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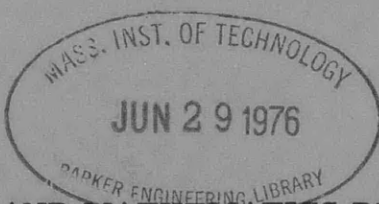
## A GENERAL EQUATION OF STATE FOR PURE MOLECULAR SUBSTANCES

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Thomas S. Walton

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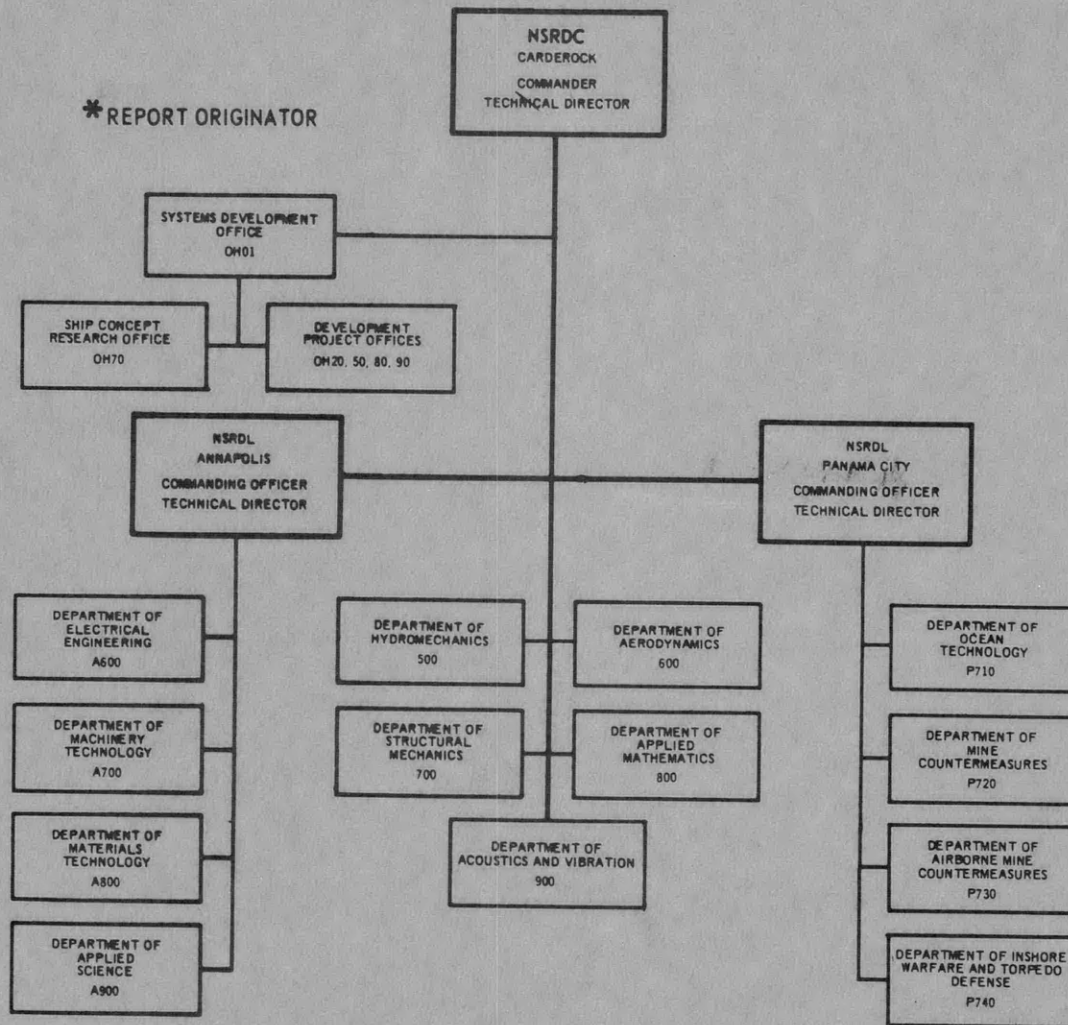
Report 3664

A General Equation of State for Pure Molecular Substances

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DEPARTMENT OF THE NAVY  
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A GENERAL EQUATION OF STATE FOR  
PURE MOLECULAR SUBSTANCES

by

Thomas S. Walton

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Report 3664

## FOREWORD

This report is an updated version of a paper (ref. 1) presented at the Seventh International Conference on the Properties of Steam in September, 1968 under the title "A General Characteristic Equation for the Thermodynamic Properties of a Pure Molecular Substance." It was pointed out by the rapporteurs for the session on Formulation of Equilibrium Properties that none of the methods for correlating experimental data proposed by the various contributors was capable of representing the specific-heat anomaly observed in the neighborhood of the critical point (because the assumption of analytic behavior at the critical point was implicit in each of the formulations). In the meantime, the author has carried out an investigation to elucidate the nature of the singularity associated with this point. The new findings are incorporated into Appendix B, which deals exclusively with this peculiar phenomenon. The original text has been corrected in a number of places, and the notation has been modified to a minor extent. Otherwise, the main part of the report is the same as that presented at the 1968 conference in Tokyo, Japan.

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## ABSTRACT

This paper describes a new analytic formulation of the thermodynamic properties of a chemically homogeneous, stable molecular substance such as water or carbon dioxide. A mathematical expression for the Helmholtz free-energy function  $f(v, T)$  is derived by starting with a form that yields the laws for ideal gases and incorporating into it a series of terms and associated parameters suggested by statistical mechanics and quantum theory considerations. The anomalous behavior of pure substances near the liquid-vapor critical point is also taken into account. This leads to a more comprehensive equation of state applicable to the condensed phases in addition to the gaseous phase. Accordingly, it is adapted for smoothing as well as interpolating observational data over a wide range of variables.

The final result may be regarded as a generalization of van der Waals' equation, modified so as to provide a more faithful representation of high-density measurements and to be consistent with Debye's theory at very low temperatures – and always, of course, reducing to the ideal gas law as the density goes to zero. Values for the parameters which enter the approximation via the molecular partition function for the substance are fixed in advance. They are usually obtained with more than sufficient accuracy by analysis of spectroscopic measurements, and therefore need no further correction. All the remaining parameters – except for a few constants that must be estimated initially from physical considerations – occur linearly in the formulas, thus facilitating their determination by a least-squares adjustment.

## ADMINISTRATIVE INFORMATION

This work was supported under Subproject SR 003 03 01, Task 10919.

## I. INTRODUCTION

The mathematical description of natural phenomena helps to advance scientific knowledge by abstracting the results of extensive observations into compact formulas. Valuable information can thus be preserved in a form allowing for easy reproduction in the future. Furthermore, such efforts have frequently led to a better understanding of the underlying principles by revealing discrepancies that otherwise would have gone unnoticed.

Investigations into the thermodynamic properties of matter have been directed toward such ends for a long time. Notable advances occurred with the discoveries by Boyle and Charles of the laws for perfect gases and, much later, with the ingenious modification by van der Waals (ref. 2) which, for the first time, supplied at least a qualitative account of behavior near the critical point as well as an interpretation of the stability of the liquid state.

With the introduction of characteristic functions into thermodynamics by Gibbs (ref. 3) came the realization that, in principle, all the thermodynamic properties of a substance could be derived from a single function of two properly chosen, conjugate variables. However, this has turned out to be far from easy in practice. The various states of matter seem, in their outward manifestations, to be governed by radically different laws, while the basic physical principles with a claim to universality are found to be abstruse and difficult to apply, even on an atomic scale.

Debye, using quantum theory to calculate the vibrational modes of the atoms in a crystal lattice, was able to construct an equation of state for the solid phase (ref. 4) expressed in terms of the Helmholtz free-energy function. The theoretical determination of this function



for liquids and dense gases has, so far, proved intractable, even though considerable progress has been made in the treatment of simplified models of fluids (ref. 5, chap. IV). On the other hand, its development for ideal gases (or for real gases in the limit as the density approaches zero) has been one of the great triumphs of statistical mechanics.

## II. OBJECTIVES

In the present investigation, we endeavor to formulate a semi-empirical equation of state for pure molecular substances which is fully in accord with the theoretical and experimental facts. The continuity of state suggests the possibility of an analytical approximation applicable to the condensed phases as well as the gaseous phase. Among the phenomena that it should take into account are: 1) the nearly ideal behavior at low densities and high temperatures; 2) the vapor-liquid equilibrium curve; 3) the vapor pressure at low temperatures, including the chemical constant; 4) the Joule-Thomson coefficient; 5) the specific heat of the condensed phases at low temperatures; and 6) the specific-heat anomaly at the critical point. Aside from its value to pure science, such a formulation would have great utility in applied science engineering.

A number of substances (e. g. , water, carbon dioxide and the more abundant constituents of the atmosphere, volatile hydrocarbons, and certain refrigerants) have considerable economic importance, and in some instances their properties have been measured over wide ranges of temperature and pressure. This is notably the case for water and steam, six international conferences having been held prior to 1968 to facilitate a careful and critical examination of its properties (ref. 6). Water has long been recognized as one of the most unusual substances in nature (ref. 7), and the representation of its properties has entailed much difficulty.

The widespread interest in this problem provided the original incentive for undertaking the research described in this paper. The application of the resulting mathematical approximation to the experimental data for water substance, as well as a computer program to carry out the fitting procedure, has been partially investigated but is not treated in this report.

### III. BASIS AND APPROACH

To arrive at a consistent and reliable description of the thermodynamic behavior of a particular substance, it is necessary to correlate the measurements of a number of its properties. This can be accomplished most effectively in terms of a fundamental equation of state, because such a formulation permits any thermodynamic quantity to be expressed as some algebraic combination of partial derivatives of an appropriate function.

Among possible choices, the Helmholtz (free-energy) function, for which the appropriate conjugate variables are volume and temperature, has the greatest appeal. There are two reasons for this. First, from a theoretical standpoint, it is the one that can be calculated most readily, on account of its close connection with the Gibbs canonical distribution of statistical physics (ref. 8, chap. 3). An explicit determination of its mathematical form has been carried out in two important limiting cases: 1) solids at low temperatures, and 2) gases at low densities. The significance of this accomplishment is apparent. Secondly, from an empirical standpoint, it is the only function which involves directly measurable quantities (such as pressure, volume, temperature, and energy in the form of heat or work) and which also has the property that all its first- and second-order differential coefficients are single-valued and finite for all physically realizable values of the two independent variables, excluding only the critical point. As a result, quantities derived from it will have unique values at every point (though in certain domains these may correspond to metastable or unstable states). Such regularity greatly simplifies the task of finding suitable interpolation formulas for the regions beyond the scope of present-day theories.

For some purposes, it would be more convenient to have pressure and temperature as independent variables and characterize the behavior of the substance in terms of the Gibbs (free-enthalpy) function. Nevertheless, an equation which gives the pressure in terms of volume and temperature poses no real obstacle to the fulfillment of such a need. Simple techniques are available for finding roots by inverse interpolation (e. g. , Newton's method) which, with the temperature held constant, will readily yield the value of the volume corresponding to a given pressure.

