THERMODYNAMIC AND FLUID-DYNAMIC PROPERTIES OF WATER FOR HIGH-TEMPERATURE NUCLEAR REACTORS

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Abstract

Many designs for advanced nuclear-fission reactors involve higher coolant temperatures than the current generation of water-cooled reactors. In this study, physical theories of the relevant properties of water are reviewed, and practical methods for calculating these properties are assessed. Special attention is given to thermodynamic stability, phase transitions, the critical point, supercritical behaviour, thermal conductivity and viscosity. The review and the assessment suggest the need for new practical methods for the critical-point neighbourhood and the supercritical thermodynamic states.

INTRODUCTION

Most of the nuclear-fission reactors used currently in electrical power generation are cooled by water. This coolant can be either light water (hydrogen oxide) or heavy water (deuterium oxide). These water-cooled reactors operate with a liquid-vapour mixture flowing through fuel channels in the reactor core. The thermodynamic properties of water restrict the maximum temperature of the coolant, and the thermal-hydraulic characteristics of liquid-vapour flow restrict the maximum vapour fraction of the flow. These restrictions limit the thermal efficiency of present water-cooled power reactors. A decrease in the cost of nuclear-generated electricity, and an increase in the efficiency of nuclear-fuel utilization, would result from overcoming these restrictions.

The development of the Canada Deuterium Uranium (CANDU) reactor by Atomic Energy of Canada Limited (AECL) provides an example of the development of water-cooled power reactors. The CANDU pressurized heavy-water reactor (CANDU PHWR) has operated successfully in generating stations for about forty years. The Advanced CANDU Reactor (ACR) is being designed as a successor to the CANDU PHWR. The ACR will have light-water coolant instead of the heavy-water coolant of the CANDU PHWR. Both types of reactor are designed to use an indirect thermodynamic cycle, with no turbines in the primary coolant loop, and a liquid-vapour flow in the reactor core. The temperatures and pressures in Table 1 indicate that the coolant is a subcritical liquid-vapour mixture in the CANDU PHWR and the ACR [1, 2].

The future development of the CANDU reactor, beyond the ACR, will involve major changes to the nuclear steam-supply system, in pursuit of greater thermal efficiency [3, 4]. A reactor with supercritical water (SCW) coolant is a likely successor to the ACR. A supercritical-water reactor (SCWR) would have many of the design features of the ACR, but an SCWR would use a gas flow in the reactor core [4]. A conceptual SCWR using an indirect thermodynamic cycle, with no turbines in the primary coolant loop, is given the type SCWR 1 in Table 1. A conceptual SCWR using a direct thermodynamic cycle, with turbines in the primary coolant loop, is given the type SCWR 2 in Table 1. The temperatures and pressures in Table 1 are for the conceptual designs CANDU-X Mark 1 (type SCWR 1) and CANDUal-X2 (type SCWR 2) [3]. The CANDU reactor appears to be evolving toward a high-temperature nuclear reactor.

Table 1. Temperature and pressure of the coolant at the outlet for various types of reactors.

	Outlet temperature		Outlet pressure
Type of reactor	T' (°C)	T (K)	p (MPa, abs)
CANDU PHWR [1]	310	583	10.0
ACR [2]	325	598	12
SCWR 1 [3]	430	703	25
SCWR 2 [3]	625	898	25

The future development of high-temperature nuclear reactors with water coolant will depend on new information about the substances and the processes at high temperatures and high pressures. The thermal-hydraulic phenomena in an SCWR are not understood sufficiently for reactor-core design, at the present time [5]. The existing correlations and models for heat transfer and fluid flow in SCW predict widely varying results [6]. New investigations of thermal-hydraulic phenomena with SCW will use experimental flow loops and computational flow simulations. The interpretation of experimental observations, and the validity of computational results, depend on an accurate knowledge of the thermodynamic and fluid-dynamic properties of water.

