

# **Chapter 4      Equation of State**

## **4.1 Introduction**

### **4.1.1 Chapter Content**

This chapter explores how to get the pressure given information from the governing conservation equations.

## 4.1.2 Learning Outcomes

Objective 4.1	The student should be able to calculate any dependent thermodynamic property given any two independent state variables using (a) the steam tables, (b) supplied codes, (c) supplied curve fits to the steam tables.					
Condition	Open book written examination.					
Standard	100%.					
Related concept(s)	Water properties.					
Classification	Knowledge	Comprehension	Application	Analysis	Synthesis	Evaluation
Weight	a	a	a			

Objective 4.2	The student should be able to develop a flow diagram and pseudo-code for the calculation of P and T given density and enthalpy.					
Condition	Open book written examination.					
Standard	100%.					
Related concept(s)	The rate form of the equation of state.					
Classification	Knowledge	Comprehension	Application	Analysis	Synthesis	Evaluation
Weight	a	a	a			

Objective 4.3	The student should be able to explain the pressure and temperature response of a volume of fluid to perturbations given the F and G functions.					
Condition	Open book written examination.					
Standard	100%.					
Related concept(s)	The rate form of the equation of state.					
Classification	Knowledge	Comprehension	Application	Analysis	Synthesis	Evaluation
Weight	a	a				

### 4.1.3 Chapter Layout

Forms of the equation of state to use for systems analysis

The iterative method of finding pressure.

The non-iterative method is offered as an improvement.

This leads naturally to the water property evaluation.

Fast, accurate curve fits are presented.

## 4.2 Thermodynamic Properties

From a thermodynamics viewpoint, the equation of state of a substance is a relationship between any four thermodynamic properties of the substance, three of which are independent.

EXTENSIVE FORM: An example of the equation of state involves pressure  $P$ , volume  $V$ , temperature  $T$  and mass of system:

$$\pi (P, V, T, M) = 0 \quad (1)$$

If any three of the four properties are fixed, the fourth is determined.

INTENSIVE FORM: The equation of state can also be written in a form which depends only on the nature of the system and not on how much of the substance is present, hence all extensive properties are replaced by their corresponding specific values. Thus

$$\pi (P, v, T) = 0 \quad (2)$$

is the specific value form of the above equation of state, where  $v$  is the specific volume.

If any two of the thermodynamic properties are fixed, the third is determined.

From a thermodynamic point of view, the appropriate way to present water properties is by tables or formula for each property expressed as a function of the independent parameters  $P$  and  $T$  (figure 4.1).

Thus given values of pressure and temperature, the calculation of other thermodynamic properties is usually straightforward.

Unfortunately,  $T$  and  $P$  are rarely the independent parameters in system dynamics since the numerical solution of the conservation equations yield mass and energy as a function of time.

Hence, from the point of view of the equation of state, it is mass and energy which are the independent parameters.

Consequently, system codes are hampered by the form of water property data commonly available.

A key point to note is that the conservation equations are all cast as rate equations whereas the equation of state is typically written as an algebraic equation.

This arises from the basic assumption that, although the properties of mass, momentum and energy must be traced or solved as a function of time and space, the corresponding local pressure is a pure function of the local state of the fluid. Process dynamics are not considered.

This is the essence of the equilibrium assumption (in a like manner, of course, we invariably use steady state heat transfer coefficients, etc. in dynamic processes).

Historically, this mixture of form arose because thermodynamics endeavours were concerned with equilibrium states and not with system processes. System modellers, on the other hand, emphasized system dynamics and used what was available for constitutive relations. System modellers are more concerned with numerical problems.



Porsching [POR71] correctly identifies the important role of flow in his work and by keying the formulation of node-link networks to flow, stable, efficient and accurate solution schemes result.

However, the role of pressure has not received the equivalent acknowledgement.

Most other popular schemes, for instance, Agee [AGE83], use the algebraic form of the equation of state.

This treatment puts the pressure determination on the same level as heat transfer coefficients.

Thus, although numerical solution of the resulting equation sets give correct answers (to within the accuracy of the assumption),

- intuition is not generated
- time consuming iterations must be performed to get a pressure consistent with the local state parameters.

We look first at such an iterative scheme and then consider a more efficient alternative (the rate method).

### 4.3 The Iterative Method

Given the density and enthalpy of a volume of water, the task at hand is to find the associated values of pressure and temperature.

Figure 4.2 shows qualitatively the relation between density,  $\rho$ , and enthalpy,  $h$ , for a given  $P$ .

At low enthalpy, the fluid is single phase liquid and the density is high.

As heat is added and the fluid reaches saturation temperature, vapour is generated to form a two-phase mixture and the density approaches the vapour density.

The curve is well behaved and continuous making it a suitable candidate for numerical search routines.

We start the iteration procedure by guessing a pressure. Usually in system transient simulation codes, the value of  $P$  at a previous time step is a good choice.

Given  $P$  we calculate  $h_{f\text{sat}}$  and  $h_{g\text{sat}}$ , the saturation enthalpies for the liquid and vapour phases, respectively.

If  $h < h_{f\text{sat}}$  then the fluid is single phase liquid.

If  $h > h_{g\text{sat}}$  then the fluid is single phase vapour.

Otherwise the fluid is a two-phase mixture with a quality,  $x \in [0,1]$ .

The case of two-phase equilibrium is considered first. Subsequently, the equations are extended to cover single phase and two-phase non-equilibrium fluid.