In principle, the location of the phase boundaries can also be deduced from either formulation, at least to the extent that the approximating functions are analytic in character (ref. 5, §4.3). But the one based on the Gibbs function is subject to inherent practical drawbacks. The metastable regions beyond the vapor-liquid equilibrium curve terminate in two loci of singularities which converge at the critical point. This gives rise to severe computational difficulties, and it becomes necessary to use piecewise approximation techniques, of which the most satisfactory is probably the cubic spline in two dimensions (ref. 9). Furthermore, the treatment of the phase boundaries then becomes a separate problem rather than an integral, albeit implicit, part of the formulation, as it is with the Helmholtz function.

#### IV. THE IDEAL-GAS APPROXIMATION

From a purely thermodynamic viewpoint, we may define an ideal gas as one for which both the pressure-volume product and the internal energy depend only on the temperature of the gas; that is, it obeys Boyle's law and exhibits no Joule effect during a free expansion (ref. 10, p. 456). The free energy per unit mass<sup>†</sup> of such a gas must be of the form

$$f(\rho, T) = RT \log \rho + f_i(T), \quad (1)$$

in which  $R$  stands for the gas constant per unit mass and  $f_i(T)$  is some (as yet unspecified) function of temperature that characterizes the thermal behavior of the molecules of the gas. Hence, using the thermodynamic definitions of pressure  $p$ , specific entropy  $s$ , specific internal energy  $u$ , and specific heat at constant volume  $c_v$ , we find

$$p = \rho^2 \frac{\partial f}{\partial \rho} = RT\rho, \quad (2)$$

$$s = - \frac{\partial f}{\partial T} = -R \log \rho - f'_i(T), \quad (3)$$

$$u = f + Ts = f_i(T) - Tf'_i(T), \quad (4)$$

$$c_v = \frac{\partial u}{\partial T} = T \frac{\partial s}{\partial T} = -Tf''_i(T), \quad (5)$$

which shows that the internal energy and specific heat of an ideal gas are completely described by the function  $f_i(T)$ . Thus, when the dependence of  $c_v$  on  $T$  is known,  $f_i(T)$  can be determined by integrating the quantity  $-c_v/T$  twice with respect to  $T$ . In particular, for  $c_v$  equal to a constant, the result after substitution in equation (1) is

---

<sup>†</sup> It is convenient to measure all extensive thermodynamic quantities in terms of a unit mass of substance and to adopt density  $\rho$  and temperature  $T$  as the independent variables.

$$f(\rho, T) = c_0 - RT \left( \frac{c_v}{R} \log T - \log \rho + c_1 \right), \quad (6)$$

where  $c_0$  and  $c_1$  are constants of integration.

According to the kinetic theory of gases, the ratio  $c_v/R$  can be related to the number of degrees of freedom that characterize the thermal motions of the molecules, each component of translation and rotation contributing half a unit to the effective value and each fully excited vibrational mode contributing a whole unit (one half for the kinetic and the other half for the potential energy associated with each normal mode). Thus we may write

$$c_v = \frac{1}{2} \nu^0 R, \quad (7)$$

where  $\nu^0$  denotes the total number of ways in which a molecule can store thermal energy under ideal-gas conditions. Translation always accounts for three of these, whereas rotation may account for 0, 2, or 3, in accordance with the molecular structure regarded as a configuration of point masses: monatomic molecules exhibit no rotational freedom; diatomic molecules can rotate about two perpendicular axes; and polyatomic molecules (excluding rigid, collinear configurations), about all three axes.

In actuality, both the translational and rotational contributions attain their classical values (i. e., as given by kinetic theory in the absence of quantum restrictions) at extremely low temperatures, but the vibrational modes are only partially excited even at moderately high temperatures. Therefore, it is not proper to take  $c_v$  as a constant, although we may certainly resolve it into a constant plus a variable term, viz.,

$$c_v = \frac{3+n}{2} R - T f''_0(T), \quad (8)$$

where  $n$  is the appropriate number of rotational degrees of freedom

and  $f''_0(T)$  designates that part of  $f''_1(T)$  in equation (5) which accounts for all contributions to  $c_v$  other than those due to translation and rotation of the molecules. Hence, on integrating and then substituting the result in equation (1), we obtain

$$f(\rho, T) = c_0 - RT \left[ \frac{3+n}{2} \log T - \log \rho + c_1 \right] + f_0(T). \quad (9)$$

In like manner, the specific entropy and internal energy of an ideal gas can be written

$$s = R \left[ \frac{3+n}{2} (\log T + 1) - \log \rho + c_1 \right] - f'_0(T), \quad (10)$$

$$u = c_0 + \frac{3+n}{2} RT + f_0(T) - Tf'_0(T). \quad (11)$$

An alternative derivation of equation (9) from the point of view of statistical mechanics and quantum theory is outlined in Appendix A. One of the significant results of that approach is that the constant  $c_1$  is found to have a definite value for each gas, which can be calculated from theory – whereas its value according to classical thermodynamics is indeterminate (ref. 11, §281). In this way, its relation to Nernst's chemical constant and the absolute value of the entropy is established. The fundamental character of equation (9) makes it the logical starting point for defining the state of a chemically homogeneous substance under more general conditions.

## V. THE VAN DER WAALS APPROXIMATION

The next stage in the development of a more widely applicable equation is the inclusion of first-order corrections in the density. The two terms introduced by van der Waals are very indicative, and a critical examination of their effects serves to motivate further modifications. The first of these terms,  $-a\rho$ , is intended to account for the long-range attractive forces between molecules, and the second one,  $-RT \log(1 - b\rho)$ , makes an allowance for the volume excluded by the finite dimensions of the molecules. Both terms are seen to vanish as  $\rho \rightarrow 0$ . When they are added to equation (9), the characteristic function becomes

$$f(\rho, T) = c_0 - a\rho - RT \left[ \frac{3+n}{2} \log T - \log \frac{\rho}{1-b\rho} + c_1 \right] + f_0(T), \quad (12)$$

from which we derive

$$p = -a\rho^2 + RT \frac{\rho}{1-b\rho}, \quad (13)$$

$$s = R \left[ \frac{3+n}{2} (\log T + 1) - \log \frac{\rho}{1-b\rho} + c_1 \right] - f_0'(T), \quad (14)$$

$$u = c_0 - a\rho + \frac{3+n}{2} RT + f_0(T) - Tf_0'(T), \quad (15)$$

$$c_v = \frac{3+n}{2} R - Tf_0''(T). \quad (16)$$

If we introduce the specific volume  $v = 1/\rho$  into equation (13) and rearrange the terms, the familiar form of van der Waals' equation results, viz.,

$$\left( p + \frac{a}{v^2} \right) (v - b) = RT. \quad (13a)$$

Since formulas (13-15) for  $p$ ,  $s$ , and  $u$  involve one or both of the quantities  $a$  and  $b$ , they will differ slightly from the formulas for ideal gases



whenever the density is greater than zero. On the other hand, formula (16) for  $c_v$  remains unchanged.

These corrections have a certain theoretical validity and beneficial effect at moderately high temperatures, provided that the density is not too great (ref. 8, § 73). However, a more detailed analysis of equation (13) reveals that it is inadequate at low temperatures for any nonzero density and at all temperatures for a sufficiently large density. Thus, by way of illustration, the isochores ( $p$  vs.  $T$  for constant  $\rho$ ) are all straight lines, and for  $\rho = 1/b$  the slope becomes infinite, contrary to experience. This equation also fails to provide an accurate description of the Joule-Thomson effect at low temperatures, for, in the limit as the density (and therefore the pressure) goes to zero, it yields the result (ref. 11, § 158A)<sup>†</sup>

$$\mu_{J.T.}^0 = \lim_{p \rightarrow 0} \left( \frac{\partial T}{\partial \rho} \right)_h = - \lim_{p \rightarrow 0} \frac{1}{c_p} \left( \frac{\partial h}{\partial p} \right)_T = \frac{1}{c_p^0} \left[ \frac{2a}{RT} - b \right], \quad (17)$$

whereas experimental measurements of this quantity (ref. 10, pp. 457-460) indicate a decidedly greater variation with  $T$  (or  $1/T$ ) as the temperature is reduced.

Finally, as shown by Planck (ref. 11, § 289), equation (13) gives for the saturation pressure  $p_s(T)$  at low temperatures the result

$$\log p_s = \log(a/b^2) - a/bRT \quad (18)$$

instead of the theoretically correct form first suggested by Kirchhoff (ref. 12), viz.,

$$\log p_s = (c_p/R) \log T - L_0/RT + i, \quad (19)$$

in which  $L_0$  is the latent heat of transformation per unit mass at absolute

---

<sup>†</sup> The symbol  $h = u + pv$  denotes the specific enthalpy;  $c_p = (\partial h / \partial T)_p$  is the specific heat at constant pressure;  $\mu_{J.T.}$  stands for the Joule-Thomson coefficient of the gas.

zero, and  $i$  is the chemical constant of the vapor in question. Equation (18) lacks a term in  $\log T$ . This circumstance can be traced to the fact that equations (12-16) are necessarily incompatible with the low-temperature behavior of liquids and solids, since, as pointed out by Nernst (ref. 13), the specific heat of any condensed system must vanish as  $T \rightarrow 0$ . The correct expression for the free energy of a perfect, nonconducting crystal close to absolute zero was deduced by Debye, viz. ,

$$f(\rho, T) = u_0 - AT^4 . \quad (20)$$

The coefficient  $A$ , as well as  $u_0$  (the limit of  $u(\rho, T)$  as  $T \rightarrow 0$ ), depends only on the density of the given crystal.

At the time that van der Waals proposed his justly famous equation of state, the constraints imposed by quantum mechanics on the behavior of matter were unknown; it would, indeed, be fortuitous if his formula were to be applicable to the extreme conditions considered here. Nevertheless, it is possible to remedy the afore-mentioned deficiencies by suitably modifying the formulation.

## VI. GENERALIZATION OF THE TERMS

As a preliminary step to obtaining a more general expression for the free energy, we replace the quantity  $\log(1 - b\rho)$  in equation (12) by its power series expansion, viz. ,

$$\log(1 - b\rho) = - \sum_{\ell=1}^{\infty} \frac{1}{\ell} (b\rho)^{\ell} \quad b\rho < 1. \quad (21)$$

That this series does not converge unless  $\rho < 1/b$  is of no consequence, since it could constitute a suitable correction only for relatively small densities, anyway. In addition, we express the term  $f_0(T)$  as

$$f_0(T) = -RT \log Q_0(T), \quad (22)$$

where  $Q_0(T)$  is the factor of the molecular partition function that characterizes all modes of thermal excitation other than translation and rigid rotation of the molecules. [See equation (A7) of Appendix A. ] Thus, equation (12) becomes

$$f(\rho, T) = c_0 - a\rho - RT \left[ \frac{3+n}{2} \log T + \log Q_0(T) - \log \rho + c_1 - \sum_{\ell=1}^{\infty} \frac{1}{\ell} (b\rho)^{\ell} \right]. \quad (23)$$

We now regard the various terms of equation (23) as belonging to one of three sets: a) those that relate to the intermolecular potential energy in the absence of thermal agitation; b) the logarithmic terms, from which the properties of ideal gases are derivable in the limit as the density approaches zero; and c) the set of temperature-dependent terms which serve to correct for the behavior of real substances, primarily in the condensed phases. For the sake of brevity, the mathematical functions to be devised for these three conceptual categories will be denoted  $u_0(\rho)$ ,  $f_1(\rho, T)$  and  $f_2(\rho, T)$ , respectively. Then we can write

$$f(\rho, T) = u_0(\rho) + f_1(\rho, T) + f_2(\rho, T) + \dots, \quad (24)$$

including such additional terms as are necessary. It will also be convenient in the subsequent analysis to employ nondimensional independent variables, as this will greatly simplify the formulas which are eventually to be used for computation. Therefore, we define

$$\begin{aligned}\theta &= T/T_c && \text{[ reduced temperature]} \\ \xi &= \rho/\rho_c = v_c/v && \text{[ reduced density]}\end{aligned}\tag{25}$$

where  $T_c$ ,  $\rho_c$  and  $v_c$  stand for the critical temperature, density, and specific volume, respectively.

a) The internal energy at absolute zero.