THERMODYNAMICS

Fundamental Relation

The theory of thermodynamics can be based on a set of postulates about a thermodynamic system and its fundamental relation [7]. This postulational formulation of thermodynamics is used widely, as an alternative to traditional formulations involving laws of thermodynamics [8]. The present study is based on the postulational formulation.

The primary fundamental relation of a simple thermodynamic system with one chemical component is the function $S(U, V, N)$, where S is the entropy, U is the internal energy, V is the volume, and N is the number of moles of substance. The equilibrium state of a system is determined by the entropy-maximum postulate. The entropy function can be inverted with respect to U, according to a postulate about the properties of entropy, so that a secondary fundamental relation is the function $U(S, V, N)$. A set of tertiary fundamental relations can be obtained with Legendre transformations. The tertiary relations obtained from the entropy function are the Massieu functions. The tertiary relations obtained from the internal-energy function are the thermodynamic potentials. Each of these fundamental relations is subject to an extremum principle; the entropy-maximum principle is the basic extremum principle.

The entropy function, the internal-energy function, the Massieu functions and the thermodynamic potentials contain individually the complete thermodynamic information about a system. In practice, a function is chosen because its independent variables are relevant to boundary conditions and significant properties of a system.

The entropy function and the internal-energy function are homogeneous first-order functions of their three independent variables. Thus, the molar (per mole) functions do not have N as an independent variable. Thus, the specific (per unit mass) functions do not have a third independent variable. Therefore, the specific entropy function $s(u, v)$ and the specific internal-energy function $u(s, v)$ are homogeneous zero-order functions of their two independent variables. Lower-case letters are used to denote specific (per unit mass) quantities, so $s = S / m$, $u = U / m$, $v = V / m$, and m represents the mass of a system.

Helmholtz Potential and Steam Tables

The specific Helmholtz potential f is obtained from the specific internal energy by the Legendre transformation

$$f = u - Ts \tag{1}$$

where T is the absolute temperature. The specific Helmholtz potential function $f(T, v)$ contains the complete thermodynamic information about a system. For a given T and a given v, f is calculated from the function, $-s$ and $-p$ are calculated from its respective partial derivatives, and u is calculated from equation (1). The specific enthalpy potential h is obtained from the specific internal energy by the Legendre transformation

$$h = u + pv \tag{2}$$

where p is the absolute pressure.

The thermodynamic system is a sample of water in the present study. The reader may be familiar with steam tables that contain numerical information about the thermodynamic properties of water. A well-known version of steam tables [9] was calculated from an equation for the specific Helmholtz potential f. The coefficients for this equation were determined from experimental data for measurable quantities, such as pressure and enthalpy change. This equation represents single-phase states for temperatures from 0°C to 1300°C (273.15 K to 1573 K), and for absolute pressures from 0 MPa to 100 MPa. The information in Table 2 is from the steam tables [9].

Table 2. Thermodynamic properties of water at the triple point and the critical point, from steam tables [9].

	Triple point		Critical point
Property	Liquid	Vapour	Gas
Temperature, T' (°C)	0.01		374.136
Absolute temperature, T (K)	273.16		647.286
Absolute pressure, p (MPa)	0.0006113		22.09
Specific volume, v (m^3/kg)	0.0010002	206.136	0.003155
Specific internal energy, u (kJ/kg)	0.00	2375.3	2029.6
Specific enthalpy, h (kJ/kg)	0.01	2501.4	2099.3
Specific entropy, s (kJ/(kg·K))	0.0000	9.1562	4.4298

The agreement of data from the steam tables [9] with experimental observations is generally within the uncertainty in the observations. The relative difference between a steam-table value and an experimental observation of specific volume is less than about

0.1% for temperatures less than 370°C, and it is less than about 1% for temperatures less than 800°C.

The evaluation of the general function for *f*, and functions for derived properties, is complicated and slow. Steam tables are useful for hand calculation, but using interpolation algorithms with stored steam tables can require a large amount of computer memory. As an alternative to approximating the functions for thermodynamic properties directly with steam tables, these functions can be approximated with simpler functions.

