

the film thickness were compared with experimental data.

It was found that the three-dimensional solution gave more accurate information on the film thickness. However, the one-dimensional solution predicts the film thickness reasonably well at the small value of  $Q^+$ .

### Nomenclature

$B$  = dimensionless coefficient in polynomials  
 $b$  = dimensionless coefficient in polynomials  
 $F$  = dimensionless radial velocity  
 $G$  = dimensionless tangential velocity  
 $H$  = dimensionless axial velocity  
 $K = \tau_y / 2\rho r\omega(\nu\omega)^{1/2}$ , dimensionless parameter  
 $Q$  = flow rate  
 $Q^+$  = dimensionless flow rate  
 $r$  = radial coordinate  
 $u$  = radial velocity  
 $v$  = tangential velocity  
 $w$  = axial velocity  
 $z$  = axial coordinate

### Greek Letters

$\mu$  = viscosity  
 $\nu$  = kinematic viscosity  
 $\xi$  = dimensionless axial coordinate  
 $\rho$  = density

$\tau$  = shear stress  
 $\tau_y$  = Bingham yield stress  
 $\omega$  = angular velocity

### Subscripts

0 = free surface  
 1 = interface between the surface flow and the shear flow  
 $zr$  =  $z-r$  plane  
 $z\theta$  =  $z-\theta$  plane  
 $'$  = derivative with respect to  $\xi$

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## An Equation for the Latent Heat of Vaporization

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An expression for the latent heat of vaporization of a fluid is formulated employing renormalization-group theory predictions for the thermodynamics of fluids in the vicinity of the critical point. A least-squares fit of the latent heat data of water is made using the general and relatively simple equation:  $L = a_1 t^\beta + a_2 t^{\beta+\Delta} + a_4 t^{1-\alpha+\beta} + \sum M_n = 1 b_n t^n$ ,  $3 \leq M \leq 5$ , yielding predicted values that are in excellent agreement with the data throughout a wide range of temperatures. The optimum value of the critical temperature, 373.92 °C, is found to be somewhat lower than the tabulated value.

### Introduction

In recent years an effort has been made to describe the anomalous thermodynamic behavior of fluids in the vicinity of the critical point through phenomenological scaling theory (Widom, 1965; Kadanoff, 1966; and Griffiths, 1967) and, more recently, via the renormalization-group approach (Wilson and Fisher, 1972). In this study we apply the results of modern critical-point theories to obtain the functional form of the latent heat of vaporization  $L$  of a pure fluid that is applicable throughout the entire domain of existence of the latent heat, i.e., from the triple point to the critical point. The resulting formula for the latent heat contains system-dependent parameters which must ultimately be fitted to data. For purposes of illustration, we perform a least-squares fit of latent-heat data of water.

### Formulation of the Latent Heat Formula

Latent-heat formulas for various substances have previously been given many times: the works of Nutting (1930) and Watson (1943) exemplify early efforts in this direction. Equations such as theirs, however, suffer in that they cannot accurately describe latent heat data over the broad domain of values that we are interested in here. Those empirical equations that are able to accurately predict latent heat values for temperatures ranging between the critical temperature  $T_C$  and the triple point temperature  $T_T$  are typically complex in form and contain a large number of terms (ASME Steam Tables, 1977). The aforementioned defects in all these empirical equations can be attributed to their not utilizing the fundamental understanding of the thermodynamic nature of the critical region that has only recently evolved.

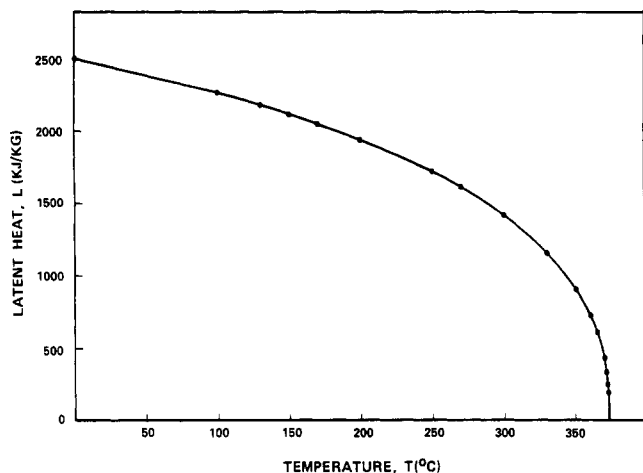


Figure 1. Predicted latent heat values using eq 9, with  $M = 3$ , compared to data of Osborne et al. (1930, 1937), as a function of temperature. Solid line denotes the predicted values and black circles the measured values.