The first group of terms in equation (23), specifically,  $c_0 - a\rho$ , may be generalized by simply forming a polynomial in the reduced density  $\xi$ ,

$$u_0(\xi) = RT_c \sum_{\ell=0}^m A_\ell \xi^\ell.\tag{26}$$

The quantity  $RT_c$  serves as a convenient unit for measuring variables having dimensions of energy per unit mass; the index  $m$  fixes the degree of the polynomial with adjustable coefficients  $A_\ell$ . On comparing the first two terms with equation (23), we identify

$$\begin{aligned}A_0 &= c_0/RT_c, \\ A_1 &= -a\rho_c/RT_c.\end{aligned}\tag{27}$$

Values of additional coefficients may (to a certain extent) be inferred from measurements of the cohesive energy, the equilibrium density at zero pressure, and the compressibility of the substance, when such data are extrapolated to very low temperatures. For  $T=0$ , these properties can all be expressed in terms of  $u_0(\xi)$  and its derivatives, evaluated at densities appropriate to the condensed phases (see ref. 14, § 5.4).

Formula (26) should give a generally adequate description of the internal energy at absolute zero. Although not immune to criticism from the standpoint of quantum mechanics, it is nonetheless capable of representing the intermolecular potentials deduced for both gases and crystals to a high degree of accuracy (ref. 15, chap. 10). At very low densities the term  $A_1 \xi$  allows for a long-range potential varying as  $r^{-3}$  ( $r$  = relative separation between molecular centers of mass), which characterizes the interaction of widely separated molecules with permanent electric-dipole moments (if such are present). The term  $A_2 \xi^2$  can take care of the forces of attraction between induced dipoles, for which the potential varies as  $r^{-6}$ . This is referred to as the van der Waals energy in the case of crystals (ref. 16, §88) and results from the phenomenon of mutual polarization, which is always present, even with the noble gases (refs. 17 and 18). The next term can accommodate itself to any short-range repulsive potential that varies approximately as  $r^{-9}$ , while such additional terms as prove necessary can represent very short-range attractive or repulsive potentials varying as  $r^{-12}$ ,  $r^{-15}$ , etc. †

b) The logarithmic term.

If we ignore, for the moment, any high-density corrections, the temperature-dependent terms of equation (23) can be written

$$-RT \left[ \frac{3+n}{2} \log \theta + \frac{1}{2} \log \frac{\zeta(\theta)}{\theta^n} - \log \xi + \epsilon \right] = RT \left[ \frac{1}{2} \log \frac{\xi^2}{\theta^3 \zeta(\theta)} - \epsilon \right], \quad (28)$$

---

† It is not yet known whether, in practice, the inclusion of such terms in the equation of state will also enable it to satisfactorily embrace the solid phases under hydrostatic pressure, but the prospect is not unlikely.

where  $\zeta(\theta) = \theta^n Q_0^2$  (29)

and  $\iota = c_1 + \frac{3+n}{2} \log T_c - \log \rho_c$  (30)

$$= 1 + \frac{1}{2} \log \left[ \frac{8\pi^3 m^5}{\rho_c^2} \left( \frac{kT_c}{h^2} \right)^{3+n} \right] + \frac{1}{2} \log \frac{(8\pi^3 I)^n}{\sigma^2 \pi^2} . \quad (30a)$$

The quantity  $\iota$  may be termed the "reduced chemical constant" of the substance since, as here defined, its value is independent of the units of measurement. [Note: The last term of formula (30a) is to be omitted in the case of a monatomic gas ( $n=0$ ). See Appendix A for the meaning of the symbols.]

The deficiencies relating to low-temperature behavior can be rectified by modifying the argument,  $\xi^2/\theta^3 \zeta(\theta)$ , of the logarithmic term in expression (28). We seek a formulation which can render an adequate account of the Joule-Thomson effect and is, at the same time, consistent with Debye's law. As pointed out in the analysis of the van der Waals approximation (cf. Section V), the isochores are straight lines and the specific heat at constant volume is independent of the density. Both these attributes are tied to the vanishing of one of the third-order partial derivatives of  $f(\rho, T)$ , as is evident from the following general thermodynamic relation:

$$\left( \frac{\partial c_v}{\partial \rho} \right)_T = - \frac{T}{\rho^2} \left( \frac{\partial^2 p}{\partial T^2} \right)_\rho = -T \frac{\partial^3 f}{\partial T^2 \partial \rho} . \quad (31)$$

For real gases the value of this derivative, though small, does not in general vanish, but approaches a finite limit as the density goes to zero.

An additional first-order correction in the density is, therefore, needed to obtain closer agreement with the facts. We have already seen,

by equations (8) and (22), that the specific heat of an ideal gas is completely determined by the partition function, or by the closely related function,  $\zeta(\theta)$ , defined in equation (29). Thus, we can write<sup>†</sup>

$$c_v^0 = \lim_{\xi \rightarrow 0} c_v(\xi, \theta) = \frac{1}{2} R [ 3 + \theta (d/d\theta)^2 (\theta \log \zeta) ]. \quad (32)$$

Now the simplest way to introduce the required correction into expression (28) is to augment  $\zeta(\theta)$  in the denominator of the argument with a linear term in  $\xi$  multiplied by some coefficient  $\eta$ . Since the magnitude of the correction will generally vary with the temperature, the coefficient must be given as a function of  $\theta$ . Secondly, to ensure conformity with Debye's formula (20), we add a quadratic term in  $\xi$ , and multiply the rest of the denominator by an adjustable coefficient  $\kappa^2$ . Lastly, to compensate at low densities for the inclusion of the factor  $\kappa^2$ , we add the quantity  $\log \kappa$  to the entire expression within the brackets. The resulting modification now reads

$$RT [ \frac{1}{2} \log \varphi(\xi, \theta) + \log \kappa - i ] , \quad (33)$$

where we define 
$$\varphi(\xi, \theta) = \frac{\xi^2}{\xi^2 + \kappa^2 \theta^3 [\eta(\theta)\xi + \zeta(\theta)]} . \quad (34)$$

For vanishingly small densities, the contributions of these new terms become negligible, and expression (33) then reduces to expression (28). Thus, the modified form will also yield the ideal gas laws, as can

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<sup>†</sup> Values of the specific heat derived from  $\zeta(\theta)$  should, where possible, be corroborated by precise measurements of thermal energy absorption by the gas in question. However, under most circumstances, the various parameters occurring in the partition function can be evaluated with far greater accuracy by analysis of spectroscopic (rather than calorimetric) data.

be verified by differentiating and taking limits as  $\xi \rightarrow 0$ . On the other hand, when  $\xi > 0$ , the term in  $\log \varphi$  (but not the additive constants) will be found to vary according to the cube of the temperature in the neighborhood of absolute zero, as required – provided, of course, that the quantity  $\eta \xi + \zeta$  does not vanish at  $\theta = 0$ . The value of the parameter  $\kappa$  will be fixed primarily by the behavior of the substance at relatively high densities and low temperatures.

It will be shown in Section VII(c) that this new form gives rise to additional temperature-dependent terms in the expressions for the virial coefficients, the quantity  $\eta$  appearing initially in the second one and  $\kappa$ , in the third, as would be expected. The selection of a particular mathematical form for the function  $\eta(\theta)$  will be taken up in Section VIII, after the proposed equation of state has been analyzed in several limiting cases.

The development of the free-energy function up to this point can be written

$$f(\xi, \theta) = u_0(\xi) + f_1(\xi, \theta) + RT(\log \kappa - i), \quad (35)$$

in which

$$f_1(\xi, \theta) = \frac{1}{2} RT \log \varphi = \frac{1}{2} RT \log \frac{\xi^2}{\xi^2 + \kappa^2 \theta^3 (\eta \xi + \zeta)}. \quad (36)$$

If  $\eta(\theta)$ , as well as  $\zeta(\theta)$ , is a positive function of temperature, then values of the function  $\varphi(\xi, \theta)$  are restricted to the unit interval. In a certain sense,  $\varphi$  measures the departure of a real gas from the perfect state [cf. equation (475) of ref. 19]. So long as both  $\varphi$  and  $\xi$  are small, i. e., for high temperatures and low densities, a stable molecular substance obeys relatively simple laws, and equation (35) will then furnish an accurate description of its thermodynamic properties. For liquids and solids, however, these properties display marked sensitivity to volume and temperature changes in certain regions, so that the above equation cannot be used without further modification. Such deficiencies as it still



possesses may be corrected by supplementing the logarithmic term with a set of terms involving combinations of powers of  $\varphi$  and  $\xi$ .

c) The temperature-dependent, high-density corrections.

This brings us to the generalization of the final group of terms in equation (23), which are intended to allow for the reduction in volume available for thermally induced motion by virtue of the physical size of the molecules. Although it follows that the frequency of collisions (and therefore the pressure) is certainly greater, this is not the only thermal effect of close aggregation. The mutual interference of the molecules at higher densities tends to restrict some of their motions, thereby decreasing the effective number of degrees of freedom; ultimately, the distances between their nuclei and the paths of their orbital electrons (or the associated wave functions) will be significantly altered. In consequence of such extremely dense packing, quantum effects analogous to those which occur at low temperatures are encountered, resulting in a reduction of specific heat (ref. 20; also ref. 13, p. 237). A quantitative account of these phenomena, whether theoretical or empirical, must clearly involve temperature as well as volume.

For constant volume, we already know that any supplemental corrections to  $c_v$  must vary with the third power of the temperature near absolute zero, whereas they ought to diminish again at much higher temperatures as a more nearly ideal state is reached. These conditions can easily be satisfied by a simple polynomial in the quantity  $\varphi$  defined in equation (34), as will be seen later in Section VII(a) and (b). For constant temperature, we conclude that the magnitudes of the corrections to  $c_v$  should initially be permitted to grow larger with increasing density but that they should eventually decline as the density becomes indefinitely great.

A first-order correction to  $c_v$  in the neighborhood of  $\xi = 0$  has been explicitly provided for as a result of incorporating the term  $\eta\xi$  into the denominator of  $\varphi(\xi, \theta)$ . Hence, the leading supplemental term (in its effect on  $c_v$ ) should be of second order in  $\xi$ . This will also follow automatically, since  $\varphi(\xi, \theta)$  varies as  $\xi^2$  for vanishingly small  $\xi$  provided that  $\kappa^2 \theta^3 \neq 0$ . With regard to the dependence of other thermodynamic quantities on density, a detailed analysis (ref. 21) of the isothermal behavior of both water and mercury up to the highest pressures attainable with precision instrumentation has shown that a polynomial in density affords the most faithful representation of the data with a limited number of adjustable constants.

