DEVELOPMENT OF A NEW EQUATION OF STATE FOR WATER AND ITS APPLICATIONS - PARTS I & II

by

PYUNG-HUN CHANG
B.S.,Seoul National University
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Signature of Author...
Department of Mechanical Engineering
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Certified by...
William C. Unkel
Thesis Supervisor

Accepted by...
Warren M. Rohsenow
Chairman, Departmental Commitee on Graduate Studies

preface

The purpose of this study was to develop a simple equation of state in the form of a thermodynamic potential function to represent the right image of pure water substance, yielding accurate thermodynamic properties. The intended use of the equation was to apply to problems in the steam power plant engineering.

The first part of this study covers the development of a new equation of state, while the second part treats the application of the equation of state to two engineering problem.

The author would like to thank Professor Henry M. Paynter for providing the motivation and the initial guidance of the study. He thanks deeply Professor William Unkel for providing timely guidances and encouragement, essential to the completion of this study. The author also thanks Professor Derek Rowell for his valuable suggestions and encouragement.

The author thanks his wife Minja for her exceptional patience and love, his two sons Chai and June for their prayers.

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PYUNG-HUN CHANG

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ABSTRACT OF PART I

An equation of state for pure water was developed in the form of a thermodynamic potential function, the Massieu Potential Function (MPF). The goal was to provide computationally simple, but accurate, expression that can be applied to problems associated with steam turbine cycle calculations, especially in control systems.

A generalized potential function was formulated after examining several theoretical equations of state including the van der Waals(VDW) equation. The potential function for water was determined from this generalized function by evaluating the accuracy as additional terms were added. Accuracy was defined in terms of agreement of the equation results with the saturation curve behavior of water.

The resulting potential function (or equation of state) consists of 4 parameters, has one more term than the VDW equation, yet gives much better accuracy. The accuracy of pressure calculated with the present equation of state, as compared to data in the Keenan-Keyes-Hill-Moore steam table, is: within 1 % deviation in the temperature range from 200 F to 1400 F, with the pressure range from 5 psia to more than 2000 psia in the superheated region; and within 9 % deviation in the pressure range from 1.5 psia to the critical point in the saturated region.

The main improvement in the accuracy in the saturated region might be made by allowing the variation of the parameter b with temperature, which could reshape the pressure-volume-temperature relationship in the saturated region. The accuracy in the superheated region might be improved by adding a few empirical terms in the form of MPF to correct the compressibility factor.

Thesis Supervisor: Dr. William C. Unkel
Title: Associate Professor of Mechanical Engineering

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PART I

DEVELOPMENT OF A NEW STATE EQUATION

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Quantitative calculations in the design and simulations of the steam power plants require reliable and computationally economical estimates of thermodynamic properties. To obtain such properties, equations of state for water are required. Equations of state for fluids can be broadly classified into three categories: empirical, semiempirical and theoretical. Simple table lookup procedures or adjustment fit fall into the class of empirical, while those correlations where the basic form is defined on theoretical grounds but where the coefficients are 'fit' to the data are termed semi-empirical equations.

Since extensive experimental measurements of thermodynamic properties are available for water, there exist many different empirical equations of state with a very large number of adjustable parameters that have essentially no physical significance. Among these are the 1967 IFC Formulation for Industrial Use and the 1968 IFC Formulation for Scientific and General Use, both of which are based on the International Skeleton Table of 1963.[1] The former consists of about 150 numerical constants and the latter about 300 constants. These two IFC formulations have crucial weakness in that the range of state is split up into 6 sub-regions, each of which has different sub-formulation. Since the formulation is a curve fit of each property rather than a fit to a thermodynamic potential function like the Helmholtz free energy, thermodynamic consistency in each sub-region is not maintained nor is continuity enforced at their boundaries. The equation by Keenan, Keyes, Hill and Moore(KKHM) uses a single fundamental function with 59 constants.[2] The fundamental function of the KKHM equation is the Helmholtz free energy as a function of temperature and specific volume, from which all the other steam properties can be derived. All the properties derived in this way are thermodynamically consistent with each other and continuous in the prescribed region. Nonetheless the larger number of constants of the KKHM equation is still disadvantageous for the computational efficiency. These totally empirical equations of state are quite accurate in making interpolative calculations of properties. For example, their accuracies are typically 0.01%. However, owing to larger number of constants, more than 90% of the CPU time is known to be spent in evaluating steam properties, when these types of state equations are used, in typical simulations of transient or steady state behavior of steam power plant components.[3] This computational disadvantage is one reason to develop theoretical or semi-empirical expressions.

A few theoretical equations exist for such simple substances such as argon or methane, although considerable mathematical and conceptual difficulties delay the rigorous theory of dense fluid. Among them is an equation proposed by Longuet-Higgins and Widom.[4] However, the complicated nature of the water molecule (such as strong polarity) makes it difficult to derive a totally theoretical equation of state. Even semiempirical equations are quite rare. One of such equations is by Whiting and Prausnitz.[5] Another is proposed by Haar and coworkers.[6] Essentially, these equations are modern expressions of well known physical concepts suggested by van der Waals [VDW] over 100 years ago. The VDW equation can be considered to consist of two terms: the first one is repulsion term and the other attraction term. The equation by Whiting et al uses the Carnahan and Starling equation[7] as the repulsion term and the molecular dynamic results of Alder[8] as the attraction term. In addition, the equation uses the simplfied assumtion proposed by Prigogine[9], i.e. that at high densities, all density-dependent rotations and vibrations can be treated as equivalent translational degree of freedom. The result of the approach of Whiting has 10 coefficients and 4 adjustable parameters. However, in spite of rather sophisticated theoretical ideas, the accuracy is not good. On the other hand, the equation by Haar et al is composed of a reference function with some theoretical basis and a purely empirical function. This reference function is an updated VDW equation which is modified in part with theoretical basis and in part empirically so that it may represent the thermodynamic behavior quantitatively at high temperatures and elsewhere at high densities.

The motivation for this study, under the direction of Professor H.M. Paynter, came from the desire to find an equation which is simpler but more accurate than those available. Thus, in engineering calculations,good accuracy could be obtained with reasonable computational expense.

1.2 PROBLEM STATEMENT

The problem investigated in this study is to construct a potential function such as the Massieu potential or Helmholtz free energy from which all thermodynamic property can be derived. Like the forementioned semi-empirical equation, the starting point is the VDW equation. The immediate objective is to improve the VDW equation by simple theoretically or empirically base terms. More specifically, the objective is to find a better functional structure as well as parameter values, so as to represent the right image of pure water ,yielding accurate thermodynamic properties with a simpler functional form for efficient calculations.

1.3 ORGANIZATION

In Chapter 2, a detailed historical background for the equation of water is given. This is followed by the direction and criteria for the development of the equation of state. Procedures of the development of the equation are presented in Chapter 3. Thermodynamical relations with regard to the Massieu Potential Function is briefly reviewed. Main procedures of the thesis are presented here. Chapter 4 contains results and discussions, and conclusions and recommendations are presented in Chapter 5.

CHAPTER 2

HISTORICAL REVIEW AND DIRECTON OF RESEARCH

In this chapter, various fluid models are introduced and reviewed so that a rational direction for a derivation of new equation of state might be found. In addition, the criteria which appear to be crucial for the development will be presented.

2.1 HISTORICAL REVIEW

The equation originally proposed by van der Waals[10]

$$(P+a/v^2)(v-b)=RT \tag{2.1}$$

can be rewritten as

$$P = RT/(v-b) -a/v^2 \tag{2.2}$$

where P is pressure, T is temperature, v is specific volume, b accounts for the excluded volume by molecules and 'a' is the constant which represents the long range attraction force. The first term in Eq.(2.2) may be interpreted as the intermolecular repulsion term Pr, the second term as the attraction term Pa respectively. In other words, the pressure is composed of

$$P = Pr + Pa \, . \qquad (2.3)$$

The VDW equation gives a moderately good description of P-V-T behavior in the gas phase where the excluded volume of each molecule does not overlap. However it gives only a qualitative description in the liquid phase since the volume v in the liquid phase is found experimentally to be considerably less than b. The improvements to the VDW equation can be either in improved repulsion or in improved attraction term.

2.1.1 Improvements To Repulsion Term

Several attempts have been made to improve the repulsion term of the VDW equation by adopting the model of hard-sphere molecules i.e. molecules where the two body potential function Γ is given by

$$\Gamma(r) = 0 \, , \text{ for } r < \sigma$$
$$\Gamma(r) = \infty , \text{ for } r > \sigma \qquad (2.4)$$

where r is radial distance and σ is the radius of hard core of each molecule. [11] For such molecules, Pa = 0. Sophisticated mathematical techniques have been applied to the model, in addition to a variety of assumptions concerning the properties of the radial distribution function.[11] Various assumptions and techniques are well reviewed in Reference 11. Relatively succesful equations of state include one by Percus-Yevic-Frisch(PYF) equation and another by

Carnahan and Starling(CS). These equations are similar with the PYF equation being

$$P = [(1+y+y^2)/(1-y)^3](RT/v) \tag{2.5}$$

and the CS being

$$P = [(1+y+y^2-y^3)/(1-y)^3](RT/v) \tag{2.6}$$

where y=b/(4v). These equations give the functional results for compressibility factor which agree well with the theoretical results by Alder. Alder solved the equations of motion of small assemblies (tens or hundreds) of hard-sphere molecules with a computer and generated the properties of this system. The properties thus obtained can be considered as those of an 'ideal liquid' comparable with the perfect gas[12], even though they may not be compared with experimental data directly, because the assumption of hard-sphere model in Eq.(2.4) is an over-simplified description of behavior of real molecules.

2.1.2 Improvements To The Attraction Term

On the other hand, as an improvement over the attraction term, Pa, the molecular dynamic results of Alder show that the constant 'a' in the attraction term of the VDW equation actually depends on temperature and density. By using the square well potential as the two-body potential function, he derived the constant 'a' as

$$a = -R(e.q/k)(r.vo)\sum_{n=1}^{4}\sum_{m=1}^{M}(m.A_{nm}/\tilde{v}^{m-1})(1/T^{n-1}) \tag{2.7}$$

where R is the gas constant,e.q is characteristic energy per molecule, k is the Boltzmann constant and r is number of segments per molecule with $\tilde{v}=v/(r.vo)$, where vo is the close-packed volume.

2.1.3 Inclusion Of Rotational And Vibrational Term

In addition to translation, larger molecules can exercise rotational and vibrational motions. Beret and Prausnitz[15] expressed the pressure with three terms, that is

$$P = Pr + Pa + Prv \quad . \qquad (2.8)$$

where Prv is the term to account for the rotation and vibration. Since it is difficult to construct a satisfying theory for evaluate Prv, Prigogine has suggested a simplifying assumption that all density-dependent degree of freedom may be considered to be equivalent translational degrees of freedom with

$$Prv = (c-1)Pr \qquad (2.9)$$

where c is an adjustable parameter for each substance. For fluids with larger molecules, c will be larger than 1, while for simple fluid with no rotation and vibration, c=1.

2.1.4 Inclusion Of Polarity

To account for orientational forces of strongly polar substance such as water, Gmehling et al[13] proposed an assumption that the substance is an equivalent mixture of monomers and dimers at chemical equilibrium and that the thermodynamic properties can be represented by the hypothetical mixture. The extent of dimerization is given by an equilibrium constant, K

$$K = (\zeta_D \phi_D)/(\zeta_M^2 \phi_M^2 P) \qquad (2.10)$$

where ζ is the true mole fraction, ϕ is the fugacity coefficient, P is the total pressure and subscripts M and D denote monomer and dimer respectively. The Eq.(2.10) is used to find the mole fractions. Once the fractions are known, a set of constants are given as a function of composition by mixing rule, which is described more in detail·in the appendix of Reference 5.

2.2 COMBINATIONS OF IMPROVED RESULTS

The more successful improvements over the VDW equation include imporvements to both the attraction and repulsion terms. They can be considered in two classes.

2.2.1 LHW And Guggenheim Equations

Longuet-Higgins and Widom(LHW)[4] combined the repulsion term given by the PYF equation, Eq.(2.5) with the VDW expression for Pa in Eq.(2.2). Both of the terms have physical meanings. Guggenheim(14) combined the same attraction term in Eq.(2.2) with an empirical repulsion term

$$Pr = [1/(1-y)^4]\ RT/v \qquad (2.11)$$

which is algebraically simpler than the PYF equation but leads to almost identical predictions. The equations are

$$P = [(1+y+y^2)/(1-y)^3]\ RT/v - a/v^2 \text{;LHW} \qquad (2.12)$$

$$P = [1/(1-y)^4]\ RT/v - a/v^2 \qquad \text{;Guggenheim} \qquad (2.13)$$

Both of them are have two free parameters a, b (or bo). Usually, excluded volume b is determined either by using the relation

$$b = 2\pi Na\sigma^3/3$$

where Na is the Avogadro's number and $\sigma/2$ is radius of hard core of each molecule , or by matching a point of interest such as critical point.. The attraction parameter 'a' is evaluated primarily by matching points of interest. Guggenheim compared the accuracies of VDW, LHW and Guggenheim(G) with experimental data on argon. The comparison is given in Table 1 [14],where c denotes critical condition, t the triple point, Tb the Boyle temperature and vl the specific liquid volume at the triple point.

Table 1. Comparison of The Three Equations with Experimental Data of Argon

	VDW	LHW	Guggenheim	Experiments
(Pv/RT)c	0.375	0.36	0.36	0.29
Tb / Tc	3.375	2.68	2.72	2.73
vl / vc	0.377	0.302	0.303	0.374
Tt / Tc	0.350	0.535	0.528	0.557

2.2.2 The Equation By Whiting Et Al

Whiting and Prausnitz used the expression of Carnahan and Starling for the repulsion term, Alder's results for the attraction term and adopt Prigogine's assumption for the rotational and vibrational term to represent water. In the form of partition function Q, their ruslt is expressed as

$$Q = (1/N!)(V/\Lambda\ )^{N} (Vf/V)^{Nc}.\exp[-\Phi/2kT]^{Nc}.(q)int^{N} \qquad (2.14)$$

where N is the number of molecules in total volume at temperature T, Vf is the free volume, k is the Boltzmann constant,Λ is the de Broglie wavelength, and $\Phi/2$ is the potential energy per molecule and where c is the parameter to account for the rotation and vibration as introduced in Section 2.1.3. The free volume

$$\ln (Vf/V) = [3(\tau/\tilde{v})^{2} - 4(\tau/\tilde{v})]/(1-\tau/\tilde{v})^{2} \qquad (2.15)$$

where $\tau = \pi/\sqrt{18}$ and

$$\Phi/2kT = \sum_{n=1}^{2} \sum_{m=1}^{5} (Anm/T^{n} V^{m}) \qquad (2.16)$$

with $\tilde{T} = T/(eq/ck)$ and all other variables are defined in Eq.(2.7). By assuming that real water can be represented by a hypothetical mixture of monomers and dimers, Whiting and Prausnitz account for orientational forces due to the strong polar nature of water. This term is expressed in the form of the partition function Q of mixture and the details are shown in Appendix A of Reference 5. The resulting equation of state has in principle 8 adjustable parameters to fit experimental data. However, by using a set of simplifying assumptions, they reduced the number of parameters to 4. The final parameters are Tm*, Vm*, ΔHo and ΔSo, where the superscript * denotes characteristic values, subscript m represents monomers, and where AHo and ΔSo are the enthalpy and entropy of dimerization in the saturated state respectively. Incidentally, the parameters 'a' and 'b' are included in Vm*, and 'Anm' respectively.