### 4.3.1 Two-Phase Equilibrium Fluid

For two-phase fluid, the density and enthalpy are functions of the pressure and quality. Since we know the density,  $\rho$ , we can estimate the quality ( $x_{\text{est}}$ ) for the guessed  $P$  (assuming a homogeneous mixture) since:

$$v = \frac{1}{\rho} = v_f(P) + x_{\text{est}} v_{fg}(P) \quad (3)$$

and thus calculate the enthalpy based on the guessed  $P$ :

$$h_{\text{est}} = h_f(P) + x_{\text{est}} h_{fg}(P) \quad (4)$$

This estimated value of  $h$  will differ from the known value of  $h$ . This difference is used to drive the iteration, ie, to update the guessed pressure as illustrated in figure 4.3:

$$\Delta P = \frac{\Delta h}{(\partial h / \partial P)_\rho} \quad (5)$$

The denominator in equation 5 must be evaluated numerically if analytical expressions are not available. The pressure is updated via:

$$P = P + \Delta P \quad (6)$$

and the iteration is repeated until the pressure has converged to some tolerance. The temperature is just the temperature of saturated fluid at that pressure.

### 4.3.2 Single-Phase Sub-cooled and Superheated Fluid

For single phase fluid, the density and enthalpy are functions of P and T, ie:

$$\rho = \rho(P, T) \quad \text{and} \quad h = h(P, T) \quad (7)$$

For a guessed P and T,  $\rho$  and h can be found directly from the water property tables.

But this is just an estimate since P and T are guessed.

The true values of  $\rho$  and h lie some distance away and, to a first approximation, the true values and the estimated values are related by a Taylor's series expansion:

$$\rho = \rho_{\text{est}} + \left. \frac{\partial \rho}{\partial T} \right|_P \Delta T + \left. \frac{\partial \rho}{\partial P} \right|_T \Delta P \quad (8)$$

$$h = h_{\text{est}} + \left. \frac{\partial h}{\partial T} \right|_P \Delta T + \left. \frac{\partial h}{\partial P} \right|_T \Delta P \quad (9)$$

Defining  $\Delta\rho = \rho - \rho_{\text{est}}$  and  $\Delta h = h - h_{\text{est}}$ , we solve for  $\Delta P$  and  $\Delta T$ :

$$\Delta P = \frac{\left(\frac{\partial h}{\partial T}\right)_P \Delta\rho - \left(\frac{\partial \rho}{\partial T}\right)_P \Delta h}{\left(\frac{\partial \rho}{\partial P}\right)_T \left(\frac{dh}{dT}\right)_P - \left(\frac{\partial \rho}{\partial T}\right)_P \left(\frac{\partial h}{\partial P}\right)_T} \quad (10)$$

$$\Delta T = \frac{\left(\frac{\partial h}{\partial P}\right)_T \Delta\rho - \left(\frac{\partial \rho}{\partial T}\right)_T \Delta h}{\left(\frac{\partial \rho}{\partial T}\right)_P \left(\frac{dh}{dP}\right)_T - \left(\frac{\partial \rho}{\partial P}\right)_T \left(\frac{\partial h}{\partial T}\right)_P} \quad (11)$$

or, more compactly,

$$\Delta P = G_{1P} \Delta \rho + G_{2P} \Delta h \quad (12)$$

$$\Delta T = G_{1T} \Delta \rho + G_{2T} \Delta h \quad (13)$$

The G functions are summarized in table 4.2. The derivatives must be evaluated numerically if analytical expressions are not available.

The pressure and temperature are updated via:

$$P = P + \Delta P \quad \text{and} \quad T = T + \Delta T \quad (14)$$

and the iteration is repeated until the pressure and temperature have converged to some tolerance.

## 4.4 The Rate Method

We next consider a scheme (called the Rate Method) that eliminates the need for iteration with no loss in accuracy.

The case of two-phase equilibrium is considered first in order to illustrate the method.

Subsequently, the equations are extended to cover single phase and two-phase non-equilibrium fluid.



#### 4.4.1 Two-Phase Equilibrium

For a two-phase homogeneous mixture we have:

$$v = v_f + x v_{fg} \quad (15)$$

$$h = h_f + x h_{fg} \quad (16)$$

where  $v_{fg} \equiv v_g - v_f$  and  $h_{fg} \equiv h_g - h_f$ .

We wish to relate rates of change of pressure to rates of change in  $\rho$  and  $h$ . Specifically, we desire:

$$dP = G_1 d\rho + G_2 dh \quad \text{or} \quad \frac{dP}{dt} = G_1 \frac{d\rho}{dt} + G_2 \frac{dh}{dt} \quad (17)$$

since  $d\rho/dt$  and  $dh/dt$  (or equivalently,  $dM/dt$  and  $dH/dt$ ) are available from the mass and enthalpy conservation equations.

First concentrating on the case of constant  $\rho$  (or  $\nu$ ), to obtain  $G_2$ , we differentiate equation (16) to gives:

$$\frac{dh}{dt} = \left( \frac{\partial h}{\partial P} \right)_\rho \frac{dP}{dt} = \left[ \frac{\partial h_f}{\partial P} + h_{fg} \frac{\partial x}{\partial P} + x \frac{\partial h_{fg}}{\partial P} \right] \frac{dP}{dt}. \quad (18)$$

Using equation (15), holding  $\nu$  constant (i.e.,  $\rho = \text{constant}$ ):

$$\frac{dx}{dP} = \frac{\partial \left( \frac{\nu - \nu_f}{\nu_{fg}} \right)}{\partial P} = - \frac{1}{\nu_{fg}} \left[ \frac{\partial \nu_f}{\partial P} + x \frac{\partial \nu_{fg}}{\partial P} \right]. \quad (19)$$

Substituting this into equation (18) gives:

$$\frac{dh}{dt} = \left\{ \frac{\partial h_f}{\partial P} + x \frac{\partial h_{fg}}{\partial P} - \frac{h_{fg}}{\nu_{fg}} \left[ \frac{\partial \nu_f}{\partial P} + x \frac{\partial \nu_{fg}}{\partial P} \right] \right\} \frac{dP}{dt} \quad (20)$$

or equally:

$$\begin{aligned} \frac{dP}{dt} &= \frac{v_{fg}}{\left\{ v_{fg} \left[ \frac{\partial h_f}{\partial P} + x \frac{\partial h_{fg}}{\partial P} \right] - h_{fg} \left[ \frac{\partial v_f}{\partial P} + x \frac{\partial v_{fg}}{\partial P} \right] \right\}} \frac{dh}{dt} \\ &= \frac{v_{fg}}{\{\text{DENOMINATOR}\}} \frac{dh}{dt} = G_2 \frac{dh}{dt}. \end{aligned} \quad (21)$$

This gives the pressure rate response due to an enthalpy rate change, holding  $\rho$  constant.

