

Interactive comment on “UV spectroscopic determination of the chlorine monoxide (ClO) / chlorine peroxide (ClOOCl) thermal equilibrium constant” by J. Eric Klobas and David M. Wilmouth

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This paper describes experimental measurements of the equilibrium constant (K_{eq}) for the gas phase reaction $ClO + ClO = ClOOCl$ at temperatures from 228 to 301 K. The measurements were performed by using wavelength-resolved UV spectroscopy to simultaneously determine the equilibrium ClO and ClOOCl concentrations. Great care was taken to identify the chemical species by their absorption spectra and to establish accurate absorption cross sections. The results for K_{eq} are in excellent agreement with the recent experimental measurements of Hume et al. (2015). The two stud-

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ies overlap in temperature to some extent and the present work extends the range to higher temperatures. (Both sets of data are in reasonable agreement with previous studies, which were not as precise and were also subject to interference from secondary reactions.) Together, the two studies constitute a set of internally consistent high-precision measurements of this important equilibrium constant over much of the atmospheric temperature range of interest. Thermodynamic parameters (entropy and enthalpy changes) were obtained from both a second-law and a third-law analysis of the data. The two approaches are in good agreement with each other and the thermodynamic parameters are in good agreement with literature values.

This is a highly important subject. The paper is very well written and the methods are clearly explained. The atmospheric context and relation of the new results to literature data are described exceptionally well.

A quibble with the third-law analysis carried out in this paper is that it assumes that K_{eq} is a pure exponential function, $K_{eq} = A \exp(B/T)$, while theoretical calculations predict that K_{eq} deviates slightly from a pure exponential. The approach taken in this paper differs from the third-law analysis carried out by the NASA/JPL Panel for Data Evaluation. The Panel evaluates every individual data point to determine the reaction enthalpy change at 0 K, $\Delta H_r(0)$, extracted from the measured $K_{eq}(T)$ at each temperature and then determines the average. $\Delta H_r(298)$ is then computed from the calculated reaction entropies and average $\Delta H_r(0)$. From $\Delta H_r(298)$, one can then obtain the standard enthalpy of formation, $\Delta H_f(298)$, for ClOOCl. Although more laborious, the approach followed by the panel does not assume a pure exponential function and is thought to be more accurate. From the Panel's approach, the combined data set consisting of the new data from the present paper and the older data from Hume et al. (2015) gives $\Delta H_r(298) = 130.1$ kJ/mol, which is 0.2 kJ/mol higher than the result reported in the manuscript, based on the pure exponential function.

In the abstract, it would be useful to state that the experimental errors are $\pm 1 \sigma$.

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In addition to the binned values for $K_{eq}(T)$, which are reported in Table 1, all of the individual K_{eq} measurements should be reported in Supporting Information.

In Figures 4 and 6, the error bounds are functions of temperature. It would be useful to report the functional forms and parameters for the error bounds in Supporting Information.

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