amount of ammonia detected in the cell after the 81 min experiment. This calculation is considering a high concentration of ammonia in the sample line obtained from a 39-vehicle fleet measured by Durbin, 2001, which is an unrealistically high upper limit for a hybrid vehicle showing much smaller emissions overall (see table 3 in the text). The low losses are thus attributed to the extremely low partial pressures of the soluble gases in the mixture.

Shi, Q., Davidovits, P., Jayne, J. T., Worsnop, D. R., and Kolb, C. E.: Uptake of Gas-Phase Ammonia. 1. Uptake by Aqueous Surfaces as a Function of pH, J. Phys. Chem. A., Vol. 103, No. 44, 8812-8823, 1999.

Plambeck, J.A.: Solutions and Solubility - Henry's Law and the Solubility of Gases. Copyright 1995. Updated November 3, 1996 jp [Intute](http://www.intute.ac.uk/sciences/reference/plambeck/chem2/p01182.htm) Science Engineering and Technology
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