Approximate functions for light-water thermodynamic properties were determined by curve fitting to accurate, steam-table properties [10]. These functions are valid for absolute pressures from 0.085 MPa to 18 MPa, and for temperatures from 90°C to 450°C. These functions can be evaluated quickly on an electronic computer. These functions have maximum errors from about 0.1% to about 5%, depending on the thermodynamic property, and the phase (liquid or vapour). The errors are generally largest for large values of pressure and temperature.

Approximate functions for heavy-water thermodynamic properties, and their derivatives, were determined by selecting piecewise Hermite polynomials that approximated a fundamental equation for heavy water [11]. These functions are valid for absolute pressures from 0.0006601 MPa to 21.600 MPa, and for specific enthalpies from 0.0 kJ/kg to 3800 kJ/kg. The corresponding temperatures are from 0°C to 800°C. These functions can be evaluated quickly on an electronic computer. These functions give maximum errors from 0.0% to 1.4% for thermodynamic properties, and from 1.5% to 5.6% for their derivatives.

Thermodynamic Stability and Phase Transitions

The reader is familiar with the transition between the liquid phase of water and the vapour phase of water. This first-order phase transition is related closely to the thermodynamic stability of the system (a sample of water).

The specific Gibbs potential g is obtained from the specific internal energy by the Legendre transformation

$$g = u - Ts + pv \quad . \tag{3}$$

For a system with one chemical component (water), the specific Gibbs potential is proportional to the electrochemical potential; the constant of proportionality is the reciprocal of the molar mass. Thermodynamic equilibrium requires equality of the electrochemical potential of the two phases (liquid and vapour), so there is equality of the specific Gibbs potential of the two phases [7]. This equality of the function $g(T, p)$ for each phase, determines a liquid-vapour coexistence curve on a graph of p versus T. One terminus of this curve is the triple point, where the solid, liquid and vapour phases coexist. The other terminus of this curve is the critical point, where the liquid and vapour phases are indistinguishable. This curve corresponds to the "saturated" states, where the liquid and vapour phases are in equilibrium.

The function $g(T, p)$ can be determined for the van der Waals model of a fluid, and isotherms of this function can be examined on a graph of g versus p [7, 12]. Stable thermodynamic states must satisfy an appropriate extremum principle, so certain portions of an isotherm must be excluded from the graph for thermodynamic equilibrium. Thus, the function $g(T, p)$ must be modified to give an equilibrium version. This consideration of stability accounts for the difference in the values of a thermodynamic property (other than g) between the liquid and vapour phases, at a given temperature and pressure.

The non-stable thermodynamic states are excluded mainly from steam tables, and from mathematical functions related to the tables. Some non-stable states can be observed experimentally and they may persist in the absence of external perturbations.

The thermodynamic properties of water at the triple point and the critical point are shown in Table 2. The difference in the values of a property between the liquid and vapour phases, at the triple point, is evident for v, u, h and s.

Critical Point and Supercritical Behaviour

The foregoing theory of the first-order phase transition between a liquid and a vapour is not valid at, or near, a critical point. A valid theory of the second-order phase transition in a small neighbourhood of a critical point was achieved in the 1970s, following precise measurements in the early 1960s that invalidated previous theories [7]. The phenomenon of critical opalescence had been observed experimentally in the 1860s, and it indicated that large fluctuations of specific volume occur in water near the critical point. The valid theory of critical phenomena incorporates a correct treatment of the correspondence between thermodynamics and statistical mechanics [7].

Recent critical-point data for light water and heavy water are shown in Table 3. There are significant differences between the values for light water and heavy water. Experimental data for specific heat capacity at constant volume versus temperature have strongly non-linear behaviour for temperatures within ±5 K of the critical temperature, for both light water and heavy water. An equation that incorporates the asymptotic behaviour from the valid theory of critical phenomena, predicts these specific-heat data correctly. The equation predicts a singularity at the critical temperature [13].