For water, the equation gives the accuracy of within: 4.5% and 4.6% deviations of saturated liquid volumes and vapor volumes from the triple point to just below the critical point; 2.2% deviation of superheated volume; 0.1% deviation of saturated pressure, up to a temperature of about 1400F and a pressure of about 14000psia.

2.3 REQUIREMENTS AND DIRECTIONS FOR THE RESEARCH

2.3.1 Requirements

Before the detailed direction of the research is discussed, it seems proper to specify the requirements for the further development of equation of state, primarily from the previous review of historical backgrounds,but also partially from consideration of the intended use of the equation.

The criteria according to which the results must be judged may be stated as follows:

1) The properties generated by the resulting equation of state must be as accurate as possible for its level of complexity.

2) The equation of state must be as simple as possible for the economy of computation.

3) The equation of state should be able to acccurately represent water in the two phase region, since the intended use of the equation is mostly to anyalyze performances of steam turbine cycles.

4) It is preferred that all terms in the equation have identifiable physical significance.

5) The properties should be generated to be selfconsistent throughout the desired interval.

2.3.2 Direction

It was shown in Eq.(2.9) that the rotational and vibrational term became an additional repulsion term. Accordingly, Eq.(2.8) reduces to Eq.(2.3) with a resulting modified repulsion term. In addtion, it is obvious that the attraction term a(v,T) in Eq.(2.7) makes the equation of state much more complicated than constant 'a'. Thus, it appears to be worth attempting:

1) to improve the accuracy of equation of state by modifying the repulsion term; and
2) to improve the simplicity of the equation by keeping 'a' in the attraction term constant.

The improvement on the repulsion term would be made by modifying the repulsion terms introduced in Section 2.1 with empirical terms (even though they may not be clearly correlated to microscopic behavior of molecules).

Since thermodynamic properties generated by a thermodynamic potential function satisfy the Maxwell's relations, they are consistent with each other. Additionally, it can give smooth and continuous transition from one state to another as well as from one phase to another phase. Therefore, it is much more desirable to construct the equation of state in the form of thermodynamic potential function such as the Helmholtz free energy or alternatively the Massieu Potential Function(MPF). According to these considerations, the direction may be stated as:

> To construct an equation of state in the form of thermodynamic potential by making improvement on the repulsion terms in a macroscopic way.

CHAPTER 3

PROCEDURES OF DEVELOPMENT

In this chapter, thermodynamical relations regarding to the Massieu Potential Function(MPF) are briefly reviewed. Then they are expressed in terms of a set of reduced properties. After various MPF are assessed, the procedure of proposed improvement is given.

3.1 REVIEW OF THERMODYNAMICAL RELATIONS

3.1.1 Thermodynamical Relations

The Massieu Potential Function(MPF) $\tilde{J}$, which has been named after its originator, is defined as

$$\tilde{J} = S - U/T = -F/T \qquad (3.1a)$$

where S, U, F and T are respectively entropy, internal energy, Helmholtz free energy and absolute temperature. The negative Massieu function J is then

$$J = -\tilde{J} = F/T \qquad (3.1b)$$

By using the well known relation

$$P = -(\partial F/\partial V)_T \qquad (3.2)$$

and Eq.(3.1), where P is pressure and V is total volume, we obtain for temperature and internal energy the expressions

$$\tau P = (\partial J/\partial V)_T \qquad (3.3)$$

or

$$\tau P = \rho^2(\partial J/\partial \rho)_T$$

and

$$U = (\partial J/\partial \tau)_\rho \qquad (3.4)$$

where τ is the inverse of temperature and ρ is the density respectively. With Eq.(3.1a), the remaining expressions for properties can be expressed as

$$S = U/T - J \qquad (3.5)$$

and

$$G = H-TS = JT + PV \qquad (3.6)$$

where G and H are the Gibbs free energy and enthalpy respectively.

The negative MPF then can be used to completely construct the thermodynamic properties of the material.

3.1.2 Reduced Form Of The Thermodynamical Relations

The negative MPF for the VDW equation can be easily derived as

$$J/m = R \ln b/(v-b) - a/v/T + J_\tau/m \quad , \quad (3.7)$$

where the first term on the right hand side can be interpreted as repulsion term, the second as attraction term and the third term J_τ/m as a part of the MPF which is function of temperature only, with m and v, mass and specific volume of the material.

If the MPF and corresponding state equations are expressed in reduced forms, not only they become more compact, but also comparisons between different terms are easier. The reduced properties are defined as

$$y \overset{\Delta}{=} bo/v; \qquad (3.8a)$$

$$\underline{P} \overset{\Delta}{=} (bo^2/a)P; \qquad (3.8b)$$

$$\underline{\tau} \overset{\Delta}{=} (a/R\ bo)/T; \qquad (3.8c)$$

$$\underline{J} \overset{\Delta}{=} (J/m)R; \qquad (3.9a)$$

$$\underline{J_\tau} \overset{\Delta}{=} (J_\tau/m)R; \qquad (3.9b)$$

and

$$\underline{Jy} \overset{\Delta}{=} \underline{J} - \underline{J_\tau} \qquad (3.9c)$$

where $\underline{Jy}$ is a part of the reduced MPF excluding $\underline{J_\tau}$ and with bo the actual volume of one mole of molecules, given as

$$bo = Na\ (\pi/6)\sigma^3 = b/4$$

where $\sigma/2$ is radius of hard core, Na the Avogadro's number and b the excluded volume in the VDW equation. The corresponding thermodynamical relations for the reduced properties become

$$\underline{P} = y^2(\partial\underline{J}/\partial y)_{\underline{\tau}} \qquad (3.10)$$

$$\underline{u} = (\partial\underline{J}/\partial\underline{\tau})y \qquad (3.11)$$

$$\underline{G} = \underline{J} + \underline{P}/y \qquad (3.12)$$

$$\underline{s} = \underline{u}\,\underline{\tau} - \underline{J} \qquad (3.13)$$

$$\underline{h} = \underline{u} + \underline{P}/y \qquad (3.13)$$

3.1.3 The MPF In Reduced Form For Existing State Equations

The MPF's of the VDW, LHW, Guggenheim(G) and CS are

$$(\underline{J}y)_{VDW} = \ln(4y) - \ln(1-4y) - y\underline{\tau} \qquad (3.15)$$

$$(\underline{J}y)_{LHW} = \ln y - \ln(1-y) - y\underline{\tau} + (3/2)(1-y)^{-2} \qquad (3.16)$$

$$(\underline{J}y)_{G} = \ln y - \ln(1-y) - y\underline{\tau} + (1-y)^{-1} + (1/2)(1-y)^{-2} + (1/3)(1-y)^{-3} \qquad (3.17)$$

and

$$(\underline{J}y)_{CS} = \ln y + 2(1-y)^{-1} + (1-y)^{-2} \qquad (3.18)$$

The similarities and differences of the relationships are clearly displayed. The resulting expressions for the pressure-volume-temperature become

$$\underline{P}_{VDW} = [y/(1-4y)]/\underline{\tau} - y^2 \qquad (3.19)$$

$$\underline{P}_{LHW} = [y(1+y+y^2)/(1-y)^3]/\underline{\tau} - y^2 , \qquad (3.20)$$

$$\underline{P}_{G} = [y/(1-y)^4]/\underline{\tau} - y^2 \qquad (3.21)$$

and

$$\underline{P}_{CS} = [y(1+y+y^2-y^3)/(1-y)^3]/\underline{\tau} \qquad (3.22)$$

3.1.4 Assessment Of Equations In Terms Of Saturation Properties

One way to assess the accuracy of the formulations is to compare the predicted and measured saturation properties. The thermodynamical relations in saturation states are given as

$$Tf = Tg \qquad (3.23a)$$

$$P(vf,Tf) = P(vg,Tg) \qquad (3.23b)$$

and

$$G(vf,Tf) = G(vg,Tg) \qquad (3.23c)$$

where f and g designate saturated liquid and vapor. For the reduced variables defined in Eqs.(3.8), the saturated expressions become

$$\underline{\tau}f = \underline{\tau}g \qquad (3,24a)$$

$$\underline{P}(yf,\underline{\tau}f) = \underline{P}(yg,\underline{\tau}g) \qquad (3.24b)$$

and

$$\underline{G}(yf,\underline{\tau}f) = \underline{G}(yg,\underline{\tau}g) \qquad (3.24c)$$

Eqs.(3.23a)-(3.23c) with Eqs.(3.12),(3.19),(3.20) and (3.21) yield the saturation properties. The saturation curves of the VDW, LHW and water are compared in Figure 1 in reduced coordinates P/Pc and T/Tc where the subscript c denotes critical condition. In these coordinates, saturation properties are independent of the parameters 'a' and 'b'. As can be seen, the equation suggested by LHW improves the agreement considerably, even though there is still significant mismatch. This may be viewed as a positive aspect. That is, since the Eq.(3.16) gives better saturation curve than Eq.(3.15) by using one more term, it may be probable that a still better saturation curve might be obtained with a relatively simple equation of state.

3.1.5 Assessment In Terms Of Compressibility Factor

From Eqs.(3.8a),(3.8b) and (3.8c) it can be shown that the compressibility factor Z is

$$Z = Pv/RT = \underline{P}\,\underline{\tau}/y \qquad (3.25)$$

The corresponding expressions for the compressibility factors of the VDW, LHW and Guggenheim equations are

$$Z_{VDW} = 1/(1-4y) \quad - y\,\underline{\tau} \qquad (3.26a)$$

$$Z_{LHW} = (1+y+y^2)/(1-y)^3 \quad - y\,\underline{\tau} \qquad (3.26b)$$

and

$$Z_G = 1/(1-y)^4 \quad - y\,\underline{\tau} \qquad (3.26c)$$

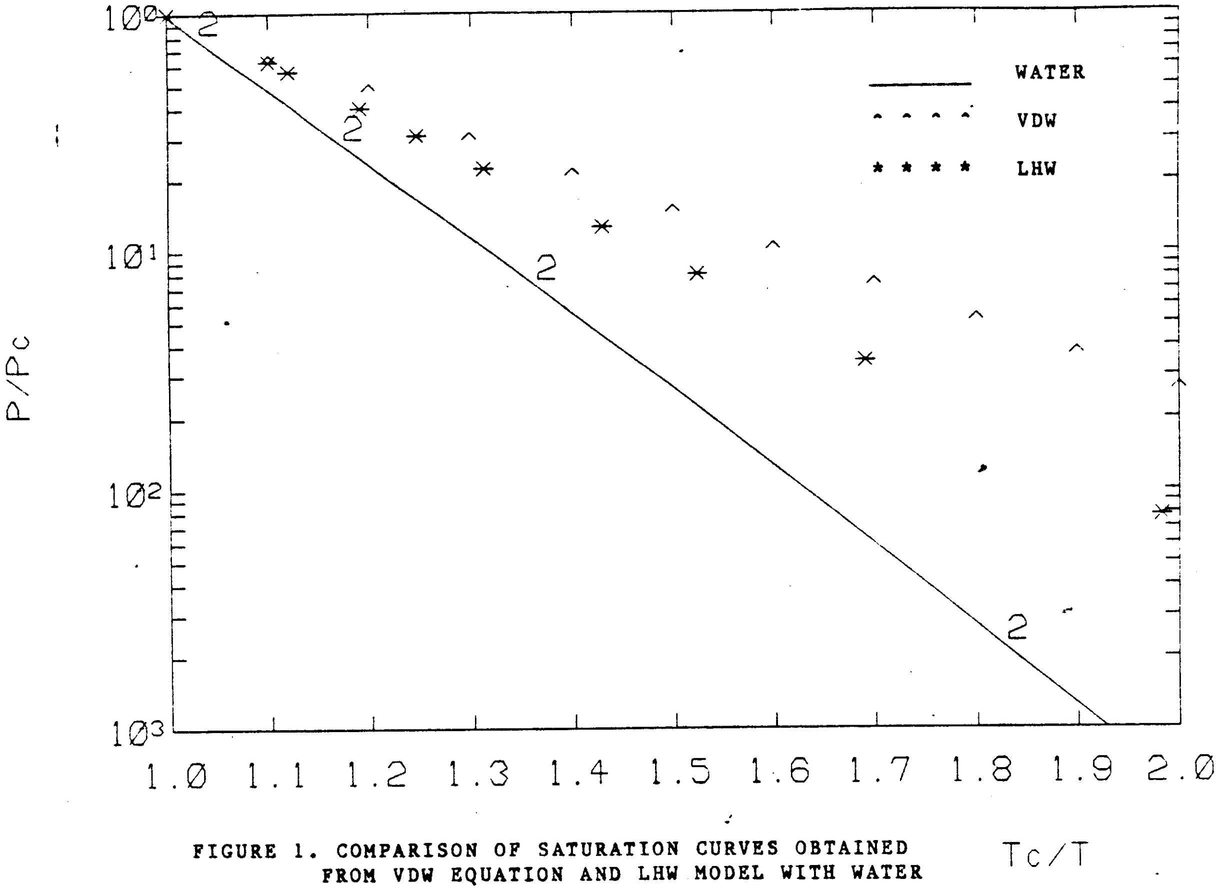

FIGURE 1. COMPARISON OF SATURATION CURVES OBTAINED FROM VDW EQUATION AND LHW MODEL WITH WATER

Each expression may be expanded in power series by using the relation

$$1/(1-x) = 1 + x^2 + x^3 + x^4 + \ldots\ldots\ldots ; \quad |x| < 1$$

The series expansions of the three equations are

$$Z_{VDW} = 1 + (4- \underline{\tau})y + 16y^2 + \ldots \qquad (3.27a)$$

$$Z_{LHW} = 1 + (4- \underline{\tau})y + 10y^2 + \ldots \qquad (3.27b)$$

and

$$Z_{G} = 1 + (4- \underline{\tau})y + 10y^2 + \ldots \qquad (3.27c)$$

Since the virial coefficients B, C, D ... are defined as

$$Z - 1 = B/v + C/v^2 + D/v^3 + \ldots$$

it can be shown from Eqs.(3.8a),(3.8c) and Eqs.(3.27) that the second virial coefficients, B of all the three equations are linear functions of inverse temperature, 1/T as

$$B = 4bo - (a/R)/T \qquad (3.28)$$

The second virial coefficient depends on values of 'a' and bo, which are determined, as described in Section 2.2.1, either by matching a point of interest or by theoretical calculations.

Measurements of water properties show that second virial coefficient of water is a complicated function of 1/T.[2] The second virial coefficient of the three equations in Eq.(3.28) is compared with water schematically in Figure 2. The comparison shows that Eq.(3.28) gives poor accuracy, especially in low temperature range. In fact, this aspect has been regarded as an intrinsic deficiency of the VDW-type equations in predicting the compressibility factor.

Since the proposed improvement in this study is to modify the

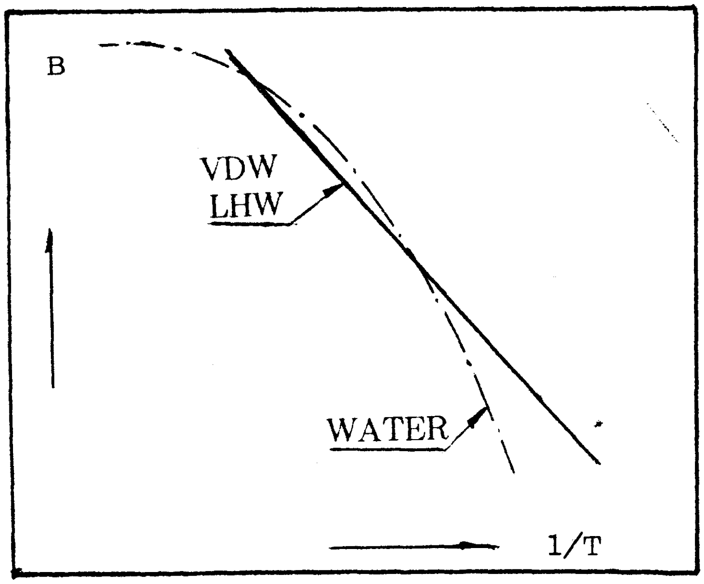

FIGURE 2. SCHEMATIC DIAGRAM OF THE SECOND VIRIAL COEFFICIENT

repulsion term with 'a' in the attraction term kept constant, the second virial has the same functional form as Eq.(3.28). Thus, the intended equation of state will have more or less the same deficiency in predicting the compressibility factor as the three discussed above. On the other hand, a significant mismatch in saturation data might be corrected without much sacrifice in the accuracy of compressibility factor. This point will be discussed later in Section 4.1.3.