In view of the foregoing considerations, it is clear that a polynomial in  $\varphi$  alone will not suffice for the corrections required at higher densities, because  $\varphi(\xi, \theta)$  approaches unity when  $\xi$  becomes indefinitely large. We therefore replace the remaining terms of equation (23), which were expressed as a power series in density, with a polynomial of degree  $m$  in the two variables  $\varphi$  and  $\xi$  multiplied, in turn, by some quantity that effects a proper transition between the low-temperature and high-temperature realms. Thus, we write

$$f_2(\xi, \theta) = -RT(1 - \varphi) \sum_{\iota=0}^m \sum_{k=0}^{\iota} B_{\iota k} \varphi^k \xi^{\iota-k}. \quad (37)$$

in which the parameter  $m$  is set to provide as many terms with adjustable coefficients  $B_{\iota k}$  as are necessary to fit the given data to within the prescribed tolerances. Also, by starting the summation with the index  $\iota$  set to 0 rather than 1, we can absorb into the coefficient  $B_{00}$  the constant  $(\log \kappa - \iota)$  which occurs in the last term of equation (35).

The common factor  $(1 - \varphi)$  in equation (37) varies with the cube of the temperature near  $T = 0$ , as does the quantity  $-\log \varphi$  to which it approximates in this region. The inclusion of such a factor ensures that

each term of  $f_2(\xi, \theta)$  will be consistent with Debye's formula, yet the inherent simplicity of a polynomial is preserved [see Section VII(a)]. Moreover, all these supplemental terms, as well as the ensuing contributions to the expressions for  $p$ ,  $s$ ,  $u$  and  $c_v$ , vanish as  $\xi \rightarrow 0$  (except for the term with coefficient  $B_{00}$ , which persists in both  $f$  and  $s$ , as it should). Consequently, none of the properties of ideal gases are in any way affected by the addition of these high-density corrections [see Section VII(c)].

d) The residual entropy.

For certain classes of substances, there is still one thermodynamic property, viz., the residual entropy of the condensed phase at absolute zero, that must be taken into account in order that the vapor pressure at low temperatures will be correctly represented. For a perfect crystal, in which each cell is occupied by an identical group of atoms in the same relative position, this quantity is zero, in agreement with equation (20). However, such exact structural periodicity is absent in glasses (which are actually supercooled liquids) and in certain crystals whose molecules can assume multiple orientations in the lattice because of negligible differences in the energies involved, examples being water, carbon monoxide, and nitrous oxide. Accordingly, the entropy of these substances does not vanish at  $T = 0$ , although their specific heats still follow the  $T^3$  law at low temperatures (provided that free electrons are not present), as can be verified from analysis of calorimetric data (ref. 10, chap. IV)<sup>†</sup>.

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<sup>†</sup> The occurrence of molecules with different combinations of isotopes and different electronic and nuclear spins also adds to the entropy, but if the ratios of the various types present in an otherwise pure substance are the same for each phase, the added entropy of mixing will have no influence on equilibrium properties (see ref. 10, pp. 556-559 and 577-578).

If the imperfection of a crystal is due to the occurrence of a multiplicity of physically distinct molecular states having essentially equal energies under the conditions of lattice formation, then the final term needed in the expression for the free energy can be written

$$-T s_0 = -RT \log \Omega_0 \quad (38)$$

where  $\Omega_0$  is the total number of such distinguishable states "frozen" into the crystal (under the assumption that their probabilities are equal). As can be shown by differentiation, this term contributes an amount  $s_0 = R \log \Omega_0$  to the entropy, but nothing to the pressure, internal energy, or heat capacity. Obviously, for a perfect crystal the value of  $\Omega_0$  must be unity.

On comparing expressions (38) and (37) with the last two terms of equation (23), and using equation (30) which links  $c_1$  with the reduced chemical constant  $\iota$ , we may now identify

$$\begin{aligned} B_{00} &= c_1 + \frac{1}{2} \log [T_c^{3+n} / (\kappa \Omega_0 \rho_c)^2] = \iota - \log \kappa \Omega_0, \\ B_{10} &= -b \rho_c. \end{aligned} \quad (39)$$

The first of these relations affords a useful check on the values found for the parameters  $B_{00}$  and  $\kappa$ , since the quantities  $\iota$  and  $\Omega_0$  can be evaluated independently on theoretical grounds. However, the relationship of the parameters  $A_1$ , previously given in equation (27), and  $B_{10}$ , given above, to the van der Waals constants  $a$  and  $b$  should be regarded as purely formal if, as is customary, comparison is made with values derived from critical data. For, in this region, equation (13) does not accurately represent the behavior of real fluids. It yields a pressure variation along the critical isotherm proportional to  $(\rho - \rho_c)^3$  in the neighborhood of the critical density, without giving any indication of the distinctive flatness observed experimentally for isotherms in this region

(ref. 22), a phenomenon that appears to be quite general<sup>†</sup>. Recent theoretical inquiries (refs. 23 and 24) have considered whether a somewhat greater exponent, possibly as high as 5, might be more appropriate, or at least allowable. Whatever may be the underlying explanation, the isotherms are very much flatter near the critical point than van der Waals' formula would indicate.

In any event, it has been found that the values obtained for  $a$  and  $b$  are quite sensitive to the temperature and density ranges of the data used (ref. 25, § 52A). Consequently, the relations involving  $A_1$  and  $B_{10}$  that are given in equations (27) and (39) can be expected to hold only if the values for the quantities  $a$  and  $b$  have been determined by fitting equation (13) to data well on the high-temperature and low-density side of the critical point, since it is only under those circumstances that the expression developed herein will reduce to such a form, as will be shown in Section VII(b).

e) The general equation of state.

For the sake of clarity and completeness, we now collect the several components of the analytic approximation for the Helmholtz free energy (per unit mass) into a compact, general formula, viz.,

$$f(\xi, \theta) = RT_c \left[ \sum_{\ell=0}^m A_{\ell} \xi^{\ell} - \theta \left( \log \Omega_0 - \frac{1}{2} \log \varphi + (1-\varphi) \sum_{\ell=0}^m \sum_{k=0}^{\ell} B_{\ell k} \varphi^k \xi^{\ell-k} \right) \right], \quad (40)$$

from which by differentiation we obtain the following expressions for the pressure-volume product, internal energy, entropy, and specific heat:

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<sup>†</sup> In all probability, such behavior is intimately connected with the existence of a singularity in the thermodynamic functions at the critical point, the influence of which is fairly localized. This topic is examined in greater detail in Appendix B.

$$pv = RT_c \left[ \sum_{\ell=0}^m \ell A_{\ell} \xi^{\ell} + \theta(1-\varphi) \left( \frac{\chi}{2} + \sum_{\ell=0}^m \sum_{k=0}^{\ell} B_{\ell k} \{ [(k+1)\varphi - k] \chi - (\ell - k) \} \varphi^k \xi^{\ell-k} \right) \right], \quad (41)$$

$$u = RT_c \left[ \sum_{\ell=0}^m A_{\ell} \xi^{\ell} + \theta(1-\varphi) \left( \frac{\mu}{2} + \sum_{\ell=0}^m \sum_{k=0}^{\ell} B_{\ell k} [(k+1)\varphi - k] \mu \varphi^k \xi^{\ell-k} \right) \right], \quad (42)$$

$$s = R \left[ \log \Omega_0 - \frac{1}{2} \log \varphi + (1-\varphi) \left( \frac{\mu}{2} + \sum_{\ell=0}^m \sum_{k=0}^{\ell} B_{\ell k} \{ [(k+1)\varphi - k] \mu + 1 \} \varphi^k \xi^{\ell-k} \right) \right], \quad (43)$$

$$c_v = R(1-\varphi) \left( \frac{\nu}{2} + \sum_{\ell=0}^m \sum_{k=0}^{\ell} B_{\ell k} \{ [(k+1)\varphi - k] \nu - [(k+1)^2 \varphi - k^2] (1-\varphi) \mu^2 \} \varphi^k \xi^{\ell-k} \right), \quad (44)$$

$$\text{where } \chi(\xi, \theta) = 2 - \frac{\eta \xi}{\eta \xi + \zeta}, \quad (45)$$

$$\mu(\xi, \theta) = 3 + \theta \frac{\eta' \xi + \zeta'}{\eta \xi + \zeta}, \quad (46)$$

$$\nu(\xi, \theta) = (1 + \mu \varphi) \mu + \theta (\partial \mu / \partial \theta) \quad (47)$$

$$= (1 + 3\varphi) \left( 3 + 2\theta \frac{\eta' \xi + \zeta'}{\eta \xi + \zeta} \right) + \theta^2 \frac{\eta'' \xi + \zeta''}{\eta \xi + \zeta} - (1-\varphi) \left( \theta \frac{\eta' \xi + \zeta'}{\eta \xi + \zeta} \right)^2,$$

and where the functions  $\eta(\theta)$ ,  $\zeta(\theta)$  and  $\varphi(\xi, \theta)$  are given by equations (107), (29) and (34), respectively. Other than the quantity  $\kappa$ , and whatever parameters appear in the functions  $\eta(\theta)$  and  $\zeta(\theta)$ , which would ordinarily

be fixed in advance, anyway, all the remaining parameters, viz., the  $m+1$  coefficients  $A_{\lambda}$  and the  $(m+1)(m+2)/2$  coefficients  $B_{\lambda k}$ , occur linearly in each of the formulas (40-44), thus facilitating their determination by a least-squares fit to the available thermodynamic data.

The functions  $\mu(\xi, \theta)$  and  $\nu(\xi, \theta)$ , which have been introduced here merely for notational convenience, are nonetheless closely connected with the number of molecular degrees of freedom that are active in taking up and storing internal energy when the density is small. For, in the limit as  $\xi \rightarrow 0$ , we find

$$\mu^0(\theta) = \lim_{\xi \rightarrow 0} \mu(\xi, \theta) = 3 + \theta \frac{d}{d\theta} (\log \zeta) = 3 + \frac{\theta \zeta'}{\zeta}, \quad (48)$$

$$\nu^0(\theta) = \lim_{\xi \rightarrow 0} \nu(\xi, \theta) = 3 + \theta \frac{d^2}{d\theta^2} (\theta \log \zeta) = 3 + 2 \frac{\theta \zeta'}{\zeta} + \frac{\theta^2 \zeta''}{\zeta} - \left( \frac{\theta \zeta'}{\zeta} \right)^2. \quad (49)$$

The first of these quantities corresponds to an average over the entire range 0 to  $\theta$ , while the second one corresponds to the value effective at the temperature  $\theta$  [cf. equation (32)]. In other words, the mean specific heat of an ideal gas is given by  $\frac{1}{2} \mu^0 R$ , while the true (incremental) specific heat is  $\frac{1}{2} \nu^0 R$ , a quantity originally introduced in equation (7), which reappears here as an explicit function of temperature. Both, evidently, depend only on the function  $\zeta(\theta)$  for the particular gas.

## VII. ASYMPTOTIC BEHAVIOR OF THE ANALYTIC FORMULATION

It is desirable to assess the adequacy of the foregoing heuristic development of a mathematical approximation for the Helmholtz free-energy function by examining the asymptotic behavior of some of the thermodynamic quantities derived from it. Furthermore, the insight thus gained will afford valuable guidance in the selection of a suitable expression for the function  $\eta(\theta)$ . Four sets of limiting conditions will be considered:

- 1) density held constant and finite with temperature approaching zero,
- 2) density constant and finite with temperature approaching infinity,
- 3) constant finite temperature with density approaching zero, and
- 4) constant finite temperature with density approaching infinity.