For most pure fluids, the first derivative  $dL/dT$  becomes infinite as  $T \rightarrow T_C$  precluding the use of a Taylor expansion of  $L$  in temperature in the vicinity of  $T_C$  (see Figure 1). In contrast, the latent heat is found to be analytic away from the critical region. Consequently, we are motivated to write the expansion

$$L = L_S + L_R \quad (1)$$

$$L_S = \sum_{n=1}^{\infty} a_n t^{\phi_n} \quad (2)$$

$$L_R = \sum_{n=1}^{\infty} b_n t^n \quad (3)$$

where the  $\phi_n$  ( $n = 1, 2, \dots$ ) are the critical exponents (which are, in general, non-integral), the  $a_n$  and  $b_n$  are system-dependent parameters, the  $t \equiv (T_C - T)/T_C$ . The term  $L_S$  is the contribution to the latent heat which describes the singular behavior near the critical point whereas the term  $L_R$  is the analytic or regular contribution to  $L$  characterizing the behavior away from the critical region. We now turn to the problem of ascertaining the critical exponents  $\phi_n$  via theories of the critical point.

The latent heat is given exactly by the Clausius-Clapeyron equation

$$L = T \frac{dP}{dT} - \frac{\rho_L - \rho_G}{\rho_L \rho_G} \quad (4)$$

where  $dP/dT$  is the slope of the vapor pressure curve and  $\rho_L$  and  $\rho_G$  denote the liquid and vapor coexisting densities, respectively. Ley-Koo and Green (1977) made use of the general form of the singular part of the thermodynamic potential proposed by Wegner (1972) for describing the critical region of fluids. From their expression, one may obtain

$$dP/dT = A_1 + A_2 t^{1-\alpha} \quad (5)$$

$$\rho_L/\rho_C = 1 + B_1 t^\beta + B_2 t^{\beta+\Delta} + B_3 t^{1-\alpha} \quad (6)$$

$$\rho_G/\rho_C = 1 - B_1 t^\beta - B_2 t^{\beta+\Delta} + B_3 t^{1-\alpha} \quad (7)$$

where  $A_i$  ( $i = 1, 2$ ) and  $B_i$  ( $i = 1, 2, 3$ ) are parameters that depend upon the particular system of interest. Here  $\alpha$  and  $\beta$  are the critical exponents describing the singularities associated with the specific heat and the difference in coexisting densities, respectively. The exponent denoted by  $\Delta$  is Wegner's first "gap" exponent.

Implicit in the form of eq 6 and 7 is the symmetry of the Ising (lattice-gas) model, a symmetry that is not expected in a real fluid (Vause and Sak, 1980). To the order that we are interested in here, however, the term accounting for the first nontrivial difference between a fluid and the Ising model will not enter. Combining 4, 5, 6, and 7 gives the singular contribution to the latent heat as

$$L_S = a_1 t^\beta + a_2 t^{\beta+\Delta} + a_3 t^{3\beta} + a_4 t^{1-\alpha+\beta} \quad (8)$$

which is eq 2 expanded up to  $n = 4$  with  $\phi_1 = \beta$ ,  $\phi_2 = \beta + \Delta$ ,  $\phi_3 = 3\beta$ , and  $\phi_4 = 1 - \alpha + \beta$ . This finite sum, for the purposes of this study, appears to contain a sufficient number of terms to accurately describe the critical region. We shall take  $\beta = 1/3$  and  $\alpha = 1/8$ ; they represent the simplest fractions that are both close to the values for the three-dimensional Ising model and within the range of experimental values for a variety of different fluids (Sengers and Levelt Sengers, 1977). The value of the gap exponent  $\Delta$  is not well established either experimentally or theoretically (from renormalization group calculations); reported values of  $\Delta$  range from as low as 0.3 to 0.65 (Chang et al., 1977; Ferer, 1977), although 0.5 from lowest-order theoretical calculations is the most commonly used value.