3.2 PROCEDURES OF THE PROPOSED IMPROVEMENT

3.2.1 The Formulation Of A Generalized MPF

Observation of functional forms of various MPF's in Eqs.(3.15),(3.16), (3.17) and (3.18) suggested to Professor H.M.Paynter a generalized repulsion term in MPF, which is expressed as

$$\underline{J}_y = \ln y - \lambda \ln(1-y) + \sum_{i=1}^{n} \mu_i/(1-y)^i$$

For example, this equation reduces to the repulsion term of the following special equations:

VDW: $\lambda = 1$; $\mu_i = 0$ for all i

LHW: $\lambda = 1$; $\mu_2 = 3/2$; $\mu_i = 0$ for all other i

Guggenheim: $\lambda = 1$; $\mu_1 = 1$; $\mu_2 = 1/2$; $\mu_3 = 1/3$; $\mu_i = 0$ for all other i

CS: $\lambda = 0$; $\mu_1 = 2$; $\mu_2 = 1$; $\mu_i = 0$ for all other i

Defining $x \overset{\Delta}{=} 4y$, $\overset{*}{P} \overset{\Delta}{=} 16(b_o^2/a)P$ and $\overset{*}{\tau} \overset{\Delta}{=} 4(a/Rb_o)/T$, then the MPF of the VDW equation, Eq.(3.15) can be expressed as

$$\underline{J}y = \ln x - \ln(1-x) - x\overset{x}{\tau} \qquad (3.29a)\ (3{,}29a)$$

If it is noticed that the MPF

$$\underline{J}y = \ln y - \ln(1-y) - y\,\underline{\tau} \qquad (3.29b)$$

and Eq.(3.29a) yield the identical saturation curves in the normalized coordinates P/Pc and Tc /T and that the saturation curve of Eq.(3.16) is closer to that of water than that of the VDW equation, effect of $\mu_i/(1-y)^i$ in the repulsion term becomes clear. This effect is shown clearly in Figure 1. If the usual VDW attraction term is included, the general MPF becomes

$$\underline{J}y = \ln y - \lambda \ln(1-y) + \sum_{i=1}^{n} \mu_i/(1-y)^i - y\,\underline{\tau} \qquad (3.30)$$

The corresponding equation of state for pressure and compressibility factor are

$$\underline{P} = [y + \lambda y^2/(1-y)^2 + y^2 \sum_{i=1}^{n} i.\, \mu_i/(1-y)^{i+1}]/\underline{\tau} - y^2 \qquad (3.31)$$

$$Z = 1 + \lambda y/(1-y)^2 + y \sum_{i=1}^{n} i.\, \mu_i/(1-y)^{i+1} - y\,\underline{\tau} \qquad (3.32)$$

The theoretical basis of the MPF given by Eq.(3.30) may be open to serious questions, but its simplicity and descriptive ability make it attractive for further use, provided that it offers some advantages in trade-off for accuracy and computation time.

3.2.2 Procedures Of Selection Of Parameter

Eq.(3.30) has i+1 explicitly shown free paramenters. The approach is to choose values of i and, by use of the saturation data, to determine the best values of x and the i's. Comparison of the results for different values of i is then used to determine if there is a best value of i. The detailed procedures adopted may be summarized as follows:

1. Determine number of terms by examining the results for several values of i in Eq.(3.30).

2. Change step by step values of λ and μi's.

3. Obtain the critical point which is uniquely determined by the above set of parameters by solving the following equations simultaneously for yc and $\underline{\tau}c$, and $\underline{P}c$ accordingly,

   $$(\partial \underline{P}/\partial y)_{\underline{\tau}} = 0; \quad (\partial^2 \underline{P}/\partial y^2)_{\underline{\tau}} = 0$$

   where c designates the critical point.

4. Determine saturation curves by solving the following two equations for several $\underline{\tau}$'s between $\underline{\tau} = \underline{\tau}c$ and $\underline{\tau} = 2\,\underline{\tau}c$,

   $$\underline{P}(yf,\underline{\tau}) = \underline{P}(yg,\underline{\tau}); \quad \underline{G}(yf,\underline{\tau}) = \underline{G}(yg,\underline{\tau}) \qquad (3.33)$$

   where f, g designates saturated liquid and vapor respectively. Thus, obtain yf, yg and $\underline{P}$ for each $\underline{\tau}$.

5. Compare these sets of saturation properties with those of water for several $\underline{\tau}$ using the quantitative measure I, as

   $$I = \sum_{i=1}^{n} \left[1 - (\underline{P}/\underline{P}c)m \,/\, (P/Pc)w \right]^2 \qquad (3.34)$$

which represents deviations between the two, where m and w represent fluid model and water respectively.

6. Repeat the steps 2 to 6 until I becomes minimum.

For the procedures, an algorithm was implemented on the computer to solve the nonlinear equations

$$\underline{P}(yf,\underline{\tau}f) = \underline{P}(yg,\underline{\tau}f)$$

$$\underline{G}(yf,\underline{\tau}f) = \underline{G}(yg,\underline{\tau}f).$$

The program is listed in Appendix A. In addition, it may be emphasized that the above procedures were done independent of the values of the parameters a and b, since in the reduced form the saturation properties are independent of these.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 RESULTS

4.1.1 The Resulting Equation Of State

After executions of the procedures described in Section 3.2, it was found that neither increasing n in Eq.(3.30) to more than two, nor chosing λ other than unity improve the accuracy significantly, at least in terms of saturation properties. Thus any serious compromise between accuracy and simplicity is not required if the values of i=1, $\lambda=1$ and $\mu_i=9$ are selected. The MPF and the equation of state for pressure become as follows:

$$\underline{J}y = \ln y - \ln(1-y) + 9/(1-y) - y\underline{\tau} \qquad (4.1)$$

$$\underline{P} = [y/(1-y) + 9y^2/(1-y)^2]/\underline{\tau} - y^2 \qquad (4.2)$$

The corresponding saturation data are shown in Table 2 and compared with those of VDW equation and water obtained from KKHM steam tables. The present results are presented and compared with VDW results of the saturation properties and water graphically in Figures 3 and 4. As can be seen, the present results accurately represents the pressure vs. temperature behavior in the two phase region and are somewhat better than the VDW equation in predicting the pressure-volume relationship in the saturated states.

Since the equation of state of P generated by the general form of MPF in Eq.(3.31) reduces to that of ideal gas as density ρ (or y) become smaller, as should be the case, the behavior in this region is not shown in great detail here. The detailed discussion of compressibility and the second virial coefficient is given in Section 4.1.3.

4.1.2 The Other Parameters 'a' And 'b'

In principle, the excluded volume b in the VDW equation may be calculated from intermolecular motions. However, the large uncertainties in the knowledge of intermolecular motions of water make it more accurate to obtain b by fitting the P,V,T data at a proper point of interest. Then the other constants a and R are determined simultaneously from Eqs.(3.8a) and (3.8b). It may be noted that since the three parameters a,b and R are interrelated to each other, they are determined only by one point of fitting. The resulting relations are

$$b = 4bo$$

$$bo = v\ y$$

$$a = bo^{2}\ (P/\underline{P})\quad \text{and}$$

$$R = \underline{\tau}(a/bo)/T$$

TABLE 2. COMPARISONS OF SATURATION DATA

WATER

Tc/T	P/Pc	vf/vc	vg/vc
1.00	1.000	1.000	1.000
1.10	0.481	0.468	5.297
1.20	0.235	0.410	12.62
1.30	0.115	0.380	25.02
1.40	5.572×10^{-2}	0.362	50.53
1.50	2.679×10^{-2}	0.349	101.4
1.60	1.272×10^{-2}	0.340	204.2
1.70	5.966×10^{-3}	0.333	415.0
1.80	2.809×10^{-3}	0.328	852.6
1.90	1.263×10^{-3}	0.324	1775.

Tc = 1165.44R, Pc = 3204 psia, vc=0.05053 ft^3/lb

PRESENT RESULT

Tc/T	P/Pc	vf/vc	vg/vc
1.00	1.000	1.000	1.000
1.10	0.512	0.656	5.049
1.20	0.256	0.530	10.21
1.30	0.123	0.463	22.24
1.40	5.934×10^{-2}	0.420	45.56
1.50	2.731×10^{-2}	0.390	94.74
1.60	1.217×10^{-2}	0.367	202.1
1.70	5.262×10^{-3}	0.349	443.0
1.80	2.029×10^{-3}	0.334	1000.
1.90	9.203×10^{-4}	0.322	2325.

$\underline{P}_c = 2.0145 \times 10^{-3}$, $\underline{\tau}_c = 18.497$, yc = 0.1062

VAN DER WAALS EQUATION

T_c/T	P/P_c	vf/vc	vg/vc
1.00	1.000	1.000	1.000
1.10	0.675	0.615	2.227
1.20	0.508	0.540	3.440
1.30	0.317	0.499	5.045
1.40	0.222	0.473	7.100
1.50	0.156	0.454	9.874
1.60	0.110	0.440	13.58
1.70	7.748×10^{-2}	0.429	18.53
1.80	5.492×10^{-2}	0.420	25.18
1.90	3.896×10^{-2}	0.413	34.11

$\overset{*}{P}_c = 3.7037 \times 10^{-2}$; $\overset{*}{\tau}_c = 3.375$, xc = 0.3333

* subscript 'c' denotes the critical point;
$\underline{\tau} \triangleq (a/Rb_o)/T$; $y \triangleq b_o/v$; x=4y; $\overset{*}{\tau} = 4\underline{\tau}$

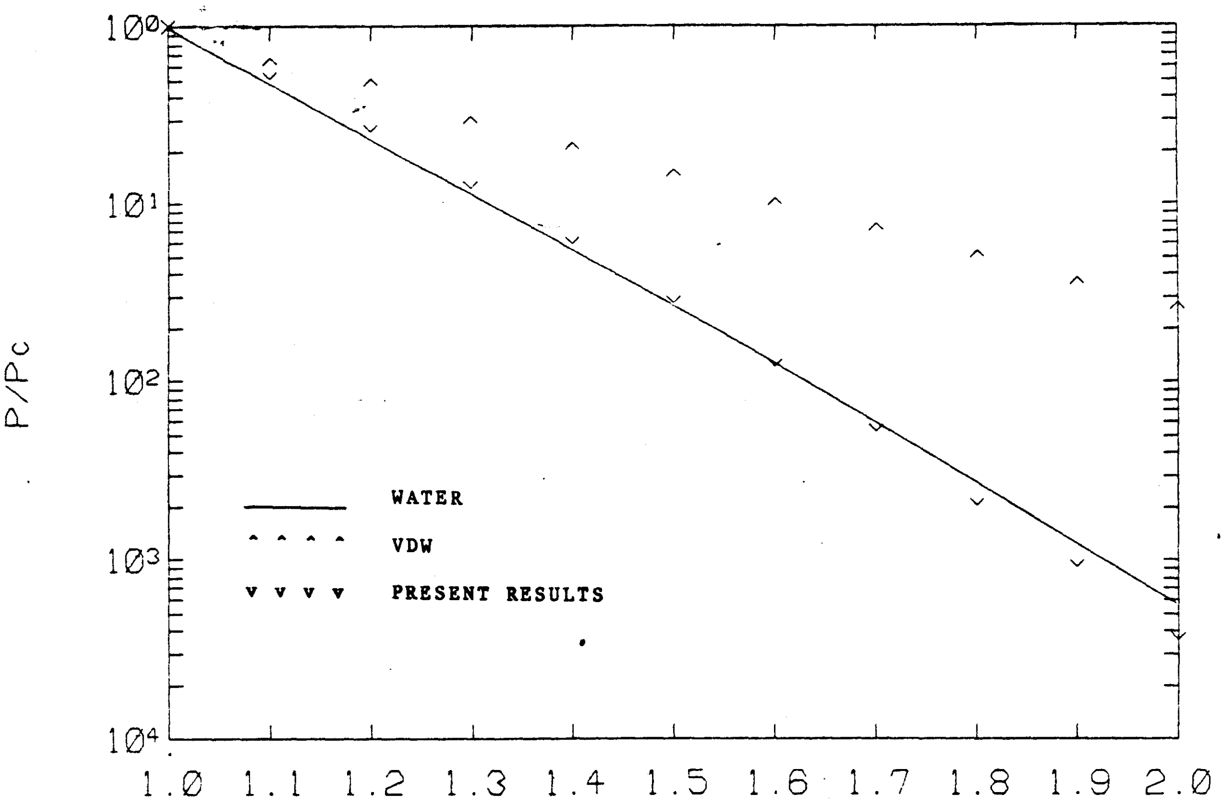

FIGURE 3. COMPARISON OF CALCULATED SATURATION DATA WITH PROPERTIES OF WATER, PRESENT RESULTS AND THE RESULTS OBTAINED FROM VDW EQUATION

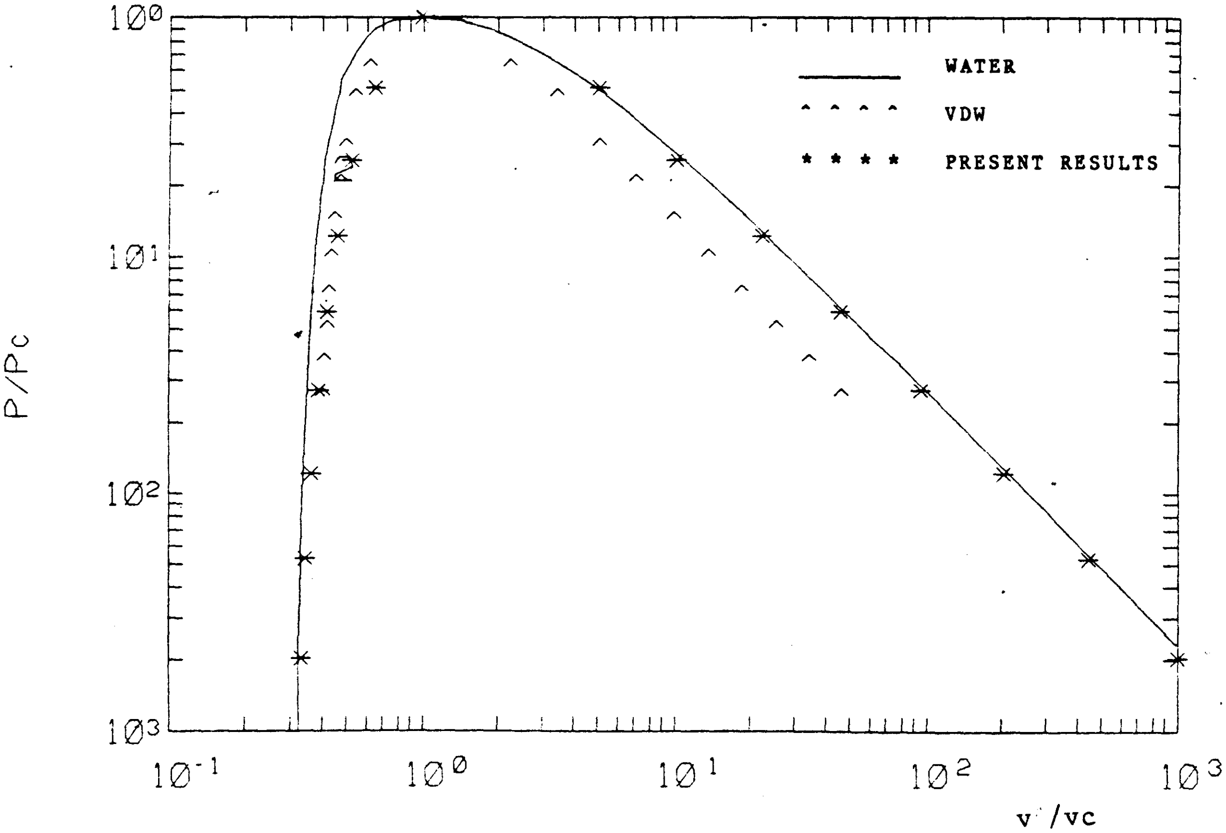

FIGURE 4. COMPARISON OF CALCULATED SATURATION DOME WITH PROPERTIES OF WATER, PRESENT RESULTS AND THE RESULTS OBTAINED FROM VDW EQUATION

where P,v,T were set properties of water at a certain state while $\underline{P}$,y and $\underline{\tau}$ were set reduced values in the MPF. One reasonable fitting points could be a state in superheated region where thermodynamical behavior of water approaches that of the ideal gas. Another would be a point on the saturation curve where the curve of water and that generated by the present equation cross. For the former case, when T=900 F and for the latter when Tc/T=1.56, the constants a,bo and R obtained are shown in Table 3.