### a) Case 1: Density finite with $\theta \rightarrow 0$ .

As previously noted, the behavior of matter in this case has been placed on a sound theoretical foundation, adequately confirmed through many experimental investigations (ref. 13, chap. III and IV). To ascertain the character of equations (40-44) under these limiting conditions, we must first expand the function  $\varphi(\xi, \theta)$ , defined by equation (34), in a power series around the value  $\theta=0$  with  $\xi$  held constant. Thus, provided that  $\xi \neq 0$ , we obtain

$$\varphi = 1 - \frac{\kappa^2(\eta_0 \xi + \zeta_0)}{\xi^2} \theta^3 + \dots \quad (50)$$

and, in like manner, for  $\log \varphi$  we have

$$\log \varphi = - \frac{\kappa^2(\eta_0 \xi + \zeta_0)}{\xi^2} \theta^3 + \dots \quad (51)$$

in which  $\eta_0 = \eta(0)$  and  $\zeta_0 = \zeta(0)$ . Substituting these approximations into equations (40-44), we find



$$f = u_0(\xi) - RT_c [(\log \Omega_0)\theta + A(\xi)\theta^4 + \dots], \quad (52)$$

$$pv = \xi u_0'(\xi) - RT_c [\xi A'(\xi)\theta^4 + \dots], \quad (53)$$

$$u = u_0(\xi) - RT_c [3A(\xi)\theta^4 + \dots], \quad (54)$$

$$s = R[\log \Omega_0 + 4A(\xi)\theta^3 + \dots], \quad (55)$$

$$c_v = R[12A(\xi)\theta^3 + \dots], \quad (56)$$

$$\text{where } A(\xi) = \frac{\kappa^2}{\xi^2} (\eta_0 \xi + \zeta_0) \left[ \frac{1}{2} + \sum_{\ell=0}^m \sum_{k=0}^{\ell} B_{\ell k} \xi^{\ell-k} \right], \quad (57)$$

$$A'(\xi) = \frac{\kappa^2}{\xi^3} \{ (\eta_0 \xi + \zeta_0) \sum_{\ell=0}^m \sum_{k=0}^{\ell} B_{\ell k} (\ell-k) \xi^{\ell-k} - (\eta_0 \xi + 2\zeta_0) \left[ \frac{1}{2} + \sum_{\ell=0}^m \sum_{k=0}^{\ell} B_{\ell k} \xi^{\ell-k} \right] \}. \quad (58)$$

As anticipated, we see that the above quantities all vary according to Debye's theory of elastic solids at very low temperatures (cf. ref. 11, § 285). In particular, the specific heat conforms to the well-established  $T^3$  law for substances which lack free electrons (ref. 8, chap. VI; ref. 16, chap. III).

b) Case 2: Density finite with  $\theta \rightarrow \infty$ .

If the temperature is allowed to become indefinitely large while the density is held constant, then the term  $\xi^2$  in the denominator of  $\varphi(\xi, \theta)$

will become relatively insignificant and we can write

$$\varphi = \frac{\xi^2}{\kappa^2 [\eta(\theta)\xi + \zeta(\theta)]} \theta^{-3} + \dots \quad (59)$$

However, the rate at which  $\varphi$  vanishes in this case depends upon the limiting behavior of  $\eta(\theta)$  and  $\zeta(\theta)$ . For a (stable) molecule with a fixed number of degrees of freedom,  $c_v^0$  must approach a constant as  $\theta \rightarrow \infty$ , and it follows that  $\zeta$  must, in the limit, vary as some power of  $\theta$ .

Let us assume that  $\zeta(\theta)$  can be expanded in a Laurent series about the point at infinity, so that

$$\zeta(\theta) = \theta^q (a_0 + a_1 \theta^{-1} + a_2 \theta^{-2} + \dots), \quad (60)$$

$$\log \zeta = q \log \theta + \log a_0 + (a_1/a_0) \theta^{-1} + \dots, \quad (61)$$

where

$$q = \lim_{\theta \rightarrow \infty} \frac{d(\log \zeta)}{d(\log \theta)} = \lim_{\theta \rightarrow \infty} \frac{\theta \zeta'}{\zeta}. \quad (62)$$

If, in addition, we assume that the ratio  $\lambda = \eta(\theta)/\zeta(\theta)$  falls off at least as fast as  $1/\theta^2$  for sufficiently large  $\theta$ , then we can write

$$\varphi = (\xi^2/\kappa^2 a_0) \theta^{-(3+q)} [1 - (a_1/a_0) \theta^{-1} + \dots] + \dots, \quad (63)$$

$$\log \varphi = -(3+q) \log \theta + \log(\xi^2/\kappa^2 a_0) - (a_1/a_0) \theta^{-1} - \dots. \quad (64)$$

Furthermore, under these conditions  $\chi \rightarrow 2$ ,  $\mu \rightarrow 3+q$ , and  $\nu \rightarrow 3+q$ , with the result that equations (40-44) take the form

$$f = u_0(\xi) - RT_c \left\{ \left[ \frac{3+q}{2} \log \theta - \log \xi + B(\xi) + C \right] \theta + a_1/2a_0 + \dots \right\}, \quad (65)$$

$$pv = \xi u_0'(\xi) + RT_c \left\{ [1 - \xi B'(\xi)] \theta + \dots \right\}, \quad (66)$$

$$u = u_0(\xi) + RT_c \left\{ \frac{3+q}{2} \theta - a_1/2a_0 + \dots \right\}, \quad (67)$$

$$s = R \left\{ \left[ \frac{3+q}{2} (\log \theta + 1) - \log \xi + B(\xi) + C \right] + \dots \right\}, \quad (68)$$

$$c_v = R \left\{ \frac{3+q}{2} + \dots \right\}, \quad (69)$$

$$\text{where } B(\xi) = \sum_{\ell=0}^m B_{\ell 0} \xi^{\ell}, \quad (70)$$

$$B'(\xi) = \sum_{\ell=0}^m \ell B_{\ell 0} \xi^{\ell-1}, \quad (71)$$

$$C = \frac{1}{2} \log \kappa^2 a_0 \Omega_0^2, \quad (72)$$

The neglected terms in the above approximations are of order  $\theta^{-1}$  (except for  $s$  and  $c_v$ , where they are of order  $\theta^{-2}$ ). Thus, we find that at sufficiently high temperatures  $pv$  and  $u$  vary linearly with  $\theta$ , while  $s$  increases as  $\log \theta$  and  $c_v$  approaches a constant. By and large, this is what is actually observed. For example, the isochores of most gases exhibit varying degrees of curvature at low temperatures, but straighten out as the temperature rises and remain so (until such temperatures are reached that ionization of the gas and/or dissociation of its molecules become appreciable).

The constant of proportionality in equation (66) includes, besides R, the factor  $1 - \xi B'(\xi)$ , which to a first order of approximation (i. e., for  $m = 1$ ) assumes the form

$$1 - B_{10} \xi = 1 + b\rho_c \xi = 1 + b\rho \approx \frac{1}{1 - b\rho} . \quad (73)$$

It was noted in equations (27) and (39) that  $A_1$  could be formally identified with the quantity  $-a\rho_c/RT_c$  and  $B_{10}$  with the quantity  $-b\rho_c$ . Accordingly, equation (66) can be written

$$pv = RT_c [ A_1 \xi + (1 - B_{10} \xi) \theta + \dots ] \quad (74)$$

$$\approx -a\rho + \frac{RT}{1 - b\rho} , \quad (74a)$$

in agreement with equation (13), which shows that this case reduces to the van der Waals approximation when the density is not too great.

c) Case 3: Temperature finite with  $\xi \rightarrow 0$ .

This case is the one most thoroughly investigated from a theoretical standpoint. Its importance derives from the fact that a proper description of the gaseous phase must reduce to the ideal gas law in the limit when  $\xi = 0$ . This law has been amply verified by experiment. Yet, even for relatively small densities, substantial deviations from this limiting behavior can be observed, especially at low temperatures. Consequently, a rigorous determination of the form of the correction terms in the neighborhood of  $\xi = 0$  is of considerable interest.

First, let us express  $\varphi(\xi, \theta)$  as

$$\varphi = \frac{\epsilon \xi^2}{\epsilon \xi^2 + \lambda \xi + 1} , \quad (75)$$

in which the coefficients  $\epsilon$  and  $\lambda$  depend on the temperature only, i. e.,

$$\epsilon(\theta) = 1/\kappa^2 \theta^3 \zeta(\theta) , \quad (76)$$

$$\lambda(\theta) = \eta(\theta)/\zeta(\theta) . \quad (77)$$

If we now expand  $\varphi(\xi, \theta)$  in a Taylor series about the point  $\xi = 0$ , holding  $\theta$  fixed, the result is

$$\varphi = \epsilon \xi^2 [ 1 - \lambda \xi + (\lambda^2 - \epsilon) \xi^2 - \lambda(\lambda^2 - 2\epsilon) \xi^3 + \dots ] , \quad (78)$$

and for its logarithm we obtain

$$\log \varphi = \log \epsilon \xi^2 - \lambda \xi + (\lambda^2/2 - \epsilon) \xi^2 - \lambda(\lambda^2/3 - \epsilon) \xi^3 + \dots . \quad (79)$$

Similarly, we find

$$\begin{aligned} \chi &= 2 - \lambda \xi / (1 + \lambda \xi) \\ &= 2 - \lambda \xi + \lambda^2 \xi^2 - \lambda^3 \xi^3 + \dots . \end{aligned} \quad (80)$$

Substituting these approximations into equations (40-44), we at length obtain

$$f = RT_c \{ A_0 - \theta(B_{00} + \log \Omega_0 - \frac{1}{2} \log \epsilon \xi^2) + [A_1 - \theta(B_{10} + \frac{1}{2} \lambda)] \xi + \dots \} , \quad (81)$$

$$pv = RT_c \{ \theta + [A_1 - \theta(B_{10} + \frac{1}{2} \lambda)] \xi + \dots \} , \quad (82)$$

$$u = RT_c \{ A_0 + \frac{1}{2} \theta \mu^0 + [A_1 + \frac{1}{2} \theta^2 \lambda'] \xi + \dots \} , \quad (83)$$

$$s = R \{ B_{00} + \log \Omega_0 + \frac{1}{2} (\mu^0 - \log \epsilon \xi^2) + [B_{10} + \frac{1}{2} (\theta \lambda' + \lambda)] \xi + \dots \} , \quad (84)$$

$$c_v = R \{ \frac{1}{2} \nu^0 + [\frac{1}{2} \theta^2 \lambda'' + \theta \lambda'] \xi + \dots \} , \quad (85)$$

$$\text{where } \mu^0 = \mu(0, \theta) = -\theta \{ d(\log \epsilon) / d\theta \} , \quad (86)$$

$$\nu^0 = \nu(0, \theta) = \mu^0 + \theta (d\mu^0 / d\theta) . \quad (87)$$

Explicit formulas for  $\mu^0$  and  $\nu^0$  are given in equations (48) and (49). The specific heat at constant pressure is also readily found for this case, viz.,

$$c_p = R \left[ \frac{1}{2}(\nu^0 + 2) + \left\{ \frac{1}{2} \theta^2 \lambda'' - 2A_1/\theta \right\} \xi + \dots \right]. \quad (88)$$

We see at once, on setting  $\xi = 0$  in the above expressions, that they reduce to the corresponding ones for an ideal gas. Thus, the equations for the pressure, internal energy, and specific heats become

$$pv = RT, \quad (89)$$

$$u = u_0(0) + \frac{1}{2} \mu^0 RT, \quad (90)$$

$$c_v = \frac{1}{2} \nu^0 R, \quad (91)$$

$$c_p = \frac{1}{2}(\nu^0 + 2)R = c_v + R. \quad (92)$$

The series of coefficients multiplying powers of the density in the expansion of  $pv$  are commonly called the virial coefficients (ref. 15, §10.3), the first one being  $RT$  (or unity if we elect to divide them all by  $RT$ ). Each subsequent coefficient of equation (82) contains a term  $\frac{1}{2}RT(-\lambda)^\ell$ , deriving from the approximation (80) for  $\chi$ ,  $\ell=1$  corresponding to the second coefficient. On account of the inverse relationship of  $\lambda$  versus  $\theta$ , these particular terms will tend to predominate in each of the successive coefficients when the temperature becomes low enough, and there will be a concurrent alternation of their algebraic signs (assuming  $\eta$ , and therefore  $\lambda$ , to be positive). This is consistent with the empirical observation that the virial coefficients of most gases do alternate in sign and become quite large at sufficiently low temperatures.