Equation 8 added to the regular part of  $L$ , eq 3, gives an equation for the latent heat that is valid in the regions both near and away from the critical point

$$L = a_1 t^\beta + a_2 t^{\beta+\Delta} + a_4 t^{1-\alpha+\beta} + \sum_{n=1}^M b_n t^n \quad (9)$$

where  $M$  is the number of terms in the regular part of  $L$ . The term containing the exponent  $3\beta$  has been absorbed by the first term in the sum, since  $\beta = 1/3$ . In order to determine the  $a_n$  and  $b_n$  one must fit eq 9 to latent-heat data of the fluid of interest. As an example of the use of eq 9, we perform a least-square analysis to fit this formula to the highly accurate latent-heat data of water of Osborne, Stimson, and Ginnings (OSG) (1937) and Osborne, Stimson, and Fiock (OSF) (1930).

## Results and Discussion

Before undertaking the general task of curve fitting the latent-heat data, we determine the optimum value of  $T_C$  and  $\Delta$  by least-squares fitting the OSG data, using eq 9 with  $M = 1$ , for temperature values within  $15^\circ$  of the critical temperature. The optimum critical temperature is found to be  $373.92^\circ\text{C}$  in contrast to the higher OSG tabulated value of  $374.15^\circ\text{C}$ . Critical temperatures determined in this manner have been shown elsewhere to be lower than the corresponding tabulated  $T_C$  value (Sengers and Greer, 1971; Sengers and Sengers, 1975). It seems that values of  $T_C$  given in steam tables are the result of smoothing which produces artificially high critical temperatures. The best value of  $\Delta$  is found to be  $0.79 - \beta \approx 0.4567$ , which is a bit lower than the value of 0.5 given by first-order renormalization-group calculations. Considering the relative simplicity of both the experimental and theoretical determinations, the agreement is remarkable and possibly fortuitous.

The latent-heat values tabulated by OSG and OSF were obtained by smoothing the corresponding experimentally measured values. In order to avoid introducing any bias as a result of smoothing on their part, we shall use the OSG and OSF experimentally measured latent values whenever possible. Such data were provided in the OSG work in the temperature range from  $200^\circ\text{C}$  to the critical temperature. The OSF study contained experimentally determined latent values in the range  $100^\circ\text{C} \leq T < 200^\circ\text{C}$ . For temperatures less than  $100^\circ\text{C}$ , only smoothed values were

Table I. Standard Error vs. Number of Terms in  $L_R$ ,  $M$ 

$M$	$\sigma$ , kJ/kg
1	2.72
2	1.57
3	0.63
4	0.42
5	0.35
6	0.23
7	0.23
8	0.23

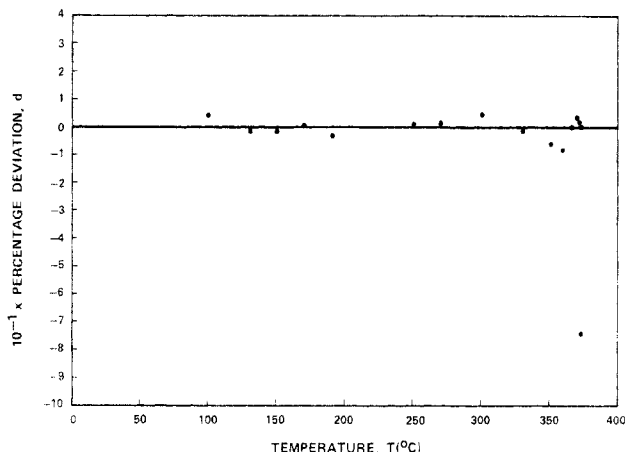


Figure 2. Percentage deviation,  $d$ , as obtained from eq 9 with  $M = 3$ , as a function of temperature. Significance of line and circles as in Figure 1.

given. Instead of utilizing all the smoothed tabulated values in the range  $0.01^\circ\text{C} \leq T < 100^\circ\text{C}$ , we used only the triple-point value (the same in both the OSG and OSF studies). Combining the OSG and OSF values in this manner gives us experimental latent heat data, for  $T_T < T < T_C$ , and a smoothed  $L$  value for  $T = T_T$ .