If we repeat the above but holding  $h$  constant we find:

$$\frac{dP}{dt} = \frac{-h_{fg}}{\{\text{DENOMINATOR}\}} \frac{dv}{dt} = \frac{h_{fg} v^2}{\{\text{DENOMINATOR}\}} \frac{d\rho}{dt} = G_1 \frac{d\rho}{dt}. \quad (22)$$

Note that  $G_1$  and  $G_2$  are functions that depend only on the local saturation fluid properties and their slopes at the local pressure.

Combining equations 21 and 22 to get the total pressure rate response when both  $h$  and  $\rho$  are varying:

$$\frac{dP}{dt} = G_1(P, x) \frac{d\rho}{dt} + G_2(P, x) \frac{dh}{dt}. \quad (23)$$

This is the rate form of the equation of state for two-phase equilibrium fluid in terms of the intensive rate properties,  $d\rho/dt$  and  $dh/dt$ , which are obtained from the continuity equations.

Equation 23 can be cast in the extensive form by noting that, since  $\rho = M/V$  and  $h = H/M$ ,

$$\frac{d\rho}{dt} = \frac{1}{V} \frac{dM}{dt} - \frac{M}{V^2} \frac{dV}{dt} \quad (24)$$

and

$$\frac{dh}{dt} = \frac{1}{M} \frac{dH}{dt} - \frac{H}{M^2} \frac{dM}{dt} \quad (25)$$

Substituting into equation 23 and collecting terms:

$$\frac{dP}{dt} = \left( \frac{G_1}{V} - \frac{G_2 H}{M^2} \right) \frac{dM}{dt} + \frac{G_2}{M} \frac{dH}{dt} - \frac{G_1 M}{V^2} \frac{dV}{dt} \quad (26)$$

After some simplification and rearrangement we find:

$$\frac{dP}{dt} = \frac{F_1 \frac{dM}{dt} + F_2 \frac{dH}{dt} + F_3 \frac{dV}{dt}}{M_g F_4 + M_f F_5} \quad (27)$$

where:

$$\begin{aligned}
 F_1 &= h_g v_f - h_f v_g \\
 F_2 &= v_g - v_f \\
 F_3 &= h_f - h_g \\
 F_4 &= \frac{\partial h_g}{\partial P} (v_g - v_f) - \frac{\partial v_g}{\partial P} (h_g - h_f) \\
 F_5 &= \frac{\partial h_f}{\partial P} (v_g - v_f) - \frac{\partial v_f}{\partial P} (h_g - h_f) \\
 M_g &\equiv x M \\
 M_f &\equiv (1 - x) M .
 \end{aligned}
 \tag{28}$$

The F functions are smooth, slowly varying functions of pressure (see appendix 4) provided good curve fits are used.

The latest steam tables [HAA84] were used to fit saturated properties to less than 1/4% accuracy using low order polynomials and exponentials [GAR88].

Considerable effort was spent on obtaining accuracy and continuous derivatives over the full pressure range.

The fact that good fits are available means that the F functions are well behaved which in turn makes the rate form of the equation of state extremely well behaved, as shown later.

The G functions are also well behaved for the same reasons.

The F and G functions have direct physical interpretations which aid in generating intuition.

The F functions relate changes in the extensive properties, M, H and V, to changes in pressure.

The G functions related changes in the intensive properties,  $\rho$  and  $h$ , to changes in pressure.

Often, a simple numerical evaluation of these functions during a simulation aids in developing an appreciation of the changing roles of the key actors in a dynamic simulation.

For instance, because  $F_1$  is negative, we immediately see that adding mass to a fixed volume of liquid with fixed total enthalpy will cause a depressurization (because the specific enthalpy,  $h = H/M$ , is decreased).

But, since  $G_1$  is positive, an increase in density in a fluid of fixed specific enthalpy causes a pressurization.

#### 4.4.2 Single-Phase Sub-cooled and Superheated Fluid

For the single-phase sub-cooled or superheated case, we do not have to account for the sorting out between phases as we did for the two phase case.

Thus the derivation is more direct and less complex. We could simply use:

$$P = \pi(\rho, h) \quad (29)$$

to give:

$$\frac{dP}{dt} = \left. \frac{\partial P}{\partial \rho} \right)_h \frac{d\rho}{dt} + \left. \frac{\partial P}{\partial h} \right)_\rho \frac{dh}{dt} \quad (30)$$

but, since the steam tables are given as a function of  $P$  and  $T$ , the slopes in equation (30) are not easily obtained.



To cast the pressure rate equation in terms of the independent variables, P and T, consider:

$$\rho = \rho(P, T) \quad (31)$$

and

$$h = h(P, T) \quad (32)$$

Note that the non-equilibrium case requires the explicit tracking of the temperature in addition to pressure. Taking derivatives of Equations (31) and (32):

$$\frac{d\rho}{dt} = \left. \frac{\partial \rho}{\partial P} \right)_T \frac{dP}{dt} + \left. \frac{\partial \rho}{\partial T} \right)_P \frac{dT}{dt} \quad (33)$$

and

$$\frac{dh}{dt} = \left. \frac{\partial h}{\partial P} \right)_T \frac{dP}{dt} + \left. \frac{\partial h}{\partial T} \right)_P \frac{dT}{dt} \quad (34)$$