It is to be particularly noted that no such temperature-dependent terms are found in the virial coefficients for van der Waals' equation, the second one, for example, being  $-a+bRT$ . As a result, equation (82)

does not approximate the van der Waals formula, even for very small densities, unless at the same time the temperature is high enough to make the contribution from  $\lambda(\theta)$  negligible<sup>†</sup>.

By contrast, it was known long ago that Callendar's equation,

$$v - b = RT/p - c/T^n, \quad (93)$$

is more nearly in accord with the facts than is van der Waals' at low temperature and moderate density (ref. 28). When solved for  $p$  in terms of  $T$  and  $v$  (or  $\rho$ ), equation (93) becomes

$$p = \frac{RT}{v - b + c/T^n} = \frac{RT\rho}{1 - (b - c/T^n)\rho}. \quad (94)$$

If we then expand the variable  $pv = p/\rho$  in a power series with  $T$  fixed, the result, through terms of the 1st power in  $\rho$ , is

$$pv = RT[1 + (b - c/T^n)\rho + \dots]. \quad (95)$$

This can now be compared with the virial expansion, equation (82), in the special case for which the coefficient  $A_1$  vanishes, and under the further assumption that the temperature is so low that  $Q_0 = 1$  in equation (29) and  $\eta$  may be regarded as constant. Thus, on making the following substitutions,

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<sup>†</sup> In this respect, the Beattie-Bridgeman equation (ref. 26) and the Benedict-Webb-Rubin equation (ref. 27) offer a distinct improvement. Both specifically include a term which appears in the second virial coefficient in a form equivalent to having  $\lambda$  vary as  $1/\theta^3$ , a feature that greatly increases their fidelity of approximation at low temperatures.

$$\begin{array}{rcl}
A_1 & = & 0 \qquad \eta = 2c\rho_c/T_c^n \\
B_{10} & = & -b\rho_c \qquad \zeta = \theta^n = (T/T_c)^n \\
\theta & = & T/T_c \\
\xi & = & \rho/\rho_c \qquad \lambda = \eta/\zeta = 2c\rho_c/T_c^n
\end{array} \quad \left. \vphantom{\begin{array}{rcl} A_1 \\ B_{10} \\ \theta \\ \xi \end{array}} \right\} \quad (96)$$

we find that equation (82) agrees with equation (95).

If the van der Waals correction  $-a\rho^2$  had been included in equation (94), the composite equation might have been even more successful in fitting the data over a limited region. In any event, it would constitute an appropriate asymptotic form of the general equation of state (41) at low temperatures and vanishingly small densities.

d) Case 4: Temperature finite with  $\xi \rightarrow \infty$ .

In judging the asymptotic behavior of the approximation in this region, little empirical or theoretical guidance of a precise nature is available for comparison. Consequently, we must largely rely on fragmentary evidence combined with intuitive reasoning. It has been shown through analysis of seismological data, along with direct measurements by Bridgman (ref. 29), that the densities of many common substances are increased by less than 50 percent at pressures of 100,000 or more atmospheres. The compressibility of matter becomes very slight under such conditions, and is attended by an increase in the velocity of sound waves.

As indicated in Section VI(c), the behavior of matter at very high densities is somewhat akin to that at very low temperatures: i. e., the contribution to the internal energy due to thermal agitation can be expected to become negligible, and  $c_v$  should then bear an inverse



relation to  $\xi$ . In particular, according to the Debye theory of elastic solids, the specific heat for any sufficiently low but fixed value of the temperature varies inversely with the density times the cube of the speed of propagation of elastic waves through the medium in question. Thus, we should expect that the terms which pertain to the intermolecular potential energy would ultimately dominate all other terms at sufficiently high densities.

According to the definition (34), the function  $\varphi(\xi, \theta)$  approaches unity as  $\xi$  increases without limit. If, in addition, it is assumed that the functions  $\eta(\theta)$  and  $\zeta(\theta)$  are finite for all finite  $\theta$ , we may write

$$\varphi = 1 - \kappa^2 \theta^3 \eta \xi^{-1} [1 + (\frac{\zeta}{\eta} - \kappa^2 \theta^3 \eta) \xi^{-1} + \dots], \quad (97)$$

$$\log \varphi = -\kappa^2 \theta^3 \eta \xi^{-1} [1 + (\frac{\zeta}{\eta} - \frac{1}{2} \kappa^2 \theta^2 \eta) \xi^{-1} + \dots], \quad (98)$$

$$\chi = 1 + \frac{\zeta}{\eta} \xi^{-1} [1 - \frac{\zeta}{\eta} \xi^{-1} + \dots]. \quad (99)$$

Substituting these approximations into equations (40-44), we find that the dominant terms in each instance are

$$f = RT_c \{ A_m \xi^m + \dots - \theta \log \Omega_0 - \kappa^2 \theta^4 \eta [ B_{m0} \xi^{m-1} + \dots ] \}, \quad (100)$$

$$pv = RT_c \{ mA_m \xi^m + \dots + \kappa^2 \theta^4 \eta [ B_{m0} \xi^{m-1} + \dots ] \}, \quad (101)$$

$$u = RT_c \{ A_m \xi^m + \dots + \kappa^2 \theta^4 \eta [ B_{m0} \mu^\infty \xi^{m-1} + \dots ] \}, \quad (102)$$

$$s = R \{ \log \Omega_0 + \kappa^2 \theta^3 \eta [ B_{m0} (\mu^\infty + 1) \xi^{m-1} + \dots ] \}, \quad (103)$$

$$c_v = R \kappa^2 \theta^3 \eta [ B_{m0} \nu^\infty \xi^{m-1} + \dots ], \quad (104)$$

$$\text{where } \mu^\infty(\theta) = \lim_{\xi \rightarrow \infty} \mu(\xi, \theta) = 3 + \theta\eta'/\eta, \quad (105)$$

$$\nu^\infty(\theta) = \lim_{\xi \rightarrow \infty} \nu(\xi, \theta) = 12 + 8\theta\eta'/\eta + \theta^2\eta''/\eta. \quad (106)$$

By comparing the terms of the two series that enter into the expression (102) for  $u$ , we find that the nonthermal portion of the internal energy will ultimately exceed the thermal contribution for any fixed temperature, provided that the leading term of  $u_0(\xi)$  is at least of degree  $m$  and its coefficient  $A_m$  is positive. It is for this reason that the same upper limit  $m$  has been assigned to the summation indices for both  $u_0(\xi)$  and  $f_2(\xi, \theta)$  in equations (26) and (37). The form of the expression (103) obtained for  $s$  indicates that  $B_{m0}$  should be positive if  $\eta(\theta)$  is positive, to avoid violating the Third Law of Thermodynamics (ref. 10, p. 512) which sets zero as a lower bound on the entropy of a substance. Also, in order that the factor  $(\mu^\infty + 1)$  in this expression should always be positive or zero, we conclude that the value of  $\mu^\infty$  (which necessarily approaches 3 as  $\theta \rightarrow 0$ ) must never at any temperature be less than -1. This imposes an additional constraint on the function  $\eta(\theta)$ : it must not decline more rapidly than the inverse fourth power of the temperature.

In order to represent empirical thermodynamic data over a fairly restricted range of variables, it is not, of course, necessary to employ a function that satisfies all the conditions detailed in this section. On the other hand, to be able to extrapolate data with some degree of confidence into a region not readily accessible to direct measurement, one should use an equation whose asymptotic behavior can be shown to be reasonable on physical grounds. Furthermore, such an equation is apt to be more effective in minimizing bias resulting from experimental errors and permit more accurate interpolation of intermediate values.

## VIII. DETERMINATION OF THE FUNCTION $\eta(\theta)$

We have at last arrived at a point where the choice of a suitable expression for the function  $\eta(\theta)$  can be put on a rational basis. The preceding analysis of the asymptotic behavior of the general equation of state reveals that the form of  $\eta(\theta)$  is subject to definite restrictions at both low temperatures (case 1) and high temperatures (case 4). Moreover, the approximations derived from the virial expansion (case 3) supply a means for quantitatively relating  $\eta$  to empirical data for gases under low pressure. These data typically indicate that its value is positive over the temperature ranges investigated.

To begin with, we may infer from equation (56) that the function  $A(\xi)$  will be  $> 0$  for all stable states, because the specific heat of matter in thermodynamic equilibrium is necessarily positive at all temperatures above absolute zero (ref. 8, §21). Under such conditions, therefore, the product of the factors on the right-hand side of equation (57) may not vanish. Now, according to equation (29), the function  $\zeta(\theta)$ , though essentially positive, becomes negligibly small as  $\theta \rightarrow 0$ , except in the case of monatomic gases, for which  $\zeta(\theta) \equiv 1$ . So, in order that the factor  $(\eta_0 \xi + \zeta_0)$  should not be identically zero, it is necessary that  $\eta(\theta)$  should approach a definite constant as  $\theta \rightarrow 0$  (presumably positive, but possibly zero or negative for certain monatomic substances). On the other hand, as  $\theta$  becomes indefinitely large,  $\lambda = \eta(\theta)/\zeta(\theta)$  must decline fairly rapidly to be congruous with measurements of the Joule-Thomson coefficient. At the same time, however, we should bear in mind the conclusion reached in Section VII(d) that the rate of decay of  $\eta(\theta)$  cannot be greater than the inverse fourth power of  $\theta$ .