Incidentally, the constant R may well be obtained from the relation:

$$R = \underline{R} / M$$

where $\underline{R}$ is the universal gas constant and M molecular weight. However, for the sake of consistency, it was determined by Eq.(3.8c). It can be observed in Table 3, however, that the two R′s are not much different, at least for the fitting points chosen either in saturated vapor region or in the superheated region. As can be predicted, the constant R gives better agreement when evaluated at a superheated (or gaseous) state than a saturated state.

Table 3. The Values Of Constants Obtained

	Superheated State Fitted	Saturated State Fitted
a (ft^4-lbf/lb^2)	1.4964×10^4	1.4184×10^4
(cm^4 - g/gm^2)	1.8854×10^7	1.7864×10^7
bo(ft^3/lb)	8.0848×10^{-3}	7.8267×10^{-3}
(cm^3/gm)	0.5044	0.4883
R (Btu/R-lb)	0.1103	0.1069
(J /K-gm)	4.622	4.476

$R = \underline{R} / M = 4.615$ (J / K-gm)

$\underline{R}$ = Universal gas constant; M = Molecular weight

4.1.3 Comparison Of The Compressibility Factor

The compressibility factor Z of the fluid model of Eq.(4.1) was calculated by using Eq.(3.32) and compared in Table 4 to the values for water as determined from KKHM steam table data.

Table 4. Comparison Of Compressibility Factor

$Tr=T/Tc$, $yr=y/yc$, $y=b/4v$

subscript c designates critical value

Tr	yr	Zwater	Zmodel
0.8	0.012	0.9760	0.9833
	0.065	0.8366	0.9103
1.0	0.010	0.9852	0.9910
	0.051	0.9266	0.9545
	0.104	0.8528	0.9085
	0.423	0.4994	0.6593
1.2	0.008	0.9930	0.9952
	0.085	0.9375	0.9527
	0.366	0.7627	0.8200
	0.816	0.6000	0.6940

To better display the discrepancies, the second virial coefficient B is derived for the present model. From Eq.(3.32), the compressibility Z is expressed as

$$Z = 1/(1-y) + 9y/(1-y)^2 - y\underline{\tau} \qquad (4.3)$$

As a power series, it is expressed as

$$Z = 1 + (10 - \underline{\tau})y + 19y^2 + \ldots \qquad (4.4)$$

From Eqs.(3.8a) and (3.8c), the second virial B becomes

$$B = 10bo - a/R/T \qquad (4.5)$$

By using the two sets of a,bo and R previously obtained, the corresponding second virial coefficients B1 and B2 obtained as

$$B1 = 4.960 - 5.9461\tau\ (\mathrm{cm}^3/\mathrm{g}) \qquad (4.6a)$$

$$B2 = 4.700 - 5.8183\tau\ (\mathrm{cm}^3/\mathrm{g}) \qquad (4.6b)$$

where B1 is for superheated water and B2 for saturated water, with

$$\tau \triangleq 1000/T\ \mathrm{K}$$

The empirically derived expression of the second virial equation for water suggested, in Reference 2, by Keyes is

$$B = 2.0624 - 2.81204\tau\ 10^{\gamma}\ (\mathrm{cm}^3/\mathrm{g}) \qquad (4.7)$$

where $\gamma \triangleq 0.1008\tau / (1 + 0.0349\tau)$

The three equations Eqs.(4.6a), (4.6b) and (4.7) are plotted in Figures 5a and 5b. Also values are tabulated in Table 5. Figure 5a shows a linear plot of B vs. c, while 5b shows a logarithmic plot.

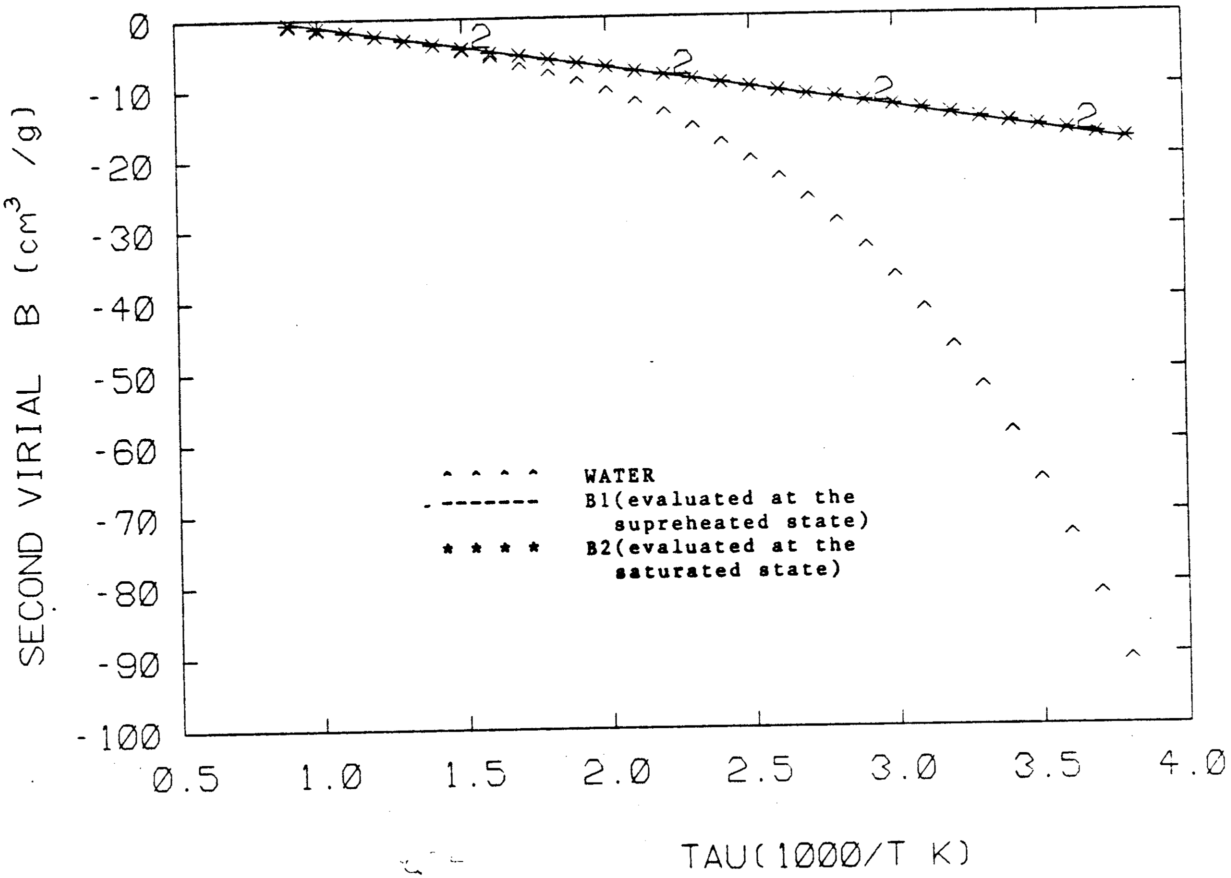

FIGURE 5a. COMPARISON OF THE SECOND VIRIAL COEFFICIENTS OF THE PRESENT RESULTS WITH WATER(LINEAR SCALE)

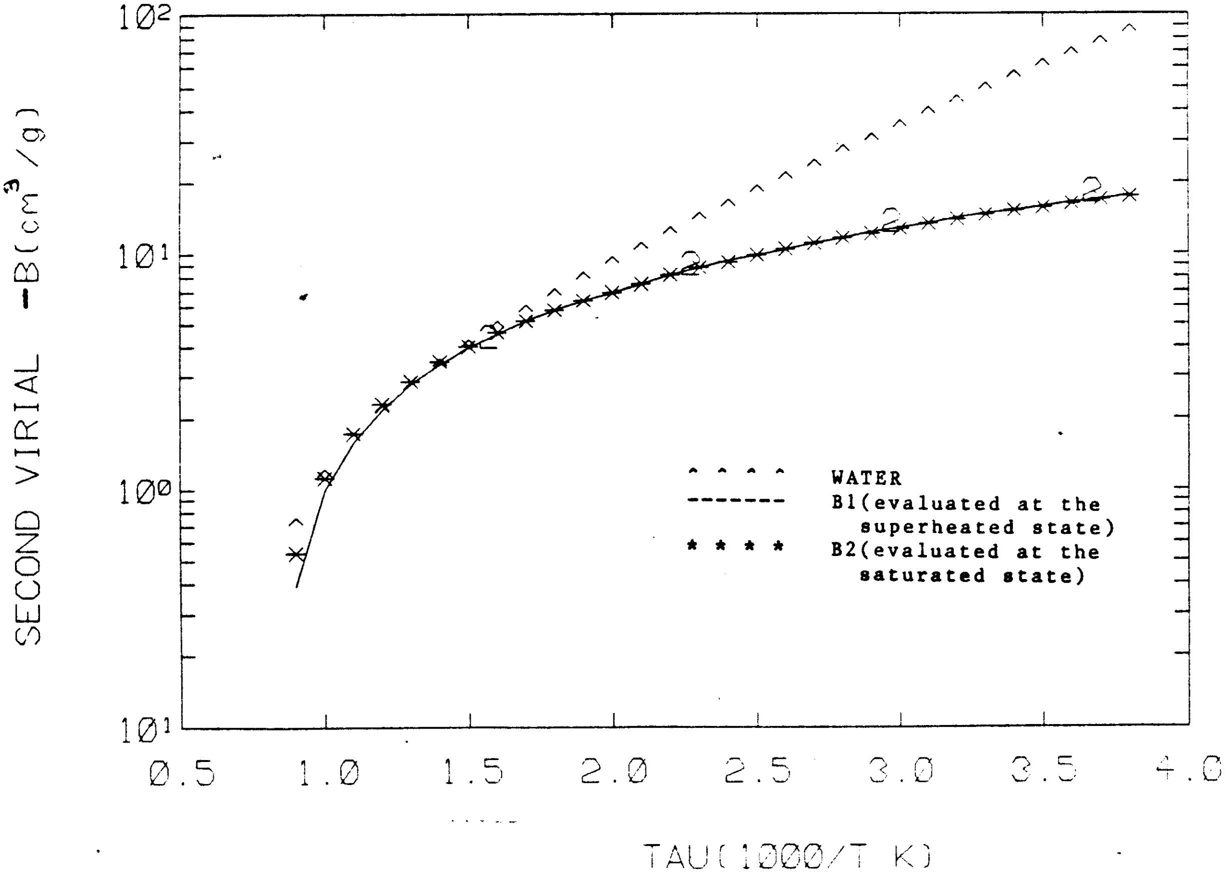

FIGURE 5b. COMPARISON OF THE SECOND VIRIAL COEFFICIENTS OF THE PRESENT RESULTS WITH WATER (LOGARITHMIC SCALE)

Table 5. COMPARISON OF SECOND VIRIAL B(cm^3/g)

(1000/T K)	(B)water	B1	B2
1.00	-1.21	-0.986	-1.12
1.40	-3.54	-3.36	-3.45
1.80	-7.18	-5.74	-5.77
2.20	-13.0	-8.12	-8.10
2.60	-22.1	-10.5	-10.4
3.00	-36.3	-12.9	-12.8
3.40	-58.0	-15.3	-15.1

The examination of the equation for the second virial coefficient obtained from the fluid model shows that the two selection techniques for a and bo do not significantly affect the compressibility factor. As has been mentioned previously, the equation of state constructed has an inherent deficiency in the compressibility factor at low temperature. It is not so surprising that the mere constant 'a' and its linear representation, Eq.(4.5) have such a deficiency when compared to the empirical expression of Keyes.

4.1.4 Techniques To Improve The Agreement Of Predicted Compressibility

One way to improve the compressibility factor would be to select a, b and R so that the deviation from measured data would be minimised for a certain temperature range. For instance, the linear regression

of the second virial between τ =0.8 and 3.0 gives

$$B = 17.32 - 15.98\,\tau\ (g/cm^3)$$

which is substantially different to the results obtained by fitting parameter points as represented by Eqs.(4.6). This requires considerably different values of a, bo and R, which will cause undesirable new inaccuracies both at the saturation states and superheated states. Thus improvements should be to incorporate additional terms with a different functional form. For example, Whiting et al[5] modified by adding an empirical term in the form of the Helmholtz free energy which is

$$Fsv = (d/Tr^{n}) \exp(-\lambda \rho) \quad , \qquad (4.8)$$

where Tr=T/Tc, d, n are constants which are determined from the second-virial-coefficient data, and λ is a positive constant for a better third virial coefficient. The correction term in Eq.(4.8) may be incorporated in Eq.(4.1) provided that it does not affect the computed saturation curve significantly. It may be worth attemptng for the future improvements of the equation of state in Eq.(4.1).

4.2 DISCUSSIONS

The new equation may be evaluated in terms of the criteria adopted, which were presented in Chapter 2.

Accuracy:

In the saturated region, for most of states from the critical point to about 1.5 atm., the agreement between calculated pressure and the KKHM steam table data is within 9%. In the superheated region, the agreements are within 1 %, with a temperature range from 200F to 1400F, a pressure range of 5 psia to more than 2000 psia.

Simplicity:

The equation has of four free parameters, which are a,bo,R and , and has only one more term than the VDW equation. In addition, it is easy to convert from one set of independent variables to another.

Saturation curve:

The present equation of state gives two phase region which is similar to water.

Physical Significance:

The theoretical basis of Eq.(3.30) and in particular the physical meaning of the term, 9/(1-y) are open to questions. It is difficult, so far, to relate them to the knowledge of intermolecular motion.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

A new equation of state for water in the form of Massieu Potential Function has been derived. The equation generates relatively accurate properties, considering its simplicity. As shown in Figures 3 , 4 and Table 2, it gives much more accurate values than the VDW equation even though it has only one more term. While it may not be adequate for calculations which require high accuracy, it may be useful when employed either for the analysis of transient response in a steam turbine cycle, where the Runge-Kutta method or a related method of solving nonlinear differential equations require simplified equation of state for the evaluation of various steam property derivatives. Further it may be employed as a reference function[6] for the further refinements. Finally, the simple closed functional form this equation of state allows explicit evaluation of formal derivatives, and this may be an advantage over the empirical equations with complicated functional form or tabulated data.