But we desire:

$$\frac{dP}{dt} = G_{1P} \frac{d\rho}{dt} + G_{2P} \frac{dh}{dt} \quad (35)$$

and

$$\frac{dT}{dt} = G_{1T} \frac{d\rho}{dt} + G_{2T} \frac{dh}{dt} \quad (36)$$

This is easily obtained by solving equations (33) and (34) for  $dP/dt$  and  $dT/dt$  to yield:

$$\frac{dP}{dt} = \frac{\left(\frac{\partial h}{\partial T}\right)_P \frac{d\rho}{dt} - \left(\frac{\partial \rho}{\partial T}\right)_P \frac{dh}{dt}}{\left(\frac{\partial \rho}{\partial P}\right)_T \frac{dh}{dT} - \left(\frac{\partial \rho}{\partial T}\right)_P \left(\frac{\partial h}{\partial P}\right)_T} \quad (37)$$

and

$$\frac{dT}{dt} = \frac{\left(\frac{\partial h}{\partial P}\right)_T \frac{d\rho}{dt} - \left(\frac{\partial \rho}{\partial T}\right)_T \frac{dh}{dt}}{\left(\frac{\partial \rho}{\partial T}\right)_P \frac{dh}{dP} - \left(\frac{\partial \rho}{\partial P}\right)_T \left(\frac{\partial h}{\partial T}\right)_P} \quad (38)$$

which is the intensive form we desire.

The extensive form is obtained as for the two-phase equilibrium case. Equations (24) and (25) are substituted into equations (37) and (38) and after rearrangement we find:

$$\frac{dP}{dt} = \frac{F_{1P} \frac{dM}{dt} + F_{2P} \frac{dH}{dt} + F_{3P} \frac{dV}{dt}}{M_v F_{4P} + M_l F_{5P}} \quad (39)$$

and

$$\frac{dT}{dt} = \frac{F_{1T} \frac{dM}{dt} + F_{2T} \frac{dH}{dt} + F_{3T} \frac{dV}{dt}}{M_v F_{4T} + M_l F_{5T}} \quad (40)$$

where



$$F_{1P} = \rho \left( \frac{\partial h}{\partial T} \right)_P + h \left( \frac{\partial \rho}{\partial T} \right)_P$$

$$F_{2P} = - \left( \frac{\partial \rho}{\partial t} \right)_P$$

$$F_{3P} = - \rho^2 \left( \frac{\partial \rho}{\partial T} \right)_P$$

$$F_{4P} = 0 \text{ for subcooled, } = \left( \frac{d\rho}{dP} \right)_T \left( \frac{\partial h}{\partial T} \right)_P - \left( \frac{\partial \rho}{\partial T} \right)_P \left( \frac{dh}{dP} \right)_T \text{ for superheated}$$

$$F_{5P} = \left( \frac{d\rho}{dP} \right)_T \left( \frac{\partial h}{\partial T} \right)_P - \left( \frac{\partial \rho}{\partial T} \right)_P \left( \frac{dh}{dP} \right)_T \text{ for subcooled } = 0 \text{ for superheated}$$

(41)

$$F_{1T} = \rho \left( \frac{\partial h}{\partial T} \right)_P + h \left( \frac{\partial \rho}{\partial T} \right)_P$$

$$F_{2T} = - \left( \frac{\partial \rho}{\partial t} \right)_T$$

$$F_{3T} = - \rho \left( \frac{\partial h}{\partial T} \right)_T$$

$$F_{4T} = - F_{4P}$$

$$F_{5T} = - F_{5P}$$

$M_v$  = mass of vapour phase = 0 for subcooled, = M for superheated

$M_l$  = mass of liquid phase = M for subcooled = 0 for superheated

### 4.4.3 Two-Phase Non-Equilibrium

The rate form for the equation of state for the two-phase non-equilibrium case is a simple extension of the single-phase non-equilibrium case.

The liquid and vapour phases are treated independently to give:

$$\frac{dP_k}{dt} = G_{1P}^k \frac{d\rho_k}{dt} + G_{2P}^k \frac{dh_k}{dt} \quad (42)$$

$$\frac{dT_k}{dt} = G_{1T}^k \frac{d\rho_k}{dt} + G_{2T}^k \frac{dh_k}{dt} \quad (43)$$

where  $k$  represents either  $\ell$  or  $v$  for the liquid or vapour phases respectively.

In general, the 6 equation model (3 continuity equations for each phase) would be used for the general unequal temperature, unequal velocity, unequal pressure situation. Thus  $d\rho_k/dt$  and  $dh_k/dt$  are available to the rate form of the equation of state.

The expressions for the  $F$  and  $G$  functions are summarized in tables 4.1 and 4.2. These expressions cover the full range from sub-cooled liquid to superheated steam.

## 4.5 H<sub>2</sub>O Property Fits

To facilitate the calculation of water properties, the 1984 standard tables were accurately curve fitted as discussed in detail in appendix 4.

These fitted functions are supplied in the files H2OPROP.FOR and H2OPROP.C for user convenience.

These FORTRAN and C functions cover a wide range of pressures and temperatures and should be sufficient for most nuclear reactor simulations, with the exception of severe accidents that generate extreme conditions.

These functions are fast and more than accurate enough given the other errors in system simulation [GAR88, GAR89, GAR92].



The basic overall approach taken in the curve fitting task was that, since the more difficult region to fit was the transition from single to two-phase and since most power plants operate at or near this region, careful attention would be paid the phase transition region at the expense of accuracy away from the saturation line, if necessary.

Thus, the first major step was to accurately fit the saturation lines.

Then, since density, enthalpy and other properties vary more strongly with T than with P (as shown in figure 4.4), the property in question, say density, would be calculated based on the deviation from the saturation value at the given T, ie:

$$\rho(P,T) = \rho_{\text{sat}}(T) + \left. \frac{\partial \rho}{\partial P} \right|_T (P - P_{\text{sat}}(T)) \quad (44)$$

Figure 4.5 illustrates the strategy.