An analytic form that exactly meets the requirements set forth is

$$\eta(\theta) = \eta_0 \left(1 - e^{-\tilde{\theta}/\theta}\right)^r \quad 0 \leq r \leq 4, \quad (107)$$

in which the parameter  $\hat{\theta}$  assumes the role of some characteristic temperature. Such a form is rather suggestive of Einstein's theory of specific heats (ref. 30; also ref. 16, §19) and, in a certain sense, allows equation (44) to take account of (or at least simulate) Einstein terms<sup>†</sup>, as well as the Debye term. If we let  $\theta$  approach either zero or infinity, we find, in accordance with our expectations, that the asymptotic forms of equation (107) are:

$$\begin{aligned} \eta(\theta) &\approx \eta_0 & \theta &\ll \hat{\theta}, \\ \eta(\theta) &\approx \eta_0(\hat{\theta}/\theta)^r & \theta &\gg \hat{\theta}. \end{aligned} \tag{108}$$

Furthermore, the inverse power behavior of  $\eta(\theta)$  for  $\theta \gg \hat{\theta}$  permits a simple evaluation of the quantities on the right-hand sides of equations (105) and (106) in this temperature range. Since  $\theta\eta'/\eta \rightarrow -r$  and  $\theta^2\eta''/\eta \rightarrow r(r+1)$  as  $\theta \rightarrow \infty$ , we obtain by substitution

$$\mu^\infty(\infty) = 3-r, \tag{109}$$

$$\nu^\infty(\infty) = 12-7r+r^2. \tag{110}$$

The assignment of the value 3 to the exponent  $r$  will cause both the above quantities to vanish. In this particular case, the thermal contributions to  $u$  and  $c_v$ , which are multiplied respectively by  $\mu^\infty(\theta)$  and  $\nu^\infty(\theta)$  in equations (102) and (104), will depend on  $\xi$  to a power less than  $m-1$  at extremely high densities whenever  $\theta$  is moderately greater than  $\hat{\theta}$ .

We now come to the final step: how to determine (or estimate) values for the parameters  $\hat{\theta}$ ,  $\eta_0$  and  $r$  from experimental data. At high

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<sup>†</sup> In the case of some molecular substances, e. g., benzene, these terms make a significant contribution to the specific heat when the temperature is not too low (ref. 10, pp. 625-626). If the data should warrant it, equation (107) could be generalized to include several such terms, each with its own characteristic temperature.

temperatures, the characteristic equation is insensitive to  $\eta$  because the term  $\kappa^2 \theta^3 \eta \xi$  in the denominator of equation (34) is overshadowed either by  $\kappa^2 \theta^3 \zeta$  if  $\xi$  is small or by  $\xi^2$  if  $\xi$  is large. The situation is different, however, at lower temperatures when  $\zeta$  is much smaller; then, if  $\xi$  is not too large, the value of this term may become quite significant, depending at first on all three parameters, while at still lower temperatures  $\eta_0$  will emerge as the controlling parameter. By and large, values for all these constants must be deduced from data taken in the region below the critical temperature of the substance.

The most direct way of finding  $\eta(\theta)$  is to first extract values of  $\lambda(\theta)$  from the available data and then use the relation  $\eta = \lambda \zeta$ . To the extent that equations (40-44) do actually characterize the behavior of real substances, it should be possible to infer  $\lambda$  by measuring either the quantity  $\rho^{-2}(\partial^2 p / \partial T^2)$  or the quantity  $T^{-1}(\partial c_v / \partial \rho)$  at several fairly small densities and by subsequently extrapolating the results to zero density. For, according to equation (31), both these quantities are related to  $\partial^3 f / \partial T^2 \partial \rho$ , the limiting value of which (in terms of reduced independent variables) can be obtained from equation (85), for example, as follows:

$$\begin{aligned} \lim_{\xi \rightarrow 0} \frac{\partial^3 f}{\partial \theta^2 \partial \xi} &= -(T_c / \theta) \lim_{\xi \rightarrow 0} \left\{ \frac{\partial c_v}{\partial \xi} \right\} / \theta \\ &= -\frac{1}{2} (RT_c) \frac{d^2}{d\theta^2} (\theta \lambda), \end{aligned} \quad (111)$$

the corresponding dimensional form being

$$\lim_{\rho \rightarrow 0} \frac{\partial^3 f}{\partial T^2 \partial \rho} = -\frac{1}{2} (R / \rho_c) \frac{d^2}{dT^2} (T \lambda). \quad (111a)$$

Thus, we see that an evaluation of this quantity for a set of temperatures extending over some suitable interval, together with the conditions that the variable  $\theta\lambda$  and its first derivative must vanish as  $\theta \rightarrow \infty$ , would suffice to establish the quantitative character of  $\lambda(\theta)$ .

The straightforward determination of such sets of limiting values from either the variation of  $c_v$  with density or the curvature of the isochores at low densities entails formidable experimental difficulties (ref. 31, §C, 3). However, there do exist a number of closely related quantities that can be measured with an acceptable degree of precision at moderately low pressures. Chief among these are 1) the deviations from Boyle's law; 2) the Joule-Thomson coefficient; and 3) the rate of change of  $c_p$  versus pressure. The limiting values of these quantities as  $p \rightarrow 0$  can be related to equations (82), (83), and (88) and their derivatives with respect to pressure (holding temperature constant). Taken in combination with equation (17), they yield the following expressions:

$$\lim_{p \rightarrow 0} \left( \frac{\partial \{pv\}}{\partial p} \right)_T = \frac{1}{\rho_c} [ A_1/\theta - B_{10} - \frac{1}{2}\lambda ], \quad (112)$$

$$\lim_{p \rightarrow 0} \left( \frac{\partial h}{\partial p} \right)_T = -c_p^0 \mu_{J.T.}^0 = \frac{1}{\rho_c} [ 2A_1/\theta - B_{10} + \frac{1}{2}(\theta\lambda' - \lambda) ], \quad (113)$$

$$\lim_{p \rightarrow 0} \left( \frac{\partial c_p}{\partial p} \right)_T = \frac{1}{T_c \rho_c} [ \frac{1}{2}\theta\lambda'' - 2A_1/\theta^2 ]. \quad (114)$$

Although the preceding formulas involve the coefficients  $A_1$  and  $B_{10}$  as well as  $\lambda(\theta)$  and its derivatives, these (as yet unknown) coefficients can be eliminated by various schemes of data analysis. This becomes particularly simple when the values of the limits are obtained at equal intervals of temperature. For, in the case of equations (112) and (113),

if we multiply them by  $\theta$  and then take 2nd differences of the results, any linear combination of  $A_1$  and  $B_{10}\theta$  will be automatically removed. Likewise, in the case of equation (114), after multiplying by  $\theta^2$  and taking 1st differences with respect to temperature, we get rid of the constant  $A_1$ . Such a detailed analysis of the data available for water vapor (refs. 32 and 33) indicates that  $\eta(\theta)$  can be accurately represented by equation (107) when the exponent  $r$  is set equal to 3. Whether this formula will give a satisfactory representation for other substances remains to be determined.

## IX. CONCLUSION

In this paper we have elaborated a semiempirical equation of state which is believed to have a greater range of validity and more general application than any heretofore devised for substances having a stable molecular structure. Much of the development has been heuristic, relying heavily on ideas suggested by statistical mechanics, quantum theory and kinetic theory, as well as on empirical knowledge. Nevertheless, the approximation has been deliberately formulated to exhibit the proper asymptotic behavior as one or the other of the independent variables approaches either zero or infinity – at least in those cases for which theory has already provided a definite answer. Consequently, the flexibility arising from the presence of adjustable parameters can be used more effectually to attain close agreement with observation in the range where accurate measurements can be made.

To test the hypothesis set forth here, some preliminary analyses of the P-V-T data for water have been carried out. These calculations have shown that the basic set of values given in the 1963 International Skeleton Table for Compressed Water and Superheated Steam can be represented over the entire grid (580 combinations of pressure and temperature) to well within the assigned tolerances at all but a few points, where the deviations exceeded the tolerances by a small margin. The resulting approximation was about as accurate as that obtained by Keenan et al (ref. 33).

The concomitant approximation for the enthalpy, however, did not produce as good a fit to the corresponding values tabulated for this quantity over the same grid points, particularly in the region lying close to the critical point. Moreover, the values calculated for the specific heat at constant volume were clearly at variance with the anomalous



behavior observed near the critical point. A subsequent investigation aimed at improving the quality of the approximating function in this area is described in Appendix B. Although funds are not currently available for writing a computer program based on the revised form of the equation of state, it is hoped that this will be possible at some future time. This would be particularly desirable, as new data are constantly becoming available.

The formulation presented herein will allow empirical thermodynamic data obtained for many different physical quantities to be correlated simultaneously. It is only necessary to determine the appropriate formula for each quantity to be included in the fit by differentiation of the fundamental equation adopted for  $f(v, T)$ . One of the chief advantages accruing from this approach is that the values of all quantities calculated from the analytic approximation will be thermodynamically consistent.

In conclusion, the author particularly wishes to cite the original contributions to the science of thermodynamics by Max Planck, who so clearly stated (ref. 11, § 289) the essential requirements which a fundamental equation of state must fulfill:

"From [the equations which give the pressure of a saturated vapor as a function of the temperature] it follows at once that the chemical constant can be calculated if the general characteristic equation of the substance is known, and that therefore the chemical constant must occur in the general characteristic equation. Already a number of forms of the characteristic equation have been proposed; besides that of van der Waals and that of Clausius, there is a series of others, which in certain limited regions fulfill their purpose with good approximation. None, as far as I see, is sufficiently comprehensive to be applicable to liquids at the lowest temperatures. . . . Before we can hope to calculate the chemical constant from the characteristic equation, a form of that equation must be found which, when  $T=0$  and the pressure is finite and positive, is consistent with Nernst's theorem."

This investigation is an attempt to answer that challenge.

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APPENDIX A  
THE FREE ENERGY OF AN IDEAL GAS

We give here a synopsis of the steps leading to equation (9) from the viewpoint of statistical mechanics. [For a more detailed treatment see, for example, ref. 8, chap. IV or ref. 19, § 143-146.]

A formula can be obtained from the Gibbs distribution that makes it possible, in principle, to calculate the free energy of any system of particles in statistical equilibrium with its surroundings, viz.,

$$F = -kT \log Z, \quad (A1)$$

where  $k$  is Boltzmann's constant and  $Z$  stands for the partition function or "sum over states" (Zustandssumme). The latter depends on the spectrum of energy states  $E_j$  of the body in question, and is given by

$$Z = \sum_j e^{-E_j/kT}. \quad (A2)$$

Such an evaluation is not feasible, however, except in a few special situations. One of these is a system consisting of  $N$  identical particles which occupy a volume  $V$  large enough that the effect of their mutual interaction is negligible at the given temperature. This characterizes an ideal gas – to which Boltzmann statistics apply, provided that distributions which differ only by a permutation of the  $N$  particles are counted only once in the enumeration of distinguishable quantum states – and we can write

$$Z = (Q^N/N!) e^{-E_0/kT}, \quad (A3)$$

where  $Q$  denotes the molecular partition function pertaining to the energy states of an individual molecule of the gas, and  $E_0$  is the zero-point energy of the system, i. e., the residual energy at  $T=0$ . Using Stirling's formula for  $\log N!$  when  $N$  is large, we find

$$\begin{aligned}\log Z &= \log Q^N - \log N! - E_0/kT \\ &= N \log Q - N(\log N - 1) - E_0/kT,\end{aligned}\tag{A4}$$

so that equation (A1) becomes

$$F = -NkT(\log Q - \log N + 1) + E_0.\tag{A5}$$

The summations necessary to obtain  $Q$  are effected with the help of quantum statistics. The process is greatly simplified by the fact that the various degrees of freedom of molecular motion act independently of one another except for a slight coupling between rotation and vibration. As a result, the partition function can be resolved into a product of factors corresponding to 1) the three components of translatory motion, 2) rotation of the molecule as a rigid structure, 3) the vibrational modes regarded as harmonic oscillators, and 4) a set of small corrections to account for the anharmonicity of the vibrations and their coupling with the rotation. [Note: There may be additional factors according to the complexity of the molecular structure.]