5.2 RECOMMENDATIONS

In the previous development of equation of state, it has been assumed that the excluded volume b is constant. However, Haar et al[6] showed that b depends on temperature. They obtained the expression of the parameter b by fitting to the steam table data. It is given as

$$b(T) = b' + c \ln \tilde{T} + d \tilde{T}^{-3} + e \tilde{T}^{-5}$$

where $\tilde{T} = T/647.073$ K and b′,c,d and e are empirically determined values. Note that since the saturated curve was obtained without regard to b, varying b with T does not change the basic shape of the curve. It would be worth attempting to examine whether and how much a variable b(T) can improve P-V-T relationship.

Another improvement might be to find an approximate representation to Alder's attraction term as represented in Eq.(2.7) by some mathematical means like least square fittings.

As suggested in Section 4.1.4, an additional term might be used to improve the accuracy of the compressibility factor.

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Appendix A

In saturated states, the relations in Eq.(3.21) hold. If Eq.(3.31) is combined with Eq.(3.24b), then

$$
\begin{aligned}
& yf - yg + \lambda (yf^2/qf - yg^2/qg) + \mu_1 (yf^2/qf^2 - yg^2/qg^2) + \\
& \quad + 2\mu_2 (yf_2/qf - yg^2/qg) + \dots \\
& \quad - \underline{\tau} (yf^2 - yg^2) \\
& = 0
\end{aligned}
\qquad \text{(A-1)}
$$

where $q \overset{\Delta}{=} 1-y$. Then

$$\underline{\tau} = \frac{yf - yg + (yf^2/qf - yg^2/qg) + (yf^2/qf^2 - yg^2/qg^2) + \dots}{yf^2 - yg^2} \qquad \text{(A-2)}$$

Besides, From Eq.(3.12) and Eq.(3.21), we can derive

$$\underline{Jf} - \underline{Jg} + \underline{\tau} (\underline{P}f/yf - \underline{P}g/yg) = 0 \qquad \text{(A-3)}$$

If we combine Eq.(A-3) with Eqs.(3.30) and (3.31), then

$$
\begin{aligned}
& \ln yf/yg - \lambda \ln qf/qg + \mu_1 (1/qf - 1/qg) + \mu_2 (1/qf^2 - 1/qg^2) + \\
& \quad - \underline{\tau} (yf - yg) + \underline{\tau} (\underline{P}f/yf - \underline{P}g/yg) = 0
\end{aligned}
\qquad \text{(A-4)}
$$

Then

$$
\begin{aligned}
& \ln (yg/yf)(qf/qg)^{\lambda} = \mu_1 (1/qf - 1/qg) + \mu_2 (1/qf^2 - 1/qg^2) + \\
& \quad + \dots\dots - \underline{\tau} (yf - yg) - ..
\end{aligned}
\qquad \text{(A-5)}
$$

If the right-hand-side of Eq.(A-5) is set X, then Eq.(A-5) becomes

$$yg = yf\ (qf/qg)^{\lambda} . \exp(X) \qquad \text{(A-6)}$$

Both Eqs.(A-6) and (A-2) constitute the algorithm, which are now

$$\underline{\tau}_i = \frac{yf_i - yg_i + \lambda (yf_i/qf_i - yg_i/qg_i) + ..}{yf_i^2 - yg_i^2} \qquad \text{(A-7)}$$

$$yg_{i+1} = yf_i\ (qf_i/qg_i)^{\lambda} . \exp(X_i)$$

where $i = 1, 2, ..$. Incidentally, yg can be determined empirically, by

$$yg_1 = e\ qf_1^2$$

where e is required to adjust. The usual values range from 0.1 to o.3

DEVELOPMENT OF A NEW EQUATION OF STATE
FOR WATER AND ITS APPLICATIONS

PART II

APPLICATIONS

ABSTRACT OF PART II

A new equation of state for pure water substance was applied to two problems associated with steam turbine cycle calculations, to evaluate the advantages of using the equation in the practical engineering situations. The evaluation was made primarily in terms of accuracy and computional speed, in comparison with another set of equations of state. This other set of equations follows a more standard development of equations of state for engineering calculations and, has 36 empirically determined coefficients for each combination of independent and dependent properties. In addition to the thermodynamic potential function describing the P-V-T behavior, it was necessary to determine the internal energy, enthalpy and entropy. This portion of the equation of state was constructed by incorporating the van der Waals expression and making a curve-fit to the Keenan- keyes-Hill-Moore(KKHM) steam table data.

The first problem was to determine thermodynamic states on the expansion line of steam partial loads. In this problem, the equations of state were used in a computer program, in conjunction with an empirical method by Spencer for evaluating the performance of steam turbines. The accuracy and computational speed with the two sets of equations of state were measured and compared.

The second problem was to simulate the transient behavior of a small part of a heat exchanger typical of steam cycle systems. The equations of state and conservation laws of were applied to model the dynamic characteristics of the component. The transient response, when subjected to load changes, was simulated using the program package DYSYS as implemented on a VAX 11/780. Comparisons of accuracy and computational speed were made for this problem, again using the two sets of equations.

The results show the advantage of the equations of state developed in this study. Compared to the more typical approach, the accuracy is equivalent or slightly better and the computational time is reduced by a factor from 2 to 6, depending on the particular problem.

Further computational advantages might be achieved by algebraic manipulation of the simple equations of state in the present study. Considering that their simple closed forms allow formal derivatives, that most terms are physically identifiable, the equations might find their usefulness in applications where functional dependences are needed and where the empirical equations with complicated expression can not be used. The accuracy of the equation of state for the internal energy would be improved by adding terms similar to those of the KKHM formulation, which should give more accurate enthalpy and entropy.

CONTENT OF PART II

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CHAPTER 1

INTRODUCTION

The equation of state in the form of the Massieu Potential Function (MPF) has been derived in Part I. The resulting equation of state was discussed in Section 4.2 of Part I, in terms of the criteria: accuracy, simplicity, identification of saturation curve and physical meaning of the equation.

In this part, the equation of state is applied to two practical problems associated with steam turbine cycle calculations. The primary reason for the application was to evaluate, in the practical engineering situations, the equation of state according to the above-mentioned criteria. The secondary reason would be to examine the feasibility of obtaining a useful scheme of computation which may be immediately used. The two problems for the application of the equation of state are:

1) the determination of states on the expansion line
   including the expansion line end point(ELEP) of
   steam turbines at partial loads; and

2) the simulation of transient behavior of a heat exchanger in a steam turbine cycle with the load changing.

The problems are chosen, because both of them require equation of state for the evaluation of steam properties. At the same time, the problems are more frequently encountered ones in practice and have their own importances in application engineering.

For the purpose of comparison, another set of equations of state was selected and used in parallel with the equation,of state obtained in this study. The set of equation of state was made at M.I.T. by Michael Packer and co-workers.[1] This equations of state have separate correlations for each combination of independent and dependent variables. Each correlation consists of 36 coefficients in the superheated region and 9 coefficients in saturated states, which were determined by fitting to the Keenan-Keyes-Hill- Moore(KKHM) steam table data. This set of equations can be taken as typical of that prepared by many people for engineering works and representing in their view a good compromise of accuracy, computational speed and programming time. Thus, it appears to be reasonable to select such equations for the purpose of comparisons.

For the evaluation of the computational efficiency, the computation times were measured in the two problems for each set of equations of state. The measuremets of CPU time were made by using a subroutine which is available in the Joint Computer Facility(JCF) at M.I.T.

Since the problems require the equations of states for such properties as internal energy, enthalpy and entropy, which the equation of state so far obtained in this study does not include, the equations of state for such properties are derived in Chapter 2. In Chapter 3, the application to the determination of ELEP is presented. Chapter 4 contains the simulation of transient behavior of a heat exchanger. Chapter 5 includes the discussions and conclusions of the part.

CHAPTER 2

NEW EQUATIONS FOR THE INTERNAL ENERGY, ENTHALY AND ENTROPY.

The equation of state was derived in the previous part in the form of the MPF $\underline{J}y$ in Eq.(4.1). The MPF yields the equation of state for pressure as a function of reduced temperature and reduced density y in Eq.(4.2). The Eqs.(4.1) and (4.2) of Part I are again

$$\underline{J}y = \ln y - \ln(1-y) + 9/(1-y) - y\underline{\tau} \qquad (4.1)$$

$$\underline{P} = [y/(1-y) + 9y^2/(1-y)^2]/\underline{\tau} - y^2 \qquad (4.2)$$

The MPF $\underline{J}$ has one more term $\underline{J}_\tau$ in Eq.(3.9) which is a function of temperature only. The term $\underline{J}_\tau$ accounts for the main portion of the internal energy and enthalpy as displayed in Eqs.(3.10) and (3.11). The relation may be expressed as

$$\underline{u} = (\partial\underline{J}/\partial\underline{\tau})y$$

or

$$= (\partial\underline{J}y/\partial\underline{\tau})y + (\partial\underline{J}_\tau/\partial\underline{\tau})y$$

or

$$\underline{u} = (\partial \underline{J}_\tau / \partial \underline{\tau}) y - y \tag{1}$$

and

$$\underline{h} = (\partial \underline{J}_\tau / \partial \underline{\tau}) y + \underline{P}/y - y \tag{2}$$

Since $\underline{J}_\tau$ is a function of temperature or equivalently τ only, the selection of $\underline{J}_\tau$ does not affect the P-V-T relationship which was already made. Thus, the $\underline{J}_\tau$ can be determined independently and separately, according to the required accuracy and to the range of applications. It is evident that the more the required accuracy and the broader the required range is, the more terms are needed. For instance, the Helmholtz free energy $\psi o(T)$ in the KKHM formulation consists of 8 terms, 6 of which are powers of 1/T, one of which is a term of ln T, the remaining one is a term of T(ln T). It is expressed as

$$\psi o(T) = \sum_{i=1}^{6} Ci/\tau^{i} + C_7 \ln T + C_8 (\ln T)/\tau \tag{3}$$

where $\tau = 1000\ R/T$ and $\psi o(T)$ is equivalent to J of the MPF formulation of state equations. On the other hand, the van der Waals(VDW) representation of $\underline{J}_\tau$ has only one term with

$$\underline{J}_\tau = c \ln \underline{\tau} \tag{4}$$

where c is a reduced specific heat at constant volume. The VDW's representation yields the internal energy from Eqs.(3.11) and (3.15) of Part I as

$$\underline{u} = c / \underline{\tau} - y \tag{5}$$

Considering that the internal energy for the ideal gas is given in the reduced variables as

$$\underline{u} = c\ /\underline{\tau} \qquad (6)$$

the Eq.(5) may be regarded as the simplest possible modification of the Eq.(6), which has a correctional term representing the reduced density y. This form for the internal energy has been known to be qualitatively accurate in representing the internal energy of some dense gases such as argon or carbon dioxide.[2] If the same $\underline{J_\tau}$ in Eq.(4) is used for the representation of internal energy in Eq.(1), the resulting equation of state for internal energy is of the same form as Eq.(5).

Although the pure water substance is different from argon or carbon dioxide, the Eq.(5) appeared to be a reasonable base upon which further improvement might be made. One way to determine the reduced specific heat c would be to make a least-square fitting to several steam table data of internal energy at superheated region where the influence of density y becomes negligible. A tentative value of c was determined by fitting ten states between temperatures of 700F and 900F with a pressure of 10 psia. The resulting value is c = 3.4362. Since 'c' denotes a reduced heat capacity, it is dimensionless. The value c and its corresponding equation of state for internal energy Eq.(5) were evaluated by generating enthalpy and entropy and by comparing with the steam table data. The resulting expressions of properties from Eqs.(3.8), (3.9) of Part I and Eq.(5) are

$$\underline{J} = \underline{Jy} + \underline{J_\tau}$$

$$= \ln y - \ln(1-y) + 9/(1-y) - y\underline{\tau} + c \ln \underline{\tau}$$

$$\underline{P} = [y/(1-y) + 9y^2/(1-y)^2]/\underline{\tau} - y^2$$

$$\underline{u} = c\ /\underline{\tau} - y$$

$$\underline{h} = \underline{u} + \underline{P}\ /y$$

and

$$\underline{s} = \underline{u}\,\underline{\tau} - \underline{J}$$

The relationships between the reduced and original properties are again

$$J/m = \underline{J}\,R + \text{constant}$$

$$P = (a/bo^{2})\,\underline{P}$$

$$T = (a/Rbo)/\,\underline{\tau}$$

$$v = bo\,/\,y$$

$$s = R.\underline{s}$$

$$h = (a/bo)\underline{h}$$

and

$$u = (a/bo)\underline{u}$$

where a, bo and R were determined in Section 4.1.2 of Part I, and had the values of

$$\begin{aligned} a &= 1.4964 \times 10^{4} \quad (ft^{4}\text{-}lbf/lb^{2}) \\ bo &= 8.0848 \times 10^{-3} \quad (ft^{3}/lb) \\ R &= 0.1103 \qquad\quad (Btu/R\text{-}lb) \end{aligned}$$

The properties generated by the above equations are listed and compared with the steam table data in Table 1. The ranges for 1% accuracy for properties are:

P = 5 psia to 2000 psia
T = 200F to 1400F for superheated vapor and
T = 100F to 400F for the saturated vapor.

Considering the accuracy that could be achieved with the selected c

Table 1. Comparison of Properties : The Present Equations of States with Steam Table

T = 300 F

(*) KKHM	p	10.0	20.0	50.0	(67.0)
	h	1193.7	1191.5	1184.4	(1180.2)
	s	1.8592	1.7805	1.6722	(1.6356)
PR	P	10.0	20.1	50.8	(68.4)
	h	1187.9	1187.1	1184.9	(1183.7)
	s	1.8527	1.7752	1.6714	(1.6375)

(*) KKHM: Steam Table Data
PR : Present Result

Units: P(psia)
h(Btu/lb)

T = 500 F

KKHM	p	10.0	20.0	50.0	100.0	200.0	500.0	(680.0)
	h	1287.7	1286.6	1284.0	1279.1	1268.8	1231.5	(1202.5)
	s	1.9690	1.8919	1.7887	1.7085	1.6239	1.4923	(1.4335)
PR	P	10.0	20.0	50.2	100.6	202.4	518.9	(722.0)
	h	1285.9	1285.4	1283.8	1281.1	1275.5	1256.5	(1242.5)
	s	1.9674	1.8905	1.7882	1.7096	1.6286	1.5115	(1.4648)

T = 700 F

KKHM	p	10.0	20.0	50.0	100.0	200.0	500.0	1000.0
	h	1384.0	1383.5	1381.9	1379.2	1373.8	1356.7	1324.6
	s	2.0601	1.9834	1.8814	1.8033	1.7234	1.6112	1.5135
PR	P	10.0	20.0	50.1	100.2	200.5	502.5	1011.5
	h	1383.9	1383.5	1382.3	1380.2	1376.0	1362.9	1338.5
	s	2.0601	1.9834	1.8816	1.8038	1.7248	1.6155	1.5233

T = 900 F

KKHM	p	10.0	20.0	50.0	100.0	200.0	500.0	1000.0
	h	1483.5	1483.2	1482.2	1480.5	1477.1	1466.5	1448.1
	s	2.1393	2.0627	1.9611	1.8838	1.8055	1.6987	1.6120
	p	2000	3000	4000				
	h	1407.6	1361.7	1315.2				
	s	1.5126	1.4414	1.3850				
PR	P	10.0	20.0	50.0	100.1	200.2	500.4	1001.6
	h	1481.9	1483.2	1480.6	1479.0	1475.7	1465.6	1448.1
	s	2.1381	2.0627	1.9598	1.8925	1.8042	1.6976	1.6114
	P	2010.8	3037.0	4100.0				
	h	1409.3	1364.6	1315.2				
	s	1.5129	1.4415	1.3769				

T = 1100F

KKHM	p	10.0	20.0	50.0	100.0	500.0	1000.0	2000.0
	h	1586.6	1586.3	1585.6	1584.5	1575.1	1562.9	1534.6
	s	2.2099	2.1334	2.0321	1.9551	1.7731	1.6908	1.5950
PR	P	10.0	20.0	50.0	100.1	500.5	1001.9	2113.0
	h	1580.0	1580.0	1579.0	1577.5	1566.7	1553.0	1521.6
	s	2.2053	2.1286	2.0272	1.9500	1.7670	1.6835	1.5850

and its corresponding equations of state, the value of c appears to be a good selection for the intended applications mentioned before, especially for the dynamic problem which usually requires less stringent accuracy than static problems. Since the selection of the value of c was made rather arbitrarily except for applying the least square fitting technique in a certain range of pressure, it can not considered to be the optimal choice. A better value of c might be expected if a more systematic study could be made. Addition of terms similar to those of the KKHM formulation would also improve accuracy. The above-quoted accuracy was calculated as

$$\%\ \text{accuracy} = 100 \times \frac{\text{Predicted Properties} - \text{Tabulated data}}{\text{Tabulated data}}$$

However, it should be noted that the accuracy of calculated in this way for the enthalpy and entropy may be less meaningful in engineering applications. In many engineering situations, what matters are changes in the enthalpy and entropy in a given process. A better way of evaluating the accuracy would be

$$\%\ \text{accuracy} = 100 \times \frac{\Delta(\text{Predicted data}) - \Delta(\text{Tabulated data})}{\Delta(\text{Tabulated data})}$$

where Δ represents the change of a property in a process. The accuracy evaluated in the latter way should give worse values. In the two problems, the accuracy was evaluated in the latter way.

