# 0-Dimensional Modelling of Thin Film Liquid Phase Chemistry with a Headspace Gas Supply

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January 14, 2016

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## 1 Introduction

Zero dimensional chemical kinetics simulations normally deal with simulating a single phase, generally liquid or gas phase. In the case where a headspace reservoir replenishes a reactant, such as in the Anton Paar PetroOxy[1], for autoxidation/fuel thermal stability tests, regular chemical kinetics simulations are thus inadequate. Given the simplifying assumption that the gas phase to liquid phase transfer is not diffusion limited, consists of a single species and that the liquid forms a thin film with a uniform distribution of the solute gas, a simple extension of a conventional solution to chemical kinetics allows for a simulation of a system which features such a headspace.

## 2 Henry's Law - Estimating Solubility

There exists a relationship between the gas pressure in a system and the amount of gas dissolved in the liquid phase, which is described by Henry's Law[2]. Henry's Law states that there exists a proportional relationship between the gas pressure $p$ and the liquid phase concentration $c$ which is described by Henry's Constant shown in Equation (1).

$$k_H = p/c \tag{1}$$

Henry's Constants are tabulated for many compounds and can be found on the web. If a test apparatus can report the headspace gas pressure, this information can thus be used for calculations as well as a comparison of the simulated system to experimental data. A caveat is that Henry's Constants are only appropriate for a finite temperature and pressure range, i.e. they would not be suitable to estimate the liquid phase concentration if the pressure or temperature changes significantly. Given that the PetroOxy tests using isothermal conditions, the temperature aspect is of little concern for the work for which the code was originally developed.

As the solver is run, it calculates the rate of change of the species concentration based on the classical Arrhenius equation as well as the species concentration. Henry's Law provides an estimate for the concentration of a dissolved gas which can therefore be adjusted prior to the rate calculation to incorporate the impact of the headspace reservoir, assuming headspace to liquid phase transfer is not diffusion limited. If the corrected current concentration is described in the liquid phase by $c_{new}$, the pressure is given by $p_{new}$, shown in Equation 2.

$$c_{new} = \frac{p_{new}}{k_H} \tag{2}$$

Using the ideal gas law, pressure in the headspace is dependent on the temperature $T$, the volume $V$, the number of moles $n$ as well as the gas constant $R$, shown in Equation 3. For the case where the test rig is a PetroOxy, the size of the dish can be measured, leading to an estimated size of $22.5 \times 10^{-6}\,\mathrm{m}^3$, where the liquid sample size is supplied by the user at the time of running the code.

$$p_{new} = n_{new}RT/V_{gas} \tag{3}$$

As numerical simulations of chemical kinetics are solved using algorithms that "step" forward, one can introduce a correction factor $c_{adjust}$ which adjusts the current concentration $c_{current}$ to the new value, $c_{new}$, shown in Equation 4.

$$c_{new} = c_{current} + c_{adjust} \tag{4}$$

As the adjustment, $c_{adjust}$ is describe as a concentration, one needs to take the volume of the sample into account to identify how many moles are dissolved during the transfer phase, shown in Equation 5

$$n_{new} = n_{curent} - c_{adjust} \times v_{sample} \tag{5}$$

One can now substitute Equation (3) into Equation (2) to obtain Equation (6).

$$c_{new} = \frac{n_{new}RT}{k_H V_{gas}} \tag{6}$$

Substituting for $n_{new}$, one obtains Equation (7).

$$c_{new} = \frac{\left(n_{curent} - c_{adjust} \times v_{sample}\right)RT}{k_H V_{gas}} \tag{7}$$

Rearranging for $c_{adjust}$, one obtains Equation (8).

$$c_{new} = \frac{\left[n_{curent} - \left(c_{new} - c_{current}\right) \times v_{sample}\right]RT}{k_H V_{gas}} \tag{8}$$

And finally rearranging for $c_{new}$, one obtains an expression that can be employed to estimate a corrected liquid phase concentration in relationship to the gas pressure in the headspace, shown in Equation 9.

$$c_{new} = \frac{\left(n_{current} + c_{current}V_{sample}\right)RT}{k_H V_{gas} + V_{sample}RT} \tag{9}$$

This formula can or is employed to adjust the concentration of the dissolved gas (such as oxygen when modelling the PetroOxy) before the reaction rates are calculated. To repeat the initial caveat, an essential assumption here is that the rate of gas consumption in the liquid is limited by the chemical reactions rates and not diffusion. It will result in very incorrect (faster) gas consumption in the case of diffusion limited reactions. Improvements on the initial algorithm may offer an opportunity for future work. In addition, in the current implementation, the volume of the test vessel is hard-coded to approximate the size of the dish in a PetroOxy, which may be inappropriate for a different test apparatus.

## 3 Where it is Implemented

At the time of writing, the implementation in the chemical kinetics solver centres around the following function:

```
void AdjustGasConcentration (
    double & GasSpeciesInLiquidConcentration ,
    double temperature ,
    double time_difference ,
    PetroOxyCalculation & PetroOxyData
)
```

# 4 Acknowledgements

# References

[1] Anton Paar GmbH, *PetroOxy Manual*, 7 2013.

[2] P. Atkins and J. de Paula, *Physical chemistry,*. W. H. Freeman and Company, eight ed., 2011.