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Studies of the Thermodynamic Properties of High Temperature and High Pressure Steam

—Mainly in the Critical Region—

Koichi WATANABE*

Recent great developments in steam power generation are ought to many factors such as the rise of the steam conditions, applications of the reheating and regenerative cycles, adoptions of the so-called unit system generation etc.. Among these many factors, the rise of the temperatures and of the pressures of utilized steam is the most eminent one, and therefore the necessity to know about the thermal properties of steam at higher temperatures and under higher pressures is becoming very important. It is well known that the thermal properties of ordinary water substance can be split into two properties, namely the thermodynamic properties to which specific volume, specific enthalpy, specific entropy and specific heat etc. are belonged and the transport properties in which viscosity, thermal conductivity and thermal diffusivity etc. are included.

Among those various thermodynamic properties, a pressure—volume—temperature relation is the most fundamental and important one, because almost all other thermodynamic properties could be derived analytically with the aid of the general relationships of thermodynamics if this pressure—volume—temperature relation is known.

Thus, in this research work, the experimental works carried out for the pressure —volume—temperature relation of superheated steam and that of water substance in its critical region, and moreover the research works of formulating an equation of state of ordinary water substance to be valid also in the critical region.

For the experiments on the pressure—volume—temperature relation of steam in its superheated steam region, a new experimental apparatus was designed and constructed. This experimental apparatus is the double vessel type which is composed both of a thick-walled pressure vessel made of heat resisting steel and of a platinum piezometer with its volume approximately 240 cm^3. And a thick-walled copper cylinder is used in order to get an uniform isothermal temperature field just around the pressure vessel in which the platium piezometer is installed.

Using this apparatus, experiments were conducted for seven isotherms such as 600°C, 650°C, 700°C, 750°C, 800°C, 850°C and 900°C in the range of pressures up to 930 kg/cm^2. The accuracy of the measurements of specific volume can be estimated

*渡 部 康 一

as 0.07—0.15 % approximately depending upon the steam conditions.

Although not many investigations have ever been carried out in these ranges of high parameters, a good coincidence between the obtained results and those by V. A. Kirillin et al., also by M. P. Vukalovich et al. is recognized.

These results obtained by the author were presented at the Sixth International Conference on the Properties of Steam, held in New York in 1963, as one of the reports of Japan Commission on the Properties of Steam.

Following after the expèriments in superheated steam region, the measurements on the pressure—volume—temperature relation of water and steam in the critical region were conducted. Although it has been well understood that the thermodynamic properties of ordinary water substance change anomalously in its critical region, enough amount of experimented data with satisfactory accuracy has not been obtained by other investigators except S. L. Rivkin et al..

Thus the two series of the measurements of specific volume in the temperature range of 360—420°C including the critical isotherm of 374.15°C, and under the pressures 210—730 kg/cm² were carried out along various kinds of isochores. Used experimental apparatus is almost the same as that was used in the previous experiments for superheated steam, except the application of a precision platinum resistance thermometer instead of platinum vs. platinum—rhodium (10 %) thermocouple. The accuracy of the measurements of specific volume in this critical region can be estimated as 0.15—0.2 % approximately for most of the measured points except the states at which the steam pressure is very close to the critical pressure.

Comparing the measured data with those by the other investigators, it was found that the coincidence of the obtained results with those by S. L. Rivkin et al. is best and also found that the deviations from those by C. J. Van Nieuwenburg et al., R. Kiyama et al. are too large in wide ranges, especially in the very proximity of the critical point. Moreover, the obtained results of specific volume along 400°C isotherm were recognized as they are exactly within the limits of tolerances given in the International Skeleton Table 1963.

In order to accomplish the pending requirements to decide the values of thermodynamic properties internationally, the Sixth International Conference on the Properties of Steam, held in New York in 1963, after careful study of the data available at that time, adopted the International Skeleton Table 1963 for the range of temeratures up to 800°C and of pressures up to 1000 bar. This conference appointed a committee, called International Formulation Committee, to prepare formulae and gave it power to approve them for international use if they would give formulations which would not deviate from the Internatinal Skeleton Table 1963 values by more than the tolerances.

In order to cooperate the tasks of this International Formulation Committee to devise formulae which is suitable for the calculations by electronic computers. two equations of state of ordinary water substance which should be valid in the critical

region were devised by the author in 1964 and in 1965.

Devised equation of state in which pressure was expressed as a function both of specific volume and of temperature, was drived by the expansion of pressure in double Taylor series just around the critical point. Substituting the well-known basic conditions for the thermodynamic consistency at the critical point to this derived expanded equation, the unknown constants were determined mainly by Least Square Method using electronic computers.

From this devised equations of state which was also transformed into dimensionless canonical form, important properties such as specific volume, specific enthalpy, isobaric specific heat and isochoric specific heat were calculated. These calculated values were recognized to be quite satisfactory in a given subregion of the International Skeleton Table 1963 within the limits of tolerances. This formulation has also a great feature that it could cover the given whole subregion including the critical point only by a single formula exactly, despite other formulations proposed by Technishe Hochshule München and also by Kyoto University have two separated formulae in almost similar subregion.

This work of formulation was presented at the Second Meeting of the International Formulation Committee, held at Glasgow in 1966, as a Report of Japan Commission on the Properties of Steam.