We fit these data, using eq 9 for various values of  $M$ . A comparison of these fits is summarized in Table I where the standard error

$$\sigma \equiv \left( \sum_{i=1}^N (L_i^* - L_i)^2 / N \right)^{1/2}$$

is given as a function of  $M$ . Here  $N$  is the number of experimental values, and  $L_i^*$  and  $L_i$  are the  $i$ th measured and predicted latent-heat values.

The largest standard error occurs when  $M$  takes on its smallest value, unity, as expected. The standard error monotonically decreases as  $M$  is made larger in such a way that very little accuracy is gained for  $M \geq 6$ . OSF indicate that the maximum experimental error in the range  $100^\circ\text{C} \leq T \leq 270^\circ\text{C}$  is one part in 1300, becoming progressively worse as the critical temperature is approached. As a result of great experimental difficulties faced by OSG in the critical region, no estimates of error were given for the vicinity of the  $T_C$ .

In light of our limited knowledge of error estimates, we conclude that the cases  $M \geq 3$  should yield predicted latent-heat values within experimental error since the  $L_i$  for  $100^\circ\text{C} \leq T \leq 270^\circ\text{C}$  are within one part in 3000 of the data in the case  $M = 3$ , based upon an average latent heat of 2000 kJ/kg in this range and  $\sigma = 0.63$  kJ/kg. A comparison of the predicted latent-heat values for this case with the corresponding measured values plotted against temperature is depicted in Figure 1. Figure 2 shows the percentage deviations  $d \equiv 100 \times (L_i^* - L_i) / L_i^*$ , associated with the preceding figure, as a function of temperature. The maximum deviation occurs at  $T = 373.5^\circ\text{C}$  (a temperature nearly equal to  $T_C$ ) where we observed the predicted value to differ from the data by about one part in

Table II. Results of Least-Squares Analysis using Eq 9 with  $3 \leq M \leq 5$ 

	$M$		
	3	4	5
$a_1$	2059.10612	2017.77302	1989.41582
$a_2$	6604.54101	9132.07411	11178.45586
$a_4$	7694.31324	17454.07847	26923.68994
$b_1$	-11318.02807	-20696.33099	-28989.28947
$b_2$	-4284.42966	-10666.82494	-19797.03646
$b_3$	2598.60251	9818.48294	28403.32283
$b_4$		-4286.78779	-30382.30642
$b_5$			15210.380
max dev	0.74%	0.40%	0.24%

100. Considering the enormous experimental difficulties one faces in this region, a percent deviation here is in all probability within the error of the experiment. In Table II we summarize some of the results of our least-squares analysis where we list the values of the coefficients  $a_n$  and  $b_n$  and the maximum percentage deviation for the instances  $3 \leq M \leq 5$  in eq 9. In all these cases the maximum deviation occurs at  $T = 373.5^\circ\text{C}$ .

### Concluding Remarks

We are able to formulate an accurate expression for the latent heat of a fluid over its entire domain of existence. A least-squares fit of latent-heat data of water using this single simple expression, over this wide temperature range, yields predicted values well within the error of the experiment. We propose that our latent-heat expression provides a highly accurate means of smoothing measured latent-heat data, as it properly accounts for behavior in the anomalous critical region. By understanding the thermodynamic behavior in this vicinity of the critical point, one may obtain more precise values for critical properties such as the critical temperature, for example, which we determine to be  $373.92^\circ\text{C}$  in this study.

Finally, it should be noted that the latent heat equation formulated in this study may be applied to other fluids which are in the same universality class as water (Stell, 1974; Sengers and Sengers, 1977). Furthermore, one may develop expressions for other saturated liquid-vapor properties using arguments very similar to the ones presented in this analysis.