It should be obvious by now that not only the properties need to be fitted but the slopes are needed as well.

Both the properties and the slopes of the properties must be free of discontinuities if numerical searches are to converge.

The supplied code is divided into 3 levels:

- Level 1: the fitted functions
- Level 2: derived functions and collections of functions (for convenience)
- Level 3: logic sorter and manager

Details on these routines are given at the end of appendix 4.

It is instructive to study appendix 4 in conjunction with the supplied code (WATERA.FOR, PROPA.FOR, H2OPROP.FOR).

## 4.6 Exercises

1. Using the spread sheet macros for Microsoft Excel supplied by G.R. McGee (as per the memo at the end of this chapter, calculate and plot the density, enthalpy, quality and void fraction for a range of pressures ( 1 to 100 atmospheres) and temperatures(50 °C to 350 °C). Make sure you cover the subcooled, saturated and superheated ranges.
2. Using the supplied code, WATERA.EXE:
  - a. Calculate  $\rho$  and  $h$  for  $P=10$  MPa and  $T=300$  °C. Increase the temperature in steps to see the approach to two-phase.
  - b. Using  $\rho$  and  $h$  slightly different than that found in (a), calculate  $P$  and  $T$ .
  - c. Practice calculating  $\rho$  given  $h$  and  $P$ .
3. Using the supplied skeleton code NODE.C:
  - a. Fill in the missing code required to calculate  $P$  and  $T$  given  $\rho$  and  $h$ .
  - b. Use the code to calculate  $\Delta P$  and  $\Delta T$  when a node experiences a  $\Delta M$ , a  $\Delta H$  or a  $\Delta V$ . Compare your answers to WATERA.EXE.
  - c. Use the code to calculate  $\Delta P$  and  $\Delta T$  when a node experiences a  $\Delta \rho$  and a  $\Delta h$ . Compare your answers to WATERA.EXE.

Table 4.1 Summary of the F functions for the rate form of the equation of state

Case	$F_1$	$F_2$	$F_3$	$F_4$	$F_5$
2 $\phi$ equilibrium (all derivatives along saturation line)	$h_g v_f - h_f v_g$	$v_{fg}$	$h_{fg}$	$\frac{\partial h_g}{\partial P} v_{fg} - \frac{\partial v_g}{\partial P} h_{fg}$	$\frac{\partial h_f}{\partial P} v_{fg} - \frac{\partial v_f}{\partial P} h_{fg}$
1 $\phi$ non- equilibrium pressure	$\rho \left( \frac{\partial h}{\partial T} \right)_P + h \left( \frac{\partial \rho}{\partial T} \right)_P$	$-\left( \frac{\partial \rho}{\partial T} \right)_P$	$-\rho^2 \left( \frac{\partial h}{\partial T} \right)_P$	$\left( \frac{\partial \rho}{\partial P} \right)_T \left( \frac{\partial h}{\partial T} \right)_P - \left( \frac{\partial \rho}{\partial T} \right)_P \left( \frac{\partial h}{\partial P} \right)_T$ 0 subcooled superheated	$\left( \frac{\partial \rho}{\partial P} \right)_T \left( \frac{\partial h}{\partial T} \right)_P - \left( \frac{\partial \rho}{\partial T} \right)_P \left( \frac{\partial h}{\partial P} \right)_T$ subcooled 0 superheated
1 $\phi$ non- equilibrium temperature	$\rho \left( \frac{\partial h}{\partial P} \right)_T + h \left( \frac{\partial \rho}{\partial P} \right)_T$	$-\left( \frac{\partial \rho}{\partial P} \right)_T$	$-\rho^2 \left( \frac{\partial h}{\partial P} \right)_T$	$-F_{4P}$	$-F_{5P}$

Table 4.2 Summary of the G functions for the rate form of the equation of state

Case	$G_1$	$G_2$
2 $\phi$ equilibrium (all derivatives along saturation line)	$\frac{h_{fg} v^2}{\left\{ v_{fg} \left[ \frac{\partial h_{fg}}{\partial P} + x \frac{\partial h_{fg}}{\partial P} \right] - h_{fg} \left[ \frac{\partial v_f}{\partial P} + x \frac{\partial v_{fg}}{\partial P} \right] \right\}}$	$\frac{v_{fg}}{\left\{ v_{fg} \left[ \frac{\partial h_f}{\partial P} + x \frac{\partial h_{fg}}{\partial P} \right] - h_{fg} \left[ \frac{\partial v_f}{\partial P} + x \frac{\partial v_{fg}}{\partial P} \right] \right\}}$
1 $\phi$ non-equilibrium pressure	$\frac{\left( \frac{\partial h}{\partial T} \right)_P}{\left[ \left( \frac{\partial \rho}{\partial T} \right)_T \left( \frac{\partial h}{\partial P} \right)_P - \left( \frac{\partial \rho}{\partial T} \right)_P \left( \frac{\partial h}{\partial P} \right)_T \right]}$	$\frac{-\left( \frac{\partial \rho}{\partial T} \right)_P}{\left[ \left( \frac{\partial \rho}{\partial P} \right)_T \left( \frac{\partial h}{\partial P} \right)_P - \left( \frac{\partial \rho}{\partial T} \right)_P \left( \frac{\partial h}{\partial P} \right)_T \right]}$
1 $\phi$ non-equilibrium temperature	$\frac{\left( \frac{\partial h}{\partial P} \right)_T}{\left[ \left( \frac{\partial \rho}{\partial T} \right)_P \left( \frac{\partial h}{\partial P} \right)_T - \left( \frac{\partial \rho}{\partial P} \right)_T \left( \frac{\partial h}{\partial T} \right)_P \right]}$	$\frac{-\left( \frac{\partial \rho}{\partial P} \right)_T}{\left[ \left( \frac{\partial \rho}{\partial T} \right)_P \left( \frac{\partial h}{\partial P} \right)_T - \left( \frac{\partial \rho}{\partial P} \right)_T \left( \frac{\partial h}{\partial T} \right)_P \right]}$

