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Calculation of the thermodynamic properties of the reactive fluid $N_2O_4 \leftrightarrow 2\ NO_2$ and its mixtures with inert gases

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Nowadays, all power plants producing electricity use inert substances (for example, CO_2 and H_2O) as working fluids in their thermodynamic cycle. That means that the molecules composing the fluid undergo only a modification of their kinetic (thermal) energy content, all along the cycle, while the molecular structure remains unaltered. In our latest research we are investigating the effect of using reactive working fluids, instead of inert ones. More specifically, the chemical reactions taking place in these *reactive* fluids consist in the reversible dissociation-association reaction of a molecule which evolves all along the thermodynamic cycle, according to the condition of thermodynamic equilibrium and to the modification of temperature and pressure in each unit operation. With this new "thermochemical cycle" we try to transform, simultaneously, the thermal and chemical energy carried by the working fluid. Preliminary calculations proved the promise of this approach [1,2]. One of such fluids is dinitrogen tetroxide N_2O_4 where the reversible reaction $N_2O_4 \leftrightarrow 2\ NO_2$ takes place. In order to assess the efficiency of a thermodynamic cycle operating with such a fluid, it is necessary to develop a thermodynamic calculation tool enabling the determination of the thermodynamic properties of these fluids, and especially when more than one phase and chemical reactions occur simultaneously. The goal of our ongoing research is to provide such a tool and we are going to present its features.

The Peng-Robinson equation of state combined with advanced mixing rules with a zero-residual excess Helmholtz energy [3] is chosen for modeling this system. To apply this model, only the properties of the critical point and the acentric factor of pure N_2O_4 and NO_2 are needed. However, it is not possible to measure the properties of the critical point of the pure N_2O_4 and NO_2. Indeed, the reaction $N_2O_4 \leftrightarrow 2\ NO_2$ being extremely fast in the two directions, this system can be considered at chemical equilibrium, meaning that its evolution with the changing in temperature and pressure is dictated by the chemical equilibrium condition and it is thus not possible to isolate N_2O_4 and NO_2 at their critical point. Critical properties and acentric factors are thus estimated by molecular Monte Carlo simulations. VLE calculations of the reactive N_2O_4-NO_2 system are then performed, solving the equations for reactional and phase equilibria, and calculated vapor pressure and densities at saturation were compared to experimental data. We have shown that the mono-variance of this reactive system in VLE conditions is the reason of the uniqueness of its critical point. The coordinates of this critical point are calculated by a modification of an algorithm proposed for non-reactive systems [4], while equilibrium calculations in the N_2O_4-NO_2-CO_2 system are performed by modified RAND method [5].

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