Modelling the Thermodynamic Properties of Reactive Working Fluids for Thermodynamic Cycles

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Thermodynamic cycles represent the backbone of current thermal energy conversion systems. Thermal power plants, heat pumps and refrigeration cycles are based on thermodynamic cycles operating with either inorganic or organic, inert, working fluids. The use of those fluids is well established for both low and high temperature applications. However, the achieved efficiencies remain much lower than the ones theoretically achievable (e.g., the Carnot and Lorentz efficiencies).

A not yet fully understood way to reduce this gap is currently under investigation [1-3]. The idea, which was initially proposed in the 1950s [4], is to adopt fluids that undergo a fast reversible chemical reaction in place of inert working fluids. One well known and studied system is the fluid $N_2O_4 \rightleftharpoons 2\ NO_2 \rightleftharpoons 2\ NO + O_2$. The occurrence of a fast reversible reaction results in the simultaneous conversion of both thermal and chemical energy along the thermodynamic transformations of the reactive fluid in the cycle, which has a positive impact on cycle performance. For example, such an effect is the result of an exothermic reaction observed to take place in the turbine, providing more work, and of an endothermic reaction along the compression process, thus demanding less compression energy [1].

The current limitation to the use of those fluids is the reduced availability in nature of such systems and our study aims to overcome such a limitation. In an on-going research project [3], we are designing novel reactive fluids and a methodology allowing the ab-initio characterisation of their thermodynamic properties under chemical equilibrium, including multiple-phase and reaction equilibrium. The challenge of this methodological characterisation is the absence of experimental data and thus the need of a predictive approach. Such a methodology includes *ab initio* Quantum Mechanics calculations, force field-based Monte Carlo simulations, and equation of state modelling. In parallel to Quantum Mechanics, Machine Learning methods are applied to characterise the thermochemistry of those fluids.

This work is intended to present the developed methodology, and the resulting thermodynamic analysis of at least two designed working fluids. For comparison and validation, we will also show the results of the methodology, applied to the N_2O_4 reactive system [5-7]. The unique behavior of monovariant two-phase binary reactive systems, such as $N_2O_4 \rightleftharpoons 2\ NO_2$, will be also highlighted, making reference to their phase equilibrium diagrams. Finally, an analysis on the impact of thermochemical, thermophysical and resulting thermodynamic properties accuracy on the assessment of cycle's performance is provided.

References

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