It follows that the approximate factored form of  $Q$  can be written

$$Q = Q_{tr} \times Q_{rot} \times Q_0\tag{A6}$$

in which all other factors are incorporated into  $Q_0$ , i. e.,

$$Q_0 = Q_{vib} \times Q_{anh} \times Q_{cpl} \times \dots.\tag{A7}$$

The value of  $Q_0(T)$  remains close to unity over the (usually appreciable) temperature range where vibrational excitation is negligible. For example, the contribution arising from a combination of simple harmonic vibrations can be expressed as

$$Q_{vib} = \prod_i \left(1 - e^{-\Theta_i/T}\right)^{-1}\tag{A8}$$

where  $\Theta_i = h\nu_i/k$ ,

$h$  is Planck's constant, and

$\nu_i$  is frequency of  $i^{\text{th}}$  normal mode.

It is clear that the value of  $Q_{\text{vib}}$  does not differ sensibly from unity so long as the conditions  $T \ll \Theta_i$  are satisfied. In contrast, at all but the very lowest temperatures the rotational, as well as the translational, degrees of freedom are fully excited (an exception being  $\text{H}_2$ ) and their contributions then reduce to

$$\begin{aligned} Q_{\text{tr}} &= A_{\text{tr}} VT^{3/2}, \\ Q_{\text{rot}} &= A_{\text{rot}} T^{n/2}, \end{aligned} \tag{A9}$$

where

$$\begin{aligned} A_{\text{tr}} &= (2\pi mk/h^2)^{3/2}, \\ A_{\text{rot}} &= (1/\sigma\pi)(8\pi^3Ik/h^2)^{n/2}, \end{aligned}$$

$m$  is the mass of a molecule,

$n$  is the number of rotational degrees of freedom,

$\sigma$  is the symmetry index (number of equivalent orientations of molecule), and

$I = I(n)$  is the geometric mean of principal moments of inertia about center of mass.

Specifically,

$$I(2) = I_A = I_B = (I_A I_B)^{1/2} \quad [\text{rigid collinear molecule}],$$

$$I(3) = (I_A I_B I_C)^{1/3} \quad [\text{rigid noncollinear molecule}].$$

In the case of a diatomic gas, rotation about the axis joining the two nuclei is suppressed, so that  $n = 2$ ; for a monatomic gas all rotational motion is suppressed, and therefore  $n = 0$ . Values of the various molecular constants that appear in the partition function (other than the mass) are deduced from the analysis of spectroscopic data.

On substituting the partial factorization displayed in (A6) for the quantity  $Q$  in equation (A5) and using the theoretical results given by equation (A9), we obtain

$$F = -NkT \left[ \log T^{(3+n)/2} + \log \frac{V}{N} + \log A_{tr} + \log A_{rot} + \log Q_0(T) + 1 \right] + E_0. \quad (A10)$$

The ratio of the volume to the number of particles therein bears an inverse relation to the mean density, viz.,

$$\rho = Nm/V. \quad (A11)$$

Moreover, since it is customary to relate extensive thermodynamic quantities to a unit mass of substance, we rewrite equation (A10) in terms of the specific free energy

$$f(\rho, T) = \frac{F}{Nm} = c_0 - RT \left[ \frac{3+n}{2} \log T - \log \rho + c_1 \right] + f_0(T), \quad (A12)$$

$$\text{where } f_0(T) = -RT \log Q_0(T),$$

$$c_0 = E_0/Nm,$$

$$c_1 = 1 + \log m + \log A_{tr} + \log A_{rot},$$

$$R = k/m = R_0/M \text{ (specific gas constant),}$$

$R_0$  is the universal gas constant, and

$M$  is the molecular weight of the gas.

## APPENDIX B

### THE SINGULARITY IN THE FREE ENERGY AT THE CRITICAL POINT

As indicated in the main part of this report, our approach is a somewhat pragmatic one: we seek a mathematical formulation that will adequately represent the empirical thermodynamic data without contradicting established theory. It was recognized, even in the time of van der Waals, that the physical properties of a fluid near its critical state were in some way peculiar and not accurately described with simple formulas. Various theoretical arguments have been advanced since then to the effect that the free energy cannot be analytic at the critical point (refs. 34 and 35), and this view is now generally accepted.

The most convincing experimental evidence for the existence of a singularity at the critical point derives from the fairly recent measurements of the isochoric specific heat  $c_v$  of a number of gases (refs. 36-44). The data for each of the substances so far investigated disclose a striking resemblance. Their most consistent characteristic is the rapid increase in  $c_v$  along the critical isochore<sup>†</sup> as the temperature is lowered to its critical value. Plots of  $c_v$  versus  $\log \tau = \log (T/T_c - 1)$  are nearly straight lines for  $\tau < .003$  (at least until the critical temperature is so closely approached that the abnormally large compressibility of the gas allows the density gradient induced by gravity to become great enough to appreciably affect the homogeneity of the sample under study). It has been noted by Fisher (refs. 23 and 45) that the data can be represented almost equally well by a small inverse power of  $\tau$  with an exponent ranging up to 0.2 if the parameters are suitably adjusted.

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<sup>†</sup> The form of the  $c_v$  curves along other isochores not too far removed from the critical density is quite similar, except that their steepest portions are abruptly ended on intersecting the coexistence curve (see, for example, the tables and graphs in ref. 44).

So far, statistical mechanics has not provided much unequivocal help in selecting an appropriate mathematical form — except for the exact solution obtained by Onsager in 1944 (ref. 46) for the two-dimensional model of a lattice gas, which yields a logarithmic infinity in  $c_v$  at the critical temperature.<sup>†</sup> The power-law formula arises from numerical studies of the three-dimensional, Ising model of a ferromagnet. An outgrowth of these studies has been the gradual development of the so-called "scaling" laws (refs. 24, 48, 49 and 50) to extend the power-law description to a function of two conjugate thermodynamic variables (e. g. , density and temperature). The type of singularity at the critical point can then be characterized as a branch point through the introduction of two independently chosen exponents. The effect of such a transformation is to reduce certain thermodynamic quantities to functions of a single variable — at least near the critical point — which would thus help to rationalize the manifestly similar behavior of so many different substances.

The final interpretation of experimental observations depends in large part on the framework of hypotheses adopted for their analysis. In keeping with the time-honored precept of introducing the minimum number of adjustable parameters required to "fit" a set of data, it would seem best to represent the specific-heat anomaly as a logarithmic function of  $\tau$ . Other than the value assigned to  $T_c$  — which should, perhaps, be determined independently to agree with observations relating to a number of other physical properties — there are then only two constants to be evaluated: the coefficient of the variable term ( $\log \tau$ ) and an additive constant. However, when the variable term is taken to be a small negative power of  $\tau$ , the value of the exponent must also be

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<sup>†</sup> Such anomalies have actually been observed in connection with other physical phenomena involving a transition from one state to another, e. g. , the  $\lambda$ -point transition in liquid helium (ref. 47).



determined. This extra degree of freedom naturally expands the universe of possible functions but does little to improve the quality of the approximation, a view shared by Voronel and his co-workers (ref. 40).

It is difficult to discriminate among these forms experimentally unless  $T_c$  can be very closely approached, but it is just in this temperature range that the trustworthiness of the data becomes questionable. Near the critical state measurements of  $c_v$  are extremely sensitive to the accuracy of the calorimeter for very small temperature increments, to the presence of slight impurities in the gas, to gravity-induced density gradients over the height of the sample container, and to whether the fluid is stirred constantly or allowed sufficient time to reach a state of equilibrium at each temperature setting. On the basis of the observations to date, no investigator seems yet prepared to positively rule out the logarithmic form, and its virtues should not be underestimated.

If the data can be accurately represented by this simpler form, then a log-log plot of  $c_v$  versus  $\tau$  should reveal a gradually decreasing, negative slope toward the left ( $\tau \rightarrow 0$ ) rather than a constant slope, which would indicate a power law. This would be true whether or not a constant is first subtracted from  $c_v$  to obtain  $c_v^*$  (the supposed value of the anomaly), at least insofar as the residue remains positive. Such a trend is exactly what the data of Voronel et al show for nitrogen (see ref. 40, Fig. 3).

To preserve the more complicated power-law representation, various devices have been tried for straightening out the log-log plots. One scheme allows a constant to be added to  $c_v$  (rather than subtracted) before fitting the data (ref. 45), thus implying that the regular part of  $c_v$  is negative at the critical point – not a very satisfying approach from a phenomenological viewpoint. A further modification allows  $T_c$  to be

adjustable, on the grounds that measurements of the small temperature differences involved are far more accurate than any absolute determination of  $T_c$ . Of course, with so many parameters available, it is not surprising that a good fit usually results, but the "best" value for  $T_c$  is often found to lie considerably below the generally accepted value obtained by other means (see ref. 43). In assessing the inconsistencies arising from different methods of locating the critical temperature of He<sup>4</sup>, Roach (ref. 51) questions the correctness of the basic power-law assumption for the region immediately adjacent to the critical point.

While the properties of ferromagnets and fluids display certain similarities near their respective critical points, there is no reason to suppose that mathematical models of their behavior should be completely analogous. There are, in fact, good arguments to the contrary: e. g., the coexistence curve of ferromagnets is inherently symmetrical about zero applied field, and may also constitute a singular locus; whereas fluids exhibit definite asymmetry about the critical isochore, and the well-established existence of metastable states suggests that the Helmholtz free energy may indeed be analytic along the coexistence curve except at the critical point (ref. 5, § 3.4, 3.5 and 3.7). Moreover, from a practical standpoint, the discovery of a reasonably simple, closed expression for the free energy, taking into account its dependence on the density variable, has proved to be a formidable task despite the apparent advantages of the scaling laws (see the examples in refs. 49 and 50). Some problems to be avoided are the possibility of a thermodynamically unstable formulation in the region just above  $T_c$  and the occurrence of unwanted singularities, e. g., along the critical isochore above  $T_c$ , as noted by Vicentini-Missoni et al (ref. 52, § 5).

Aside from the specific-heat measurements, some additional information about the nature of the singularity can be deduced from

investigating the shapes of the critical isotherm and the coexistence curve<sup>†</sup>. When very accurate observations of the former are approximated by a power of  $|\sigma| = |\rho/\rho_c - 1|$ , the exponent usually turns out to be a little less than 5 (with, however, considerable uncertainty because of the very large compressibility of the gas under these circumstances). On the other hand, the exponent for the coexistence curve is generally found to be slightly less than 3 (again, however, a conclusion largely based on density measurements somewhat removed from the critical value). Although for most gases such results are widely accepted, there is, nonetheless, some doubt as to their validity and consistency (ref. 57, sec. V). It is not precluded — as we shall see in what follows — that the critical isotherm (which has a point of inflection at  $\sigma=0$ ) may have the character of a function with a very small third derivative but a fairly large fifth derivative at  $\sigma=0$ , while the coexistence curve (which has a maximum there) may behave like a function with a small second derivative the effect of which is masked by the influence of higher derivatives when  $\sigma$  is appreciably different from zero (refs. 58-61).

For the various reasons cited above (and until more conclusive evidence is available), we prefer to adopt the simpler hypothesis that the specific-heat anomaly  $c_v^*$  involves a logarithmic singularity, and then seek a closed expression for the corresponding free-energy anomaly  $f^*$  which does not contain any undetermined functions of temperature. Accordingly, by straightforward analysis, the mathematical and physical consequences that follow can be fully assessed, and it can be shown that the behavior near the critical point is thermodynamically stable. