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<tbody>
<tr>
<td><strong>Author</strong></td>
<td>小沢, 寛恭(Ozawa, Hiroyasu)</td>
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<tr>
<td><strong>Publisher</strong></td>
<td>慶應義塾大学藤原記念工学部</td>
</tr>
<tr>
<td><strong>Publication year</strong></td>
<td>1967</td>
</tr>
<tr>
<td><strong>Jtitle</strong></td>
<td>Proceedings of the Fujihara Memorial Faculty of Engineering Keio University (慶應義塾大学藤原記念工学部研究報告). Vol.20, No.81 (1967. ) ,p.204(28)- 204(28)</td>
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<tr>
<td><strong>Abstract</strong></td>
<td>Summaries of Doctor and Master Theses</td>
</tr>
<tr>
<td><strong>Genre</strong></td>
<td>Departmental Bulletin Paper</td>
</tr>
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Study on the Thermodynamic Properties of Ordinary Water Substance near the Critical Point

Hiroyasu OZAWA*

According to the resolution taken at the meeting of IFC (International Formulation Committee), the formulation of the thermodynamic properties of ordinary water substance has been made. It describes them throughout the region that extends in the pressure from 165.35 bar to 1000 bar, in the temperature from 350°C to 650°C. The region mentioned above includes the critical point, and the thermodynamic properties in this region varies exceedingly so that the Van der Waals form of \( P = f(V, T) \) is applied fundamentally for the formulation. The formulation obtained is

\[
P = P_c + (\rho - \rho_c) \sum_{j=0}^{9} C_{0j} \rho^j + (T - T_c) \sum_{j=0}^{9} C_{1j} \rho^j + (T - T_c)^2 \sum_{j=0}^{7} C_{2j} \rho^j + (T - T_c)^3 \sum_{j=0}^{7} C_{3j} \rho^j + (T - T_c)^4 \sum_{j=0}^{7} C_{4j} \rho^j + (T - T_c)^5 \sum_{j=0}^{7} C_{5j} \rho^j + (T - T_c)^6 \sum_{j=0}^{7} C_{6j} \rho^j + (T - T_c)^7 \sum_{j=0}^{7} C_{7j} \rho^j + (T - T_c)^8 \sum_{j=0}^{7} C_{8j} \rho^j + (T - T_c)^9 \sum_{j=0}^{7} C_{9j} \rho^j
\]

The thermodynamic conditions at the critical point are to be satisfied by the above equation, and the calculated values of the derived thermodynamic properties such as Enthalpy, Entropy and Specific Heats at constant pressure and at constant volume were taken into consideration in the process to complete above formulation. After getting above original formulation, the reduced Canonical Formulation is derived theoretically by utilizing well-known thermodynamic equation of Helmholtz function (free energy). As it is described by the above equation, the value of specific volume \( v = 1/\rho \) at specified pressure and temperature is to be the solution of the equation \( P = f(V, T) \), and in order to get the proper solution \( v \), mathematically well-known Newton method was employed. At that time besides the calculation for Skeleton Table grid points, the calculation for specified points near the critical point was made to know correctly the behavior of the thermodynamic properties that varies quite largely in that region.

Getting the values of specific volume as mentioned above, some thermodynamic properties such as Adiabatic Exponent, Isothermal Exponent, Ratio of Specific Heats, Joule-Thomson Coeff. and Sonic Velocity were calculated by using them. These values of properties are calculated by each equation of the thermodynamic properties that can be derived from the original formulation.

In order to examine the formulation, the values of the differential quotients at the critical point were calculated. As results, it was found, comparing with some other references, that the formulation gives the reasonable values for thermodynamic boundary conditions at the critical point.

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