### Nomenclature

$A_1, A_2$  = constants in eq 5  
 $a_1, a_2, a_3, a_4$  = constants in eq 8  
 $B_1, B_2, B_3$  = constants in eq 6 and 7  
 $b_1, b_2, b_3, b_4, b_5$  = constants in eq 9  
 $d = 100 \times (L_i^* - L_i) / L_i^*$   
 $L$  = latent heat of vaporization  
 $L_i$  =  $i$ th predicted  $L$  value  
 $L_i^*$  =  $i$ th measured  $L$  value  
 $L_R$  = regular part of  $L$   
 $L_S$  = singular part of  $L$   
 $M$  = number of terms in  $L_R$   
 $N$  = number of measured  $L$  values  
 $P$  = pressure  
 $T$  = temperature  
 $T_C$  = critical point temperature  
 $T_T$  = triple point temperature  
 $t = (T_C - T) / T_C$

### Greek Letters

$\alpha$  = scaling exponent in eq 6  
 $\beta$  = scaling exponent in eq 6  
 $\Delta$  = scaling exponent in eq 6  
 $\phi_m$  = scaling exponent in eq 2  
 $\rho$  = density  
 $\rho_G$  = saturated vapor density  
 $\rho_L$  = saturated liquid density

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# Parametric Pumping with pH and Electric Field: Protein Separations

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A new parametric pumping process for the separation of protein mixtures has been developed, based on cyclic variation of pH and electric field. The model system used is human hemoglobin plus human serum albumin on CM Sepharose ion exchanger. Experimental results are presented. They indicate that the process is a useful method for splitting proteins from each other.

## Introduction

Parametric pumping is a separation process which involves reciprocating flow of a mixture to be separated through a fixed bed and simultaneous, synchronous cyclic variation of intensive variables, such as gas pressure, solution temperature, solution ionic strength, solution pH, electric field, etc. The intensive variables most often used to motivate parametric pumping have been temperature and pressure. Electric field or pH has been used less often.

Parametric pumping via pH variation usually involves the so-called "recuperative mode" of operation of the process (Sabadell and Sweed, 1970; Shaffer and Hamrin, 1975). In this mode, various levels of pH are set in the streams entering either end of the parametric pumping column. As the entering streams penetrate the column, a pH change in the column occurs. This is opposed to the "direct mode", in which the intensive variable is changed uniformly over the entire length of the column.

Unlike pH, changes in the electric field as an intensive variable can be immediately and speedily applied to the parametric pumping system. Electrochemical parametric pumping has been shown to be a promising technique for desalination of water (Thompson and Bass, 1974; Oren and Soffer, 1978).

Chen et al. (1977, 1979, 1981) have studied the separation of hemoglobin and albumin by one-column pH parametric pumping. The experimental data have shown that a pH-driven parapump is capable of yielding high separation factors. Also, Chen et al. (1980a,b) have indicated that the multicolumn parapump (columns packed alternately with cation and anion exchangers) has a much higher separation capability than the one-column unit. In this paper, separation of protein mixtures is experimentally investigated by pH and electric field-driven parametric

pumping. Emphasis is placed on the problem of separating two proteins from each other.

## Experimental Section

The experimental apparatus is shown in Figure 1. An LKB 7900 Uniphor column electrophoresis system was modified for continuous operation by the addition of a second elution stopper. Minor modifications were made on the elution stopper and the filter in order to supply adequate support for the solid phase. The column (0.026 m i.d. and 0.15 m height) was packed with CM Sepharose, a cation exchanger. The system was maintained at 278 K by circulation of cooling water through the jacket of the Uniphor column and the jackets of the Uniphor buffer chambers. The external buffer reservoirs (2 L volume) were kept at 288 K.

Reciprocating flow through the system was obtained by use of a reversible peristaltic pump (manufactured by Pharmacia Fine Chemicals). A higher capacity peristaltic pump (manufactured by Bio-Rad laboratories) was used for buffer circulation. A Buchler 3-1500 power supply was used for a direct current source to maintain constant voltage across the column. The feed pump and the power supply were connected to a timer for precise control of reservoir displacements and feed volumes. Valves were placed on each inlet channel of the feed pump in order to introduce the reservoir liquids, to introduce the high or low-pH feeds, and to take product samples.

Each product stream was analyzed at the end of every cycle using a Bausch and Lomb spectrophotometer. Hemoglobin concentration was determined by absorbance at a wavelength of 403  $\mu\text{m}$  and total protein was determined at a wavelength of 595  $\mu\text{m}$ . Albumin concentration was then determined by difference.

## pH Parametric Pumping

The first system to be considered (Figure 2) is a one-column parametric pump (Chen et al., 1979). Two pH

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