CHAPTER 3

THE DETERMINATION OF THE EXPANSION LINE END POINTS

3.1 INTRODUCTION

One of the more frequently encountered problems in the steam power plant engineering is the determination of the expansion line end point(ELEP) of the turbine, or more generally, the states on the expansion line. The reasons are that:

1) the ELEP of higher pressure sections gives the inlet conditions of reheaters, while that of lower pressure section gives the inlet conditions of condensers; and
2) the ELEP and the states of stages in the turbine are used for the design of extraction lines and they give

necessary data for the prevention of reverse flows from the feedwater heaters.

Therefore, it is important to accurately determine the ELEP's and the states on the expansion line for the calculations of:

1) the heat balance(or the static performance) of a given steam turbine cycle at both design and partial loads; and
2) the dynamic response of heat exchangers such as reheaters and condensers.

To accurately and quickly determine the ELEP's or the states on the expansion line, the proper equation of the state is required. In addition to the equation of state, a reliable estimation of non-extraction performance(or efficiency) of the turbine is indispensible. Therefore, the methods for the estimation will be reviewed to some extent first, and the use of the equation of state will be discussed later.

3.2 THE METHODS OF ESTIMATION OF NON-EXTRACTION PERFORMANCE OF STEAM TURBINES

A. The Stage by Stage Method

The overall non-extraction performance of a turbine can be determined by calculating the performance of each individual stage and then by combining them. However, the stage by stage calculation method is not, in general, practical for predicting the performance of new designs in the stage of proposition, since the detailed knowledge of the particular turbine design is not available at that time. In addition, the method is usually long and tedious. Therefore, the method is not preferred except for a particularly unusual case.

B. The Empirical Methods

On the other hand, the overall performance of a turbine may be calculated by empirical methods which are based on observations and tests. More specifically speaking, it was observed from experiences that the performance of a turbine is closely related to the type of design and that the type of design is related, in turn, to the rating of the turbine as well as the steam conditions. Therefore, it was observed that the overall performance of the turbine is predictable to a certain degree, if the rating, the type of design and the steam conditions are given.

Warren and Knowlton used these facts to present a general method for the calculation of the overall performance of nonreheat turbine-generator units.[3] Elston and Knowlton extended the area of application by including reheat unit.[4] Hegetschweiler and Bartlett[5] improved the method by extending the prediction for the part load performance of nonreheat and reheat turbine. Spencer and Cotton[6] presented a method which is essentially a modified and updated version of the Hegetschweiler's method. That is, the area of application of Spencer's method is same, but the method is based on the updated experimental results of 24 performance tests in power plants, which were done according to the ASME Power Test Code No.6 requirements. In addition, the method is the more useful for the analysis of performance with a computer, since it provides mathematical expressions for computer applicatons. Spencer's method predicts the overall performance of modern steam turbine with an accuracy of less than 0.5% deviations.

Spencer's method predicts the efficiencies of a given turbine at each section both at the design flow and partial flows, if the following informations given:

1) volume flow;
2) pressure ratio of steam at a point or a stage of interest to the throttle pressure;
3) initial steam conditions at the governing stage; and

4) governing stage design.

The 'section' in this context means a group of similar stages. It is well known that modern large turbines frequently are composed of three sections: the high pressure, the intermediate and the low pressure section. The detailed formula and the procedures for the calculations are well described in Reference 6.

3.3 THE DETERMINATION OF THE ELEP'S

As mentioned before, the efficiencies estimated are used to determine the pressure and temperature of steam(or states of steam) at various stages and the expansion line end points(ELEP). However, it is not so simple to determine the states, because the pressures at the stages, in addition to efficiency, vary simultanously, as the flow rate of the steam(or equivalent load) varies. The phenomena are shown in Figure 1. Thus the states can be obtained by considering the variations of both the pressure and the efficiency.

Since the efficiency depends on the flow rate, it may be expressed as

$$E = E(w) \qquad (7)$$

where E is the efficiency of sections of the turbine and w is the mass flow rate. On the other hand, the efficiency E is defined as

$$E = (h1 - h2)/(h1 - h2s) \qquad (8)$$

where h1 is the inlet steam enthalpy at the section, h2 is the enthalpy of a state on the expansion line including the ELEP, h2s is the isentropic enthalpy at the pressure of the state P2. The

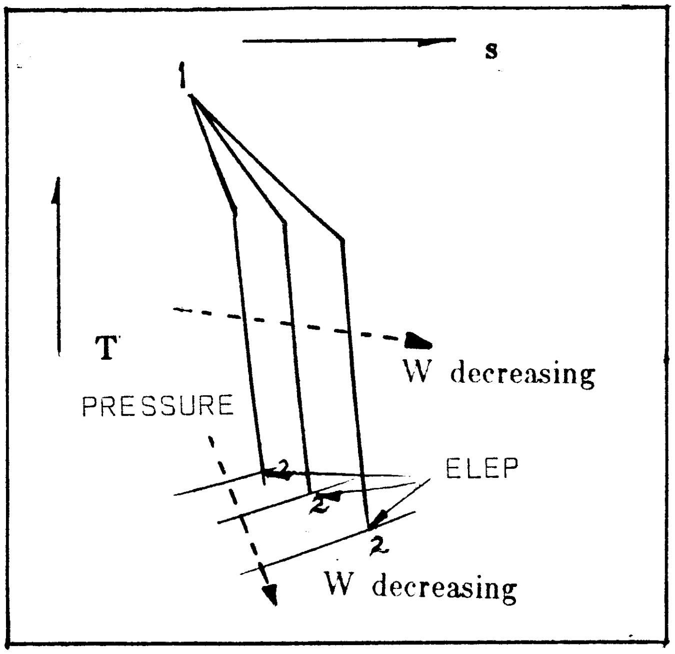


FIGURE 1. TURBINE EXPANSION LINE WITH CHANGES OF FLOW

isentropic enthalpy h2s is determined by the constitutive relation or the equation of state

$$h2s = h2s(s1,P2) \tag{9}$$

where s1 is the inlet entropy. Then the enthalpy of the state on the expansion line including the ELEP is given as

$$h2 = h1 - E(w)(h1 - h2s) \tag{10}$$

Meanwhile, the flow rate at the load gives another relationship between the pressure P2 and the specific volume v2 as

$$w = C1\sqrt{P2/v2} \tag{11}$$

or alternatively, gives the relationship between the pressure and the temperature as

$$w = C2\ P2/\sqrt{T2} \tag{12}$$

where C1 and C2 are the constants determined by the pressure ratio of the pressure at the state to that of the state at the next stage, as well as the adiabatic exponent k. The two relationships (11) and (12) hold for the perfect gas, when a pressure ratio is given. Even though the superheated steam is not a perfect gas, the two equations are valid provided that the values C1 and C2 are correct for the region under considerations.[7] Therefore the states on the expansion line including the ELEP are determined so that their thermodynamic properties might satisfy Eqs.(10) and (11) or alternatively Eqs.(10) and (12) simultaneously. Thus the determination of such states require iterative calculations of the two equations (10) and (11) as well as the estimation of properties at each iteration. To determine the states on the expansion line including the ELEP accurately and quickly a proper equation of state is required. Among the criteria mentioned before, the accuracy of the equation of state is more important than other factors in the problem of determining the ELEP. The simplicity is also valuable not that the computation becomes economical, but that the equation of state can be easily programmed and implemented to any computer. That is because the states to be determined including the ELEP are less than about 30; a few ELEP's, several extraction points and about 15 to 30 turbine stages. The computation time could be at most in the order of magnitude of 0.1 seconds in a modern minicomputer. At the same time, it is necessary for the computation scheme to be able to recognize in which phase a state lies, or equivalently where the saturation line is located.

3.4 THE PROCEDURES FOR THE COMPUTATION

By utilizing the relationships and discussions introduced in the previous sections, a scheme for the determination of the state on the expansion line including the ELEP can be set up. In the scheme, the input data are assumed to be:

1) The inlet steam conditions and the reheat pressure of the turbine;
2) The type and rating of the turbine; and
3) The pressures at states of interest at the design flow, including the pressures at the ELEP's of each section.

The detailed procedures adopted may be summarized as follows.

1. Determine efficiencies of sections of the turbine

at the design flow(or the rated load) Eo's by using Spencer's method, where the subscript o denotes the conditions at the design flow.

2. Determine the inlet steam conditions of the section of interest. If the section is the high pressure section, the inlet steam conditions given as the input data are the inlet conditions of that section. If the section is other than high pressure section, the steam conditions can be determined by using the equation of state and Eq.(10) successively.

3. Determine the isentropic enthalpy of the state of interest on the expansion line including the ELEP, by using the equation of state in Eq.(9) as

$$h2so = \psi\,(s1, P2o)$$

   where ψ denotes the equation of state, subscript 1 the inlet condition of the section, subscript 2 the state of interest in that section, while s denotes the isentropic path.

4. Determine the enthalpy of the state at the design flow by using Eq.(10) as

$$h2o = h1 - Eo(h1 - h2so)$$

5. Determine other properties at state 2, by using the equation of state as

$$T2o,\ S2o,\ v2o = \psi\,(h2o, P2o)$$

6. Determine the efficiency E(w) at the partial flow by using Spencer's method.

7. Guess a tentative pressure at state 2, P2

8. Determine the isentropic enthalpy h2s which corresponds to P2 and s1, by the equation of state as

$$h2s = \psi\ (P2, s1)$$

9. Determine the enthalpy at state 2, by using the Eq.(10) as

$$h2 = h1 - E(w)(h1 - h2s)$$

10. Since P2 and h2 are known, other properties can be determined by using the equation of state as

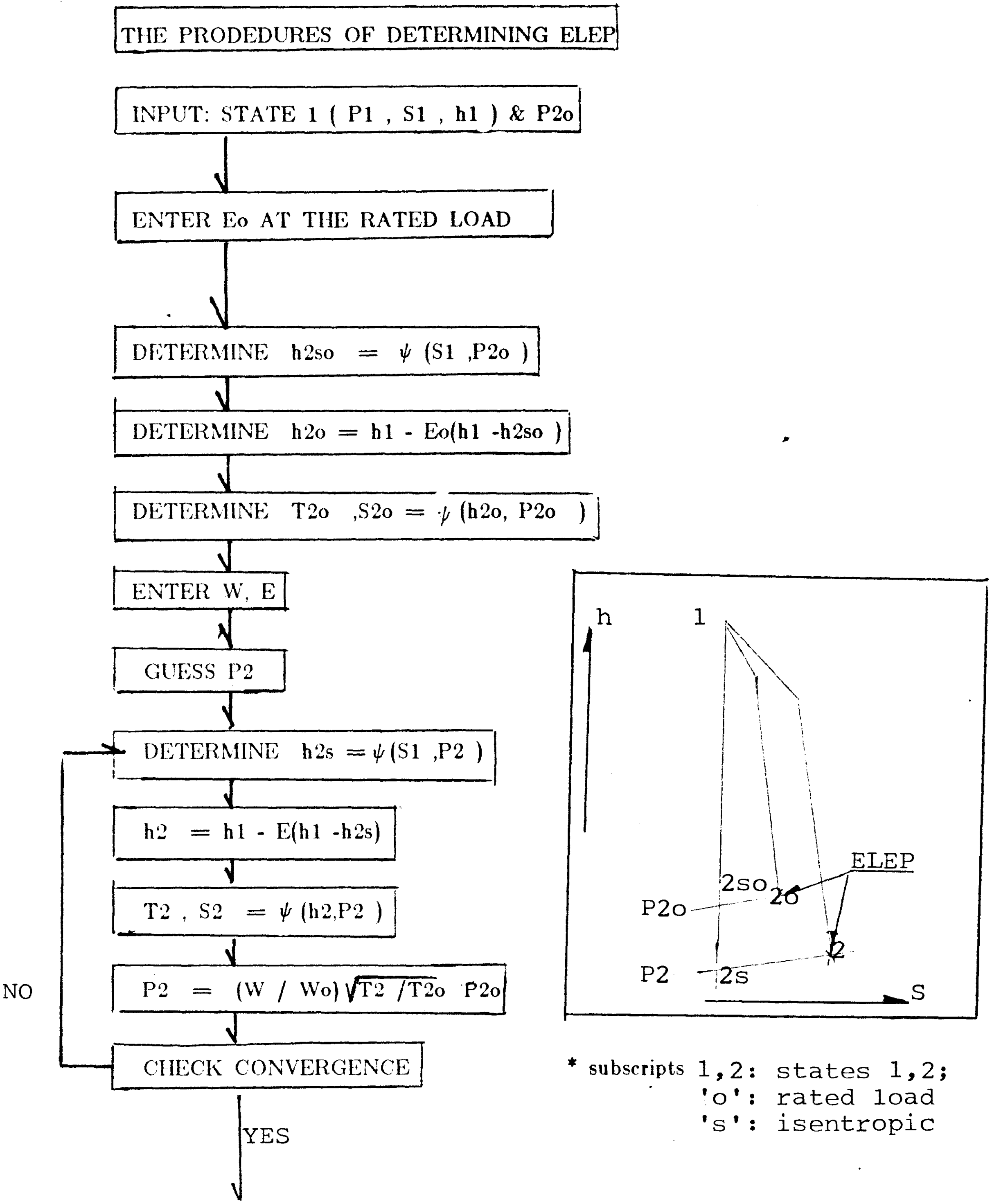
$$T2,\ s2,\ v2 = \psi\ (h2,\ P2)$$

11. By using the equation (12), update P2 such as

$$P2 = (w/wo)\sqrt{T2/T2o}\ P2o$$

12. Repeat procedures 7 to 10 until a satisfactory convergence is made.

The procedures are described in the flow chart in Figure 2



* subscripts 1,2: states 1,2;
'o': rated load
's': isentropic

FIGURE 2. THE FLOWCHART OF PROCEDURES DETERMINING ELEP'S

3.5 AN ILLUSTRATIVE EXAMPLE AND THE RESULTS

As an example of the application of the equation of state to the determination of ELEP, a relatively large turbine and corresponding steam conditions are given. The given conditions and basic assumptions are listed as follows.