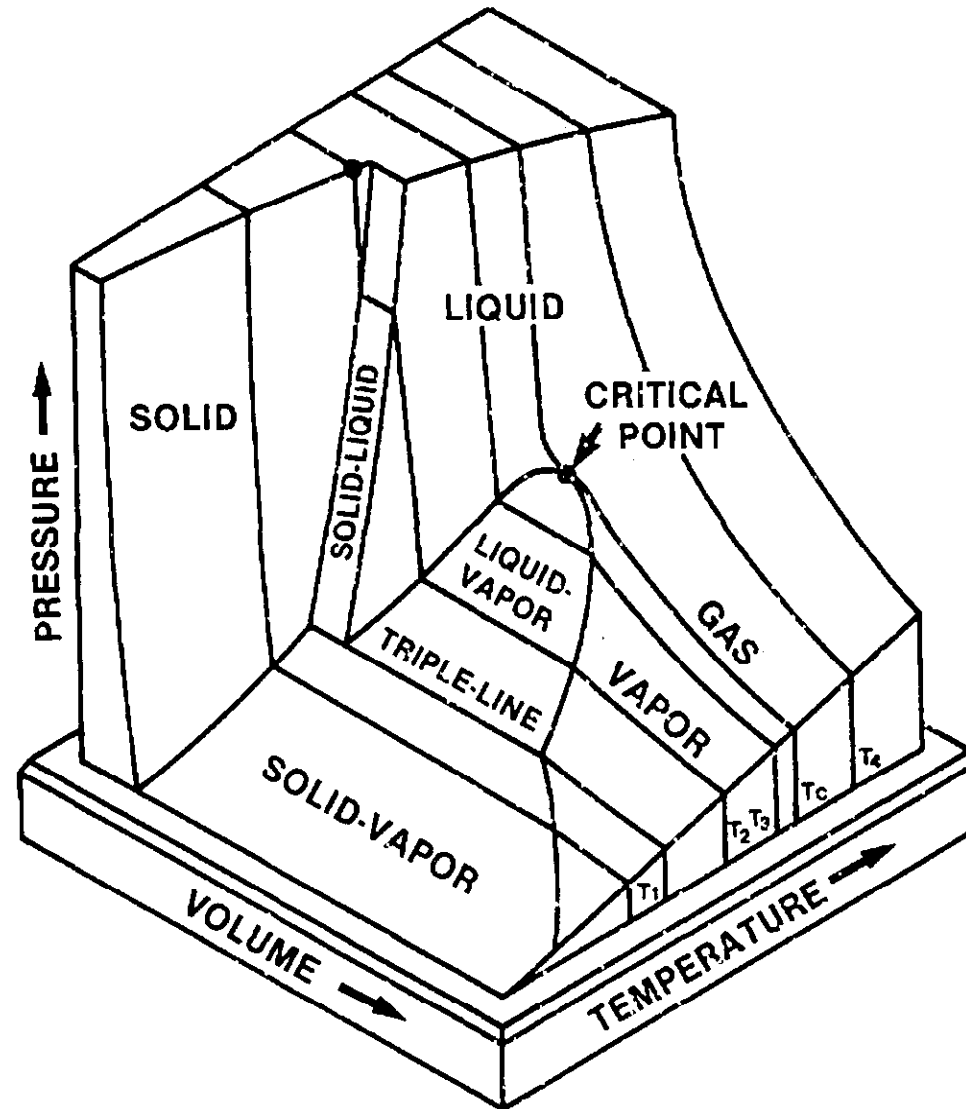


Figure 4.1 P-v-T surface for water.