The reader may want to exercise caution in performing thermodynamic calculations, and in designing thermodynamic cycles, near a critical point. The reader may realize that performing thermodynamic calculations for a supercritical fluid is less troublesome.

A supercritical fluid exists at a temperature and a pressure greater than the critical values; this fluid is called a "gas", in contrast to "liquid" and "vapour". The steam tables, and the related equation for f, are valid for temperatures up to 1300°C (1573 K) and for pressures up to 100 MPa, so calculations for supercritical water (SCW) can be performed [9]. The approximate functions for light water [10] and heavy water [11] are not valid for supercritical conditions.

Table 3. Thermodynamic properties of light water and heavy water at the critical points, from a recent publication [13].

Property	Light water (hydrogen oxide)	Heavy water (deuterium oxide)
Temperature, T' (°C)	373.946	370.697
Absolute temperature, T (K)	647.096	643.847
Absolute pressure, p (MPa)	22.064	21.671
Specific volume, v (m^3/kg)	0.003106	0.002809

Thermal Conductivity

The subject of non-equilibrium thermodynamics includes heat transfer by conduction. The thermal conductivity, K, is a non-equilibrium thermodynamic property of a substance. Thermal conduction in a fluid involves molecular motion and the transport of molecular kinetic energy. The kinetic theory of gases predicts thermal conductivity and this prediction can be used to estimate K for high-temperature vapour and supercritical gas [12]. Accurate values of K can be obtained from tables for water [9, 14]. Tables and equations for the thermal conductivity of water are available for temperatures from 0°C to 800°C (273 K to 1073 K), and for absolute pressures from 0 MPa to 100 MPa [14]. Relevant values of thermal conductivity are shown in Table 4.

Information on the thermal conductivity of heavy water, and a description of high-temperature estimates of the thermal conductivity of heavy water, are available [15].

FLUID DYNAMICS

Viscosity

The viscosity, μ', is a fluid-dynamic property of a fluid. Viscous stresses in a fluid involve molecular motion and the transport of molecular momentum between fluid elements moving at different velocities. The kinetic theory of gases predicts viscosity and this prediction can be used to estimate μ' for high-temperature vapour and supercritical gas [12]. Accurate values of μ' can be obtained from tables for water [9, 14]. Tables and equations for the viscosity of water are available for temperatures from 0°C to 800°C (273 K to 1073 K), and for absolute pressures from 0 MPa to 100 MPa [14]. Relevant values of viscosity are shown in Table 4.

Information on the viscosity of heavy water, and a description of high-temperature estimates of the viscosity of heavy water, are available [15].

Fluid Flow and Heat Transfer

The reader may know that this description of fluid properties is only a part of a larger story about fluid flow and heat transfer in water-cooled nuclear reactors. That story also includes thermal-hydraulic phenomena and reactor-core design.

Table 4. Thermal conductivity and viscosity of light water at relevant temperatures and pressures [14].

Temperature		Pressure	Thermal conductivity	Viscosity
T' (°C)	T (K)	p (MPa, abs)	K (mW/(m·K))	μ' (µPa·s)
25	298	0.1	607.5	890.1
300	573	10.0	548.1	86.46
350	623	12.5	81.1	22.37
425	698	25.0	118.9	28.45
650	923	25.0	106.4	36.42

CONCLUSION

The thermodynamic and fluid-dynamic properties of water, and the related physical theories, are known well. Most of the information about these properties for high-temperature nuclear reactors is readily available. Three concerns are identified in this study: (1) calculations near a critical point can be difficult and uncertain; (2) approximate functions may not be valid for supercritical water; (3) accurate information for very high temperatures in accident scenarios is not readily available. These concerns suggest the need for new practical methods for the critical-point neighbourhood and the supercritical thermodynamic states.

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