(A) Turbine nameplate rating: 250,000KW

(B) Turbine Type: cross compound double-flow,
3600/1800 rpm,
43 inch last-stage backet, 247.6
sq. ft. total last-stage annulus
area.

(C) Steam Condition: Initial 2400psia, 1000F; exhaust
pressure 1.0in-Hg

(D) Estimated design throttle flow: 1,559,000 lb/hr

(E) Point of interest in expansion line and its pressure
at design flow: ELEP of high pressure section with
480psia at design flow

By using Spencer's method, the efficiencies of high pressure section at the design flow and partial flows are given in Table 2

Table 2 The efficiency calculated

w	efficiency
1.0	0.8495
0.9	0.8446
0.8	0.8305
0.7	0.8087
0.6	0.7808
0.5	0.7483
0.4	0.7128
0.3	0.6750

0.2 0.6392

w = perunit mass flow rate.

The calculation of efficiencies was made by using various formula given in Reference 6.

The ELEP are obtained first at design flow and then at four partial flows according to the procedures explained before. The properties are evaluated at two points: the one is the isentropic expansion line at the pressure of ELEP, the other is the ELEP as illustrated in Figure 1. In the former state, the enthalpy and other properties are evaluated for given entropy and pressusre, while in the latter state the temperature and other properties are evaluated for given enthalpy and pressure. The criteria for the convergence of iteration at partial loads were less than 0.1%.

Three methods were used to evaluate the steam properties:

1. the steam table by Keenan-Keyes-Hill-Moore,
   designated KKHM.
2. the equations of state obtained in this study,
   designated PR.
3. the equations of state by Michael Packer et al,
   designated MP.

The evaluation by looking up the steam table was made mainly to provide a reference data for the comparison of accuracy of the two sets of equations of state:the equations obtained in this study and the MP equations.

The computation time is not so important in this problem, because the total amount of CPU time required for determining all the necessary states in the expansion line of the larger turbine including the ELEP's would be at most in the order of magnitude of 0.1 seconds in a modern minicomputer. However, the CPU time was measured to compare the computational efficiencies, by using the FORTRAN subroutine 'JPI.FOR' in the Joint Computer Facility at M.I.T. More than 50 repetitions of the same program were made to get a reliable estimation of CPU time for each set of equations of state. The measurements for the two sets of equations were done at the same time when the computation load of the VAX-11/780 system is relatively small.

At partial flows of 40% and 20% of the design flow, the isentropic expansion lines fell into the two phase region. Both the sets of equations are able to recognize which phase a state belongs to. More specifically, these two sets of equations can compute the entropy of saturated vapor Sg for a given pressure; the present equations in this study can compute the entropy by making use of the algotithm in Appendix A of Part I, the MP equations by computing the function subprogram SGSAT(P).[1] Then the phase can be recognized by comparing the entropy of steam before the expansion (s1 in Figure 1) with the Sg. The criterion in Section 2.3 of Part I which requires the capability to give two phase region can be justified in this example.

The resulting ELEP's and the accuracies of the two sets of equations are compared in Table 3, the measured CPU times are also given. The equations of state obtained in this study give more accurate pressure, enthalpy and entropy than the MP equations, while the latter yields somewhat more accurate temperature. Considering that the more important properties are pressure and enthalpy in practice, the present equations are more useful. The average CPU time when using the present equations is 6 times shorter than that using the MP equations.

Table 3 The Expansion Line End Point Obtained with Three Methods of Generating steam Property Values and the cpu Time

The ELEP's Obtained with Three Formula

W	P (psia)	S (Btu/lb.R)	h (Btu/lb)	T (F)	
	480.	1.5609	1296.4	594.1	KKHM
1.0	480.(0.0)	1.5612(1.05)	1298.2(1.1)	573.9(3.4)	PR
	480.(0.0)	1.5711(36.0)	1308.3(7.2)	605.7(1.8)	MP
	376.2	1.5701	1280.4	551.8	KKHM
0.8	376.2(0.0)	1.5706(1.33)	1280.9(0.3)	532.5(3.5)	PR
	366.6(2.5)	1.5773(19.2)	1285.4(2.8)	554.4(0.5)	MP
	277.1	1.5903	1269.3	515.6	KKHM
0.6	277.6(0.2)	1.5911(1.39)	1270.3(0.5)	517.2(0.3)	PR
	261.7(5.6)	1.5924(3.64)	1265.7(1.9)	505.2(2.0)	MP
	181.4	1.6227	1260.3	480.9	KKHM
0.4	181.7(0.2)	1.6237(1.11)	1263.0(1.3)	481.7(0.3)	PR
	168.0(7.4)	1.6289(6.88)	1256.2(2.0)	470.6(2.1)	MP
	88.6	1.6830	1244.6	429.9	KKHM
0.2	89.0(0.5)	1.6841(0.73)	1247.6(1.4)	421.0(2.1)	PR
	79.5(10.)	1.6945(7.65)	1243.5(0.5)	424.8(1.2)	MP

* W = perunit mass flow rate

*The values in the parenthesis denote the % error from the KKHM steam table data

* % error of P, T = 100 x (predicted - tabulated)/tabulated value

* % error of h, s = 100 x [Δ(predicted) -Δ(tabulated)]/Δ(tabulated) where Δ represents the variation of properties in a process

* The three formula are denoted as:
KKHM: KKHM steam Table data, PR: The Present Equations of state
MP: The Equations of state by Michael et al.

The Average cpu Time Required for Each Calculations with The Two Sets of Equations

The Present Equations of state : 1.88 msec.
The MP Equations : 10.86 msec.

CHAPTER 4

THE APPLICATION TO THE SIMULATION OF A HEAT EXCHANGER

4.1 INTRODUCTION

One of important problems in the power plant engineering is the simulation of transient response of heat exchangers. This is important for the study of dynamic characteristics of a power plant when subjected to normal and abnormal disturbances.

The dynamic model of a heat exchanger requires a set of physical laws such as the conservation of mass, momentum and energy. The dynamic model also requires a set of equations of state to evaluate unknown thermodynamic properties with known properties at each time step.

Among the criteria, the simplicity of the equation of state is desired primarily for the economical reason. A typical simulation of transient response of a section of heat exchanger would require more than 1000 timesteps. An average dynamic model of a realistic problem might have more than 150 sections with 2 iterations per timestep. Since two or three steam properties must be evaluated at each iteration, 1/2 to 1 million steam property evaluations are required in this case. Thus economical computation is crucial in this problem. The accuracy is also important

In this section, a part of heat exchanger is selected as the system and the simple dynamic model is made under various assumptions. The transient response is simulated with this model first by the present equations of state obtained in this study and second the MP equations. The computation time and accuracy of properties are compared to evaluate the equation of state.

4.2 THE PROCEDURES OF MODELLING AND SIMULATION OF A SELECTED SYSTEM

System

A section of a heat exchanger in a steam turbine cycle was selected as the system (the control volume) to be analyzed. It is assumed that the section was so chosen that it can be regarded as 'a lumped parameter system'. For the selection of sufficient number of 'lumped sections' to adequately describe the 'distributed parameter system', various existing techniques and criteria can be used. However, since the main purpose of this study is to examine how the equations of state are applied to practical engineering situations, the lumping techniques and criteria are not treated here. A good review of these techniques and criteria appears in Reference 8.

Figure 3 shows a schematic diagram of the selected system, which is 'a representative tube' instead of bank of tubes.

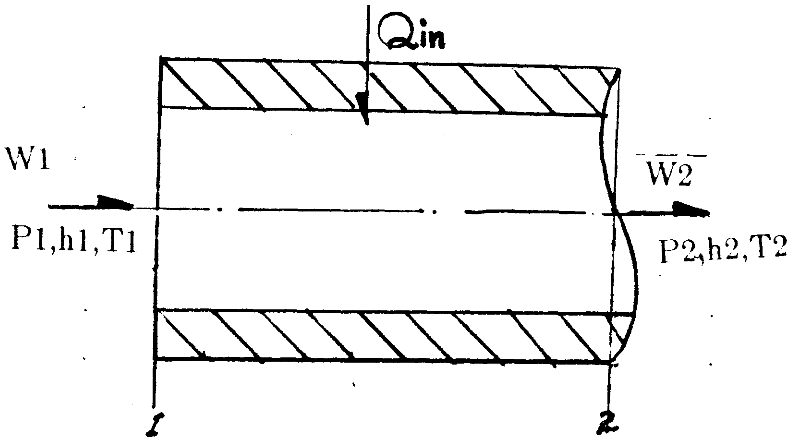


FIGURE 3. A SCHEMATIC DIAGRAM OF THE SYSTEM

Table 4 Properties and Parameters of System

Property	Section 1	Inside	Section 2
P(psia)	50	48	46
T(F)	500	600	600
h(Btu/lb)	1284.0	1332.9	1332.9
s(Btu/lb/R)	1.7887	1.8417	1.8464
u(Btu/lb)	1179.4	1216.9	1216.9
v(ft^3/lb)	11.305	13.055	13.627

with
W = 1000lb/s
Vcv = 4000 ft^3
Qin = 4.89×10^4 Btu/s

Some of data and thermodynamic properties necessary to describe the system at an equilibrium state correspond to a load point are listed in Table 4, where 'Qin' is the heat transfer rate from the tube wall to the system, 'Vcv' designates the control volume and 'W' is the mass flow rate. The size and capacity of the system roughly correspond to those of a section of the second reheater of modern larger steam turbine cycle (about 500 to 1000 MW), but are not a precise representation of a practical piece of equipment.

Modelling

By using the physical laws of mass, momentum and energy conservation as well as the equations of state and the constitutive relationship imposed by the turbine control valve, the system can be modelled. The governing equations are given in the section below.

Continuity:

$$Vcv\ d\rho/dt = W1 - W2 \qquad (13)$$

where subscripts 1 and 2 denote cross-sections 1 and 2, respectively.

Momentum:

$$P1 - P = K1\ W1^2 / \rho \qquad (14)$$

$$P - P2 = K2\ W2^2 / \rho \qquad (15)$$

where coeffiecients K1 and K2, determined from the given data in Table 4, are

$$K1 = 1.769 \times 10^{-7} \quad (ft^3 psi\ sec^2/lbm)$$
$$K2 = 1.532 \times 10^{-7} \quad (ft^3 psi\ sec^2/lbm)$$

Energy:

$$V_{cv}\, d(\rho u)/dt = W1\, h1 - W2\, h2 + Q_{in} \quad (16)$$

If the enthalpy and temperature inside the tube are assumed to be same as outlet properties h2 and T2, then Eq.(16) becomes

$$V_{cv}\, d(\rho u)\, dt = W1\, h1 - W2\, h + Q_{in} \qquad (17)$$

Equations of state:

Since the density and the product of density and internal energy are computed and known at each time step, the density and the internal energy can be selected as the independent variables. Then other properties are obtained by

$$P, h, T = \psi\, (\rho\, , u) \qquad (18)$$

where ψ represents the equation of state.

Constitutive relationship of control valve:

Since the steam generated from heat exchangers such as a superheater or reheater passes the turbine control valve, it is governed by a certain law imposed by control valve which is

$$W_c = C\, P_c/\sqrt{T_c} \qquad (19)$$

where C is a constant determined by the valve area and other factors; the subscript 'c' denotes the control valve. If there are other sections from the selected section to the turbine control valve, the pressure drop are summed from P to Pc to yield another equation by summing Eq.(15) and the same equations in the subsequent sections. If it is assumed,for the sake of simplicity, that the selected section is the last section before the control valve, then the Eq.(19) becomes

$$W2 = C\ P2/\sqrt{T2} \qquad (20)$$

where C ,determined from the given data, is

$$C = 707.78\ (\mathrm{lb}\ R^{1/2}/\mathrm{psia\ sec})$$

Eqs.(15) and (20) give the relationship

$$W2 = \sqrt{\beta \rho T\ /2}\ [\ (1+4P/k2\beta^{2}\rho T)\ -1] \qquad (21)$$

where $\beta = 1/(C\ K2)$

W2 is determined iteratively so that it may be compatible with thermodynamic properites. Additional assumptions which were made implicitly are:

(1) The properties inside the tube are well mixed and uniform.
(2) The effect of gravity are negligible and the flow is one directional.
(3) The heat transfer rate Qin is controllable.

Simulation

One of the inputs or disturbances to the system can be the incoming mass flow rate which represents changes or variations of load in the cycle. The inlet mass flow rate was chosen as a ramp input which increases 10 % in 5 minutes; i.e.

$$W1 = Wo + a\ t$$

where Wo = 1000 lb/sec and a = 0.3333 $\mathrm{lb/sec}^{2}$.

The simulation of the model of the system was made by using the program DYSYS (DYnamic SYstem Simulator) within the Joint Computer Facility(J.C.F.) at M.I.T. The program solves the time response of systems described by a set of ordinary differential equations with the fourth order Runge-Kutta method. The user supplied subroutine called EQSIM was used to describe the system with governing equations (14) through (21). At each time step, the governing equations were computed four times to ascertain adequate convergence of W2 (mostly within 0.1 %).

The two sets of equations of state were used to evaluate the properties in Eq.(18). However the MP equations do not have the correlations in Eq.(18). Meanwhile, the equations of state in the present study predict the pressure and temperature P,T with independent variables ρ, u with an accuracy of better than 0.5% inside the range of computation, which is less than the upper limit of error(1%) in the MP equations.[1] Thus the equations of state in this study were substituted for the missing relationships. More specifically, at the inlet section 1, the missing relationship

$$T1 = \psi(\rho_1, u1)$$

was substituted. Then the enthalpy was evaluated by the existing correlation in the MP equations,

$$h1 = \psi(P1, T1)$$

while, inside the tube, the missing relationship

$$P = \psi(\rho, u)$$

was substituted and then the enthalpy h was calculated by

$$h = u + P/\rho$$

Temperature only could be obtained by the existing correlation in MP equations

$$T = \psi(P, h)$$

The time step was kept less than 0.5 seconds. Otherwise, the solution diverged in the simulation, owing to the nonlinear governing equations.

4.3 THE RESULTS

The transient response of the system when subjected to the ramp input was computed and plotted in Figures 4 and 5. Figure 4 shows the transient response of pressure inside the tube, and Figure 5 shows the response of temperature and the ramp input, which is the incoming mass flow rate. In the figures, simulations using each set of equations of state are plotted together to compare them. To force stronger transient response, a simulation ,with the control volume exaggerated 100 times, was made by using the equations of state in this study and the results are plotted in Figures 6 and 7. The Figures 6 and 7 show that the system behaves like a typical linear second order system with a damping ratio of about 0.5. The results may be discussed according to the two criteria;the accuracy and the computational efficiency.

The Accuracy:

It is hard to examine the absolute accuracy of the properties, because there is no proper reference data available for comparisons. Instead, the relative discrepancies between the two sets of equations of state were calculated by comparing the intermediate states between the initial state and final state. The agreements are mostly less than 0.1% and no more than 0.5% . Also the thermodynamic consistency was checked at the final state (or another equilibrium state) by comparing the resulting values of enthalpy in the simulation with the value obtained by letting d(properties)/dt =0. The agreements are better than 0.5% in both cases.