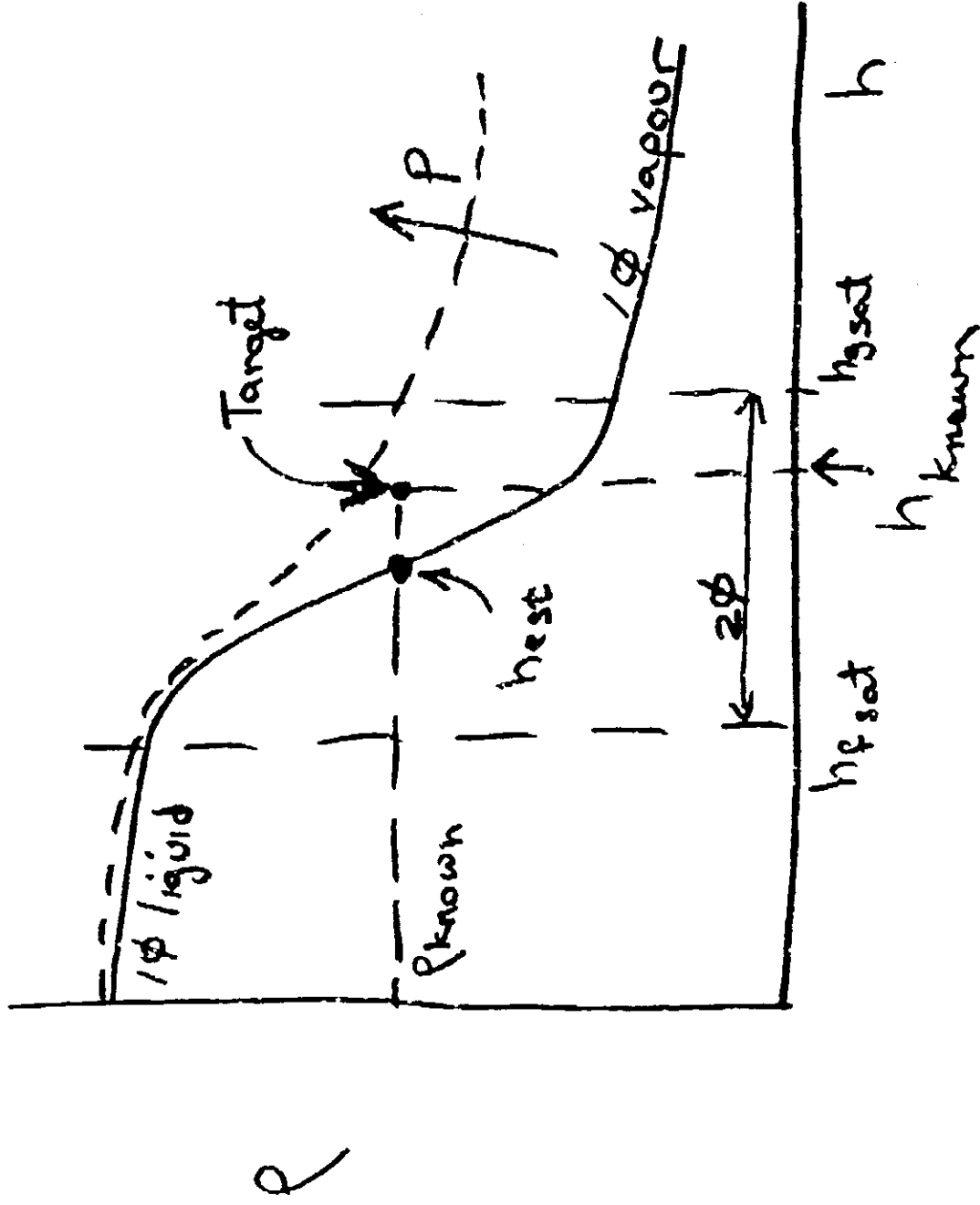


Figure 4.2 Numerical search for  $P$  given  $\rho$  and  $h$  for a two-phase mixture.

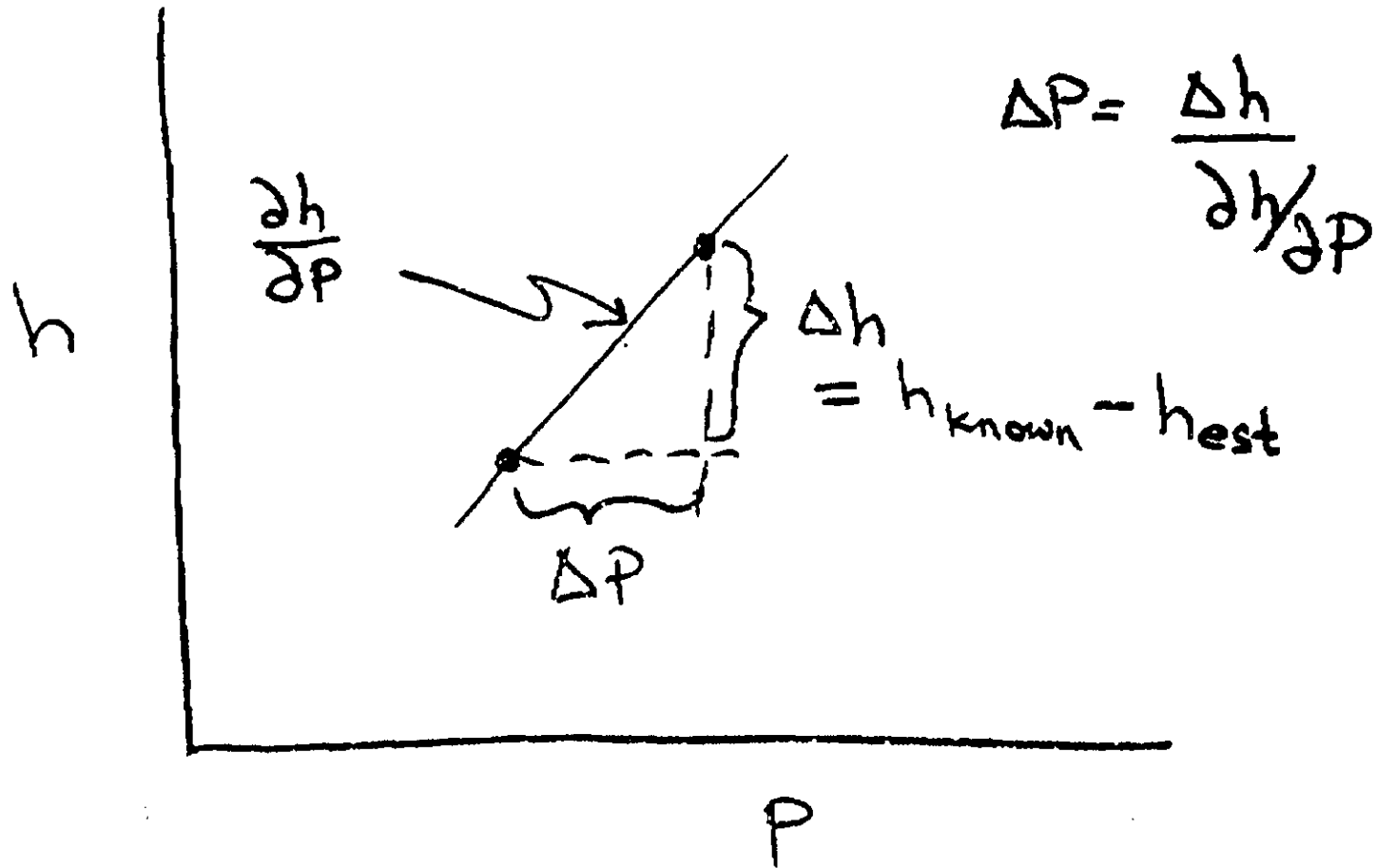


Figure 4.3 Error correction scheme for pressure in two-phase.