The Computational Efficiency:

Since the CPU-time measuring subroutine (JPI) was not working

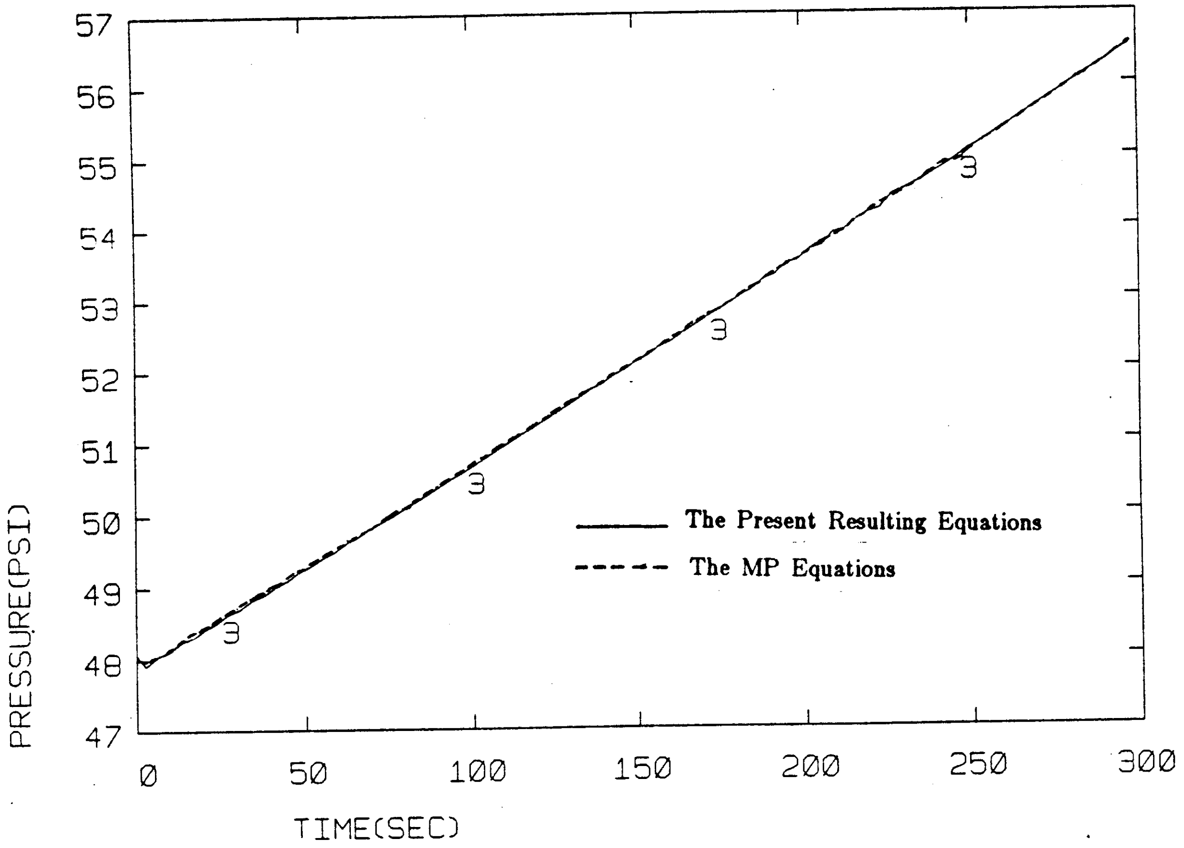


FIGURE 4. COMPARISON OF TRANSIENT RESPONSES OF PRESSURE INSIDE THE SYSTEM

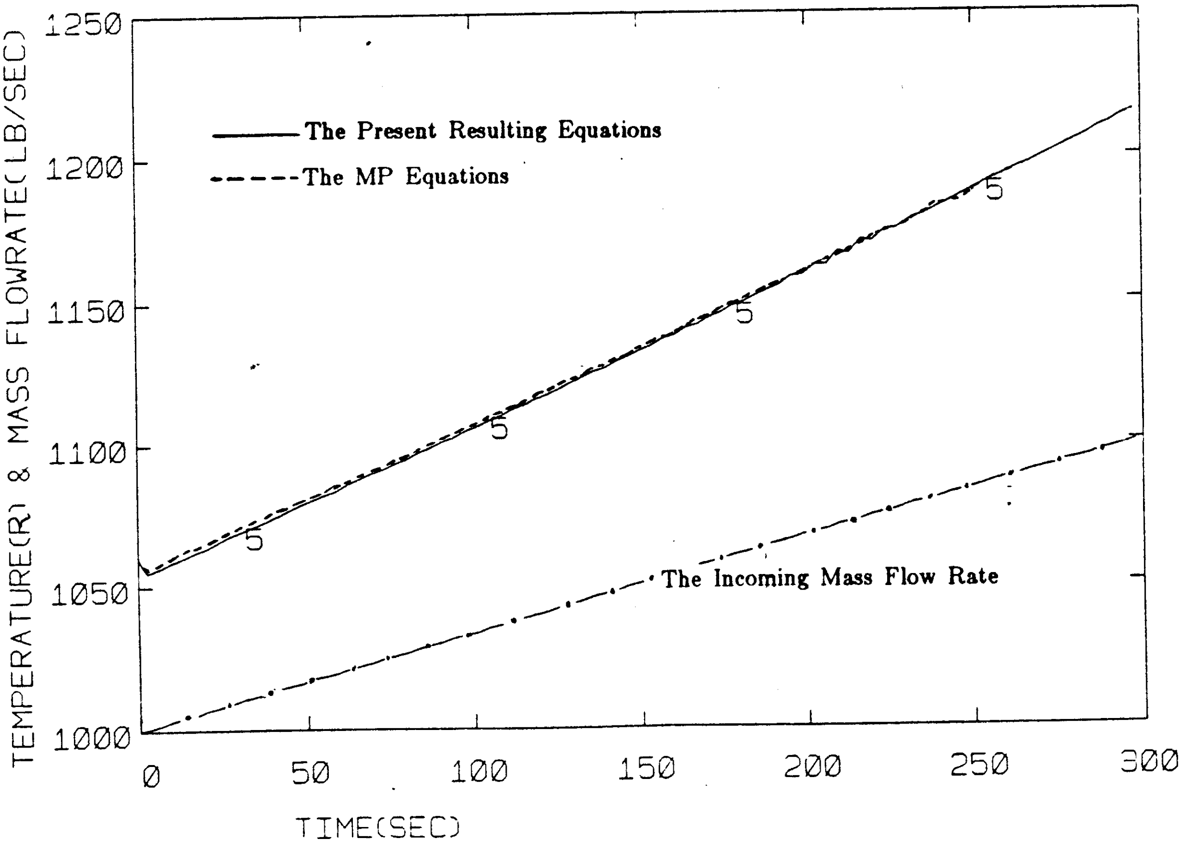


FIGURE 5. COMPARISON OF TRANSIENT RESPONSES OF TEMPERATURE INSIDE THE SYSTEM

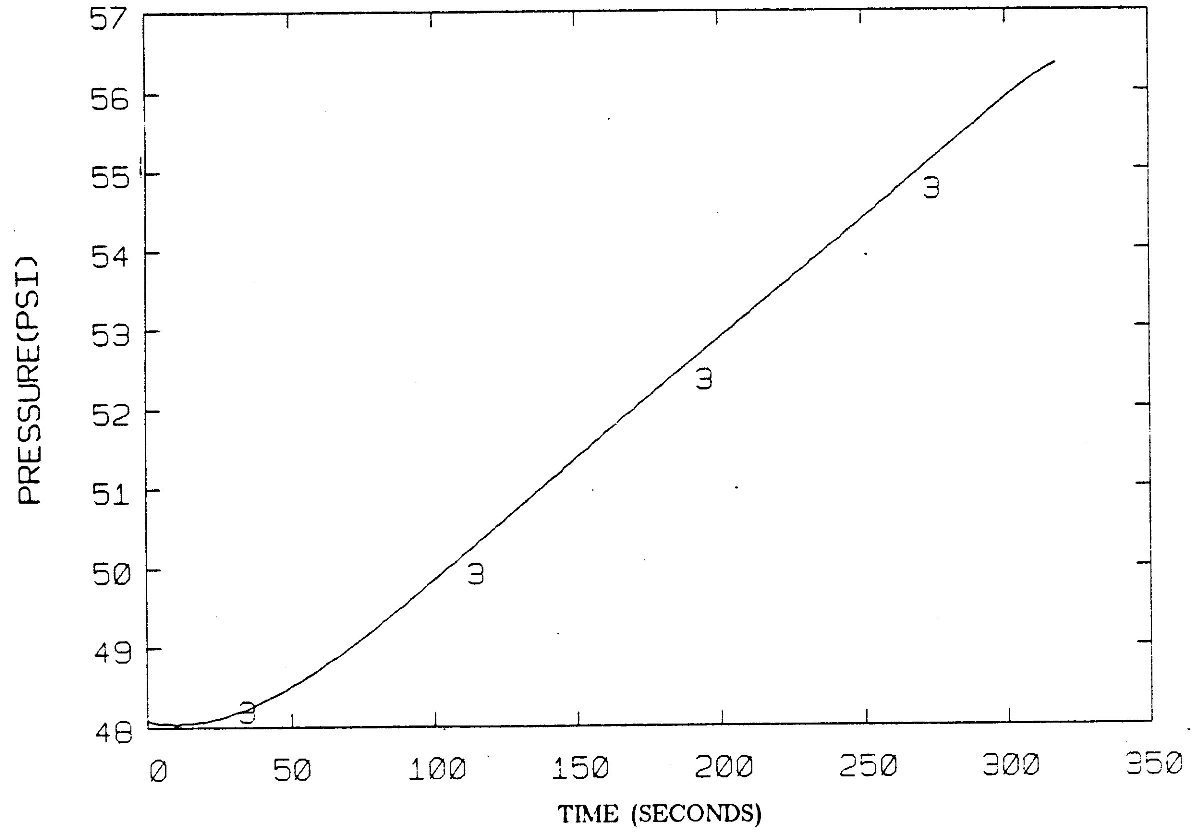


FIGURE 6. TRANSIENT RESPONSE OF PRESSURE WITH EXAGGERATED CONTROL VOLUME

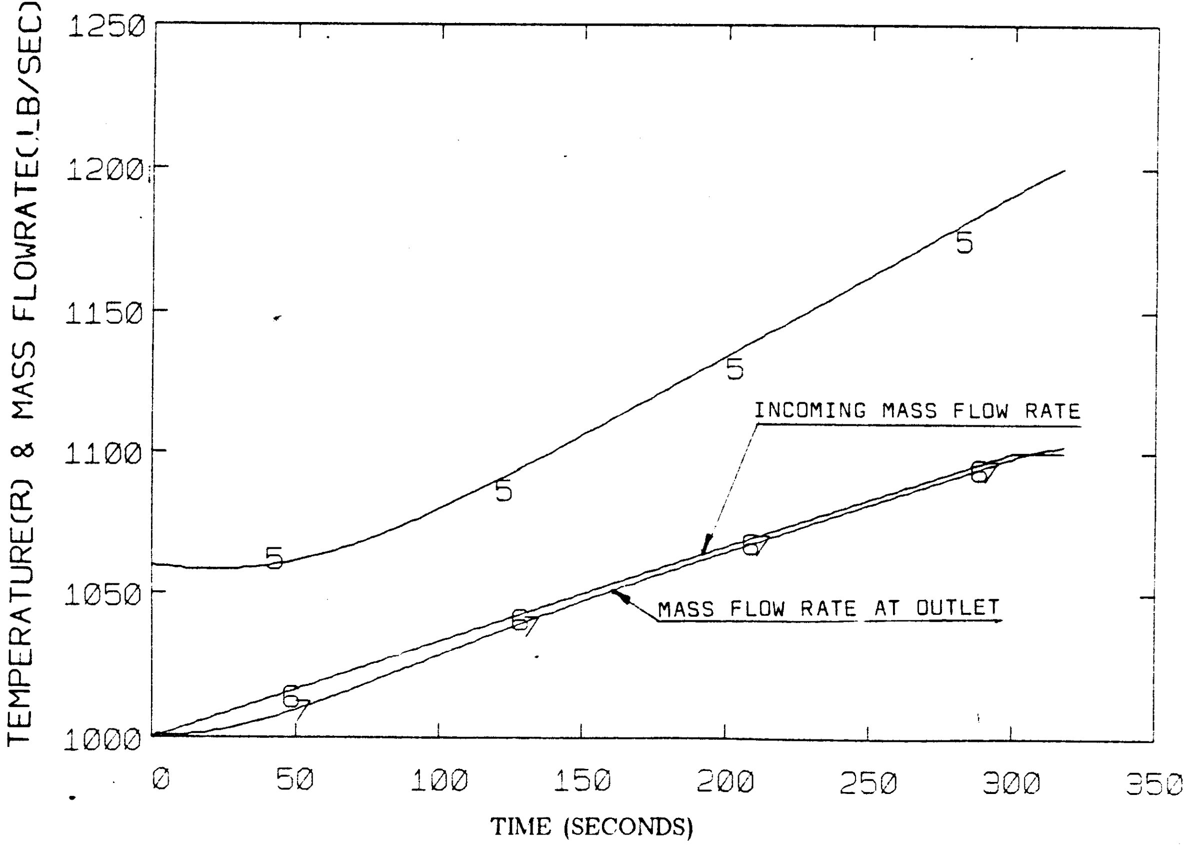


FIGURE 7 TRANSIENT RESPONSE OF TEMPERATURE WITH EXAGGERATED CONTROL VOLUME

with the program DYSYS, the subroutine EQSIM which calculates the properties at each time step was separated into a DO-loop of a simple main program and repeated 200 times. The measured CPU times are 36 msec with the present equations of state obtained in this study and 70msec. with the MP equations. Therefore, the computational efficiency with the former is about twice higher than that with MP equations.

CHAPTER 5

CONCLUSIONS

In this study, the equations of state were applied to the problems associated with steam turbine cycle calculations. The purpose for the applications is to evaluate the equations of state in terms of the criteria: the accuracy, the simplicity as represented by computational speed and identification of the saturation states. The equations of state obtained in the present study were assessed by comparing with a typical set of empirical equations developed by Packer et al.[1]

In the problem determining the ELEP's, the accuracy achieved by the present equations of state is somewhat better than that by the fully empirical equations of Packer. This is encouraging, especially considering that the equations of state have only 5 coefficients; a, bo, R, μ and c, while the empirical equations have 36 coefficients for each correlation. The computational efficiencies were compared by measuring the CPU time of the computer. The CPU time for the property calculations alone as required with the present equations is about 6 times less than with the method of Packer. Both equations have the capability to recognize the saturation lines. This capability was required when the isentropic expansion line fell into the two phase region.

A simple heat exchanger problem was used to investigate the performance for transient calculations of steam system performances. The results of measurements indicate that the simulation with the present equations of state requires about half of the CPU time than with the empirical equations. Although the result is not as dramatic as expected, it is still significant. The comparison of the accuracy with each other indicates that the results are equivalent. Further computational advantages might be achieved by algebraic manipulations of the present equations of state.

The results clearly show the advantages of employing the present equation of state rather than developing a set of curve-fits to each property: accuracy is slightly better or equivalent and computation time is reduced by a factor of 2 to 6 depending on the particular problem being invetigated. It may be concluded that the present equations of state can be utilized effectively in certain classes of problems as demonstrated in this study, owing to the accuracy and simplicity as well as the intrinsic ability to recognize the two phase region. Thus it may be also concluded that the purpose and criteria for developing the present equations of state can be considered relevant in the practical engineering situations.

Considering that the present equations of state yield relatively accurate properties with a simple functional form, it would not be hard to expect that the further improvements may be made on the basis of these equations of state. The improvements could be made by adding a few terms to the equation representing the internal energy such as

$$\underline{u} = c1/\underline{\tau} + c2/\underline{\tau}^2 + \ldots - y\,.$$

which should give more accurate internal energy, enthalpy and entropy than the equation

$$\underline{u} = c/\underline{\tau} - y.$$

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