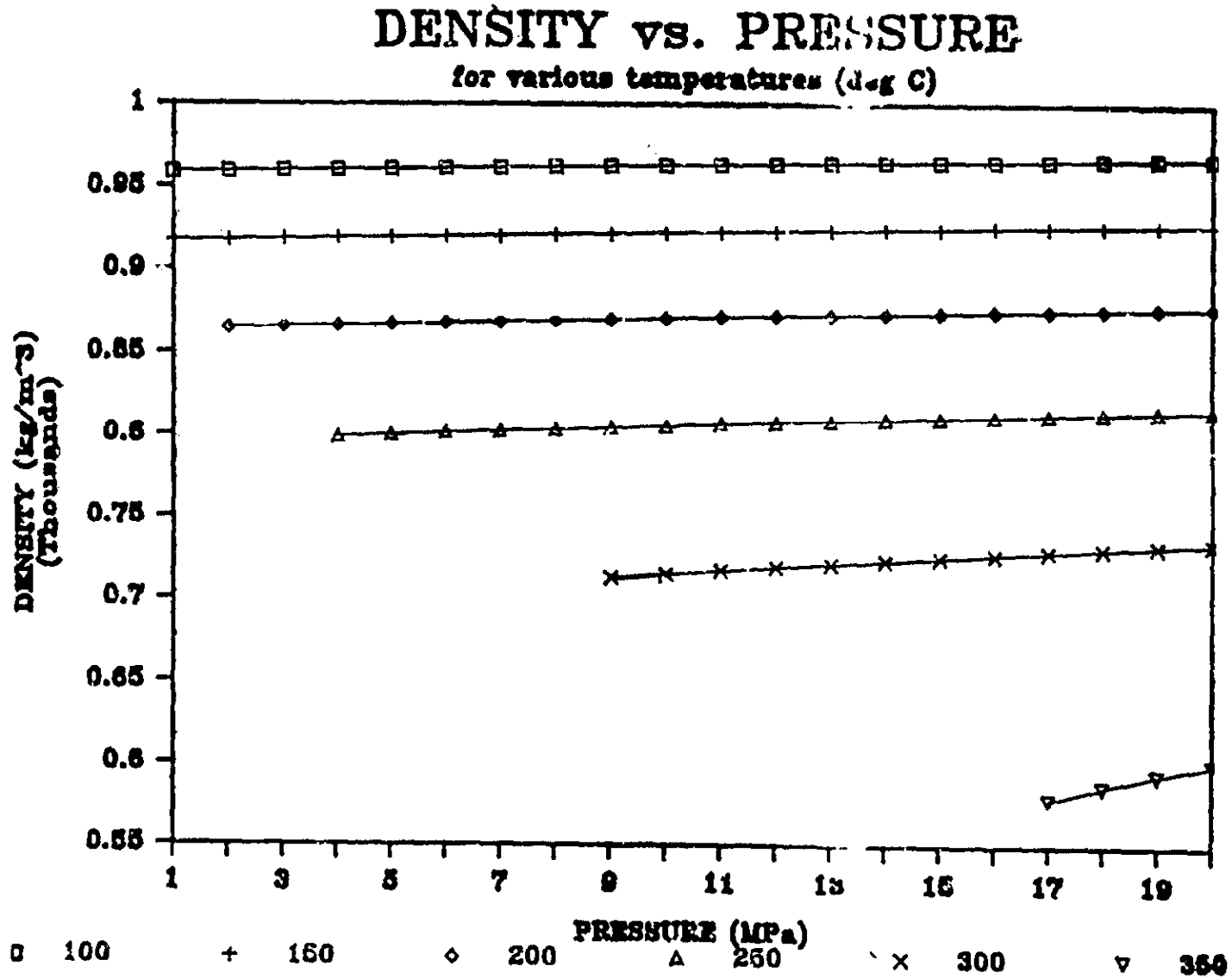
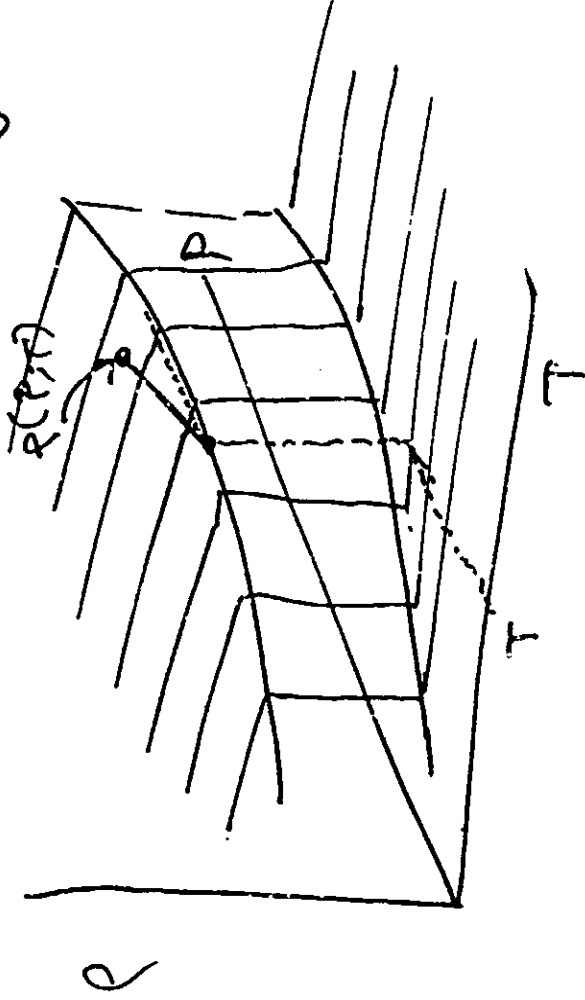


Figure 4.4 Density vs. pressure at various temperatures in subcooled water.

Based on saturation fits by Haskins



$$p(P, T) = p_{\text{sat}}(T) + \frac{\partial p}{\partial P} \Big|_T (P - p_{\text{sat}}(T))$$

Superheat & Subcooled fits by Hand.

Figure 4.5 Basis for curve fitting in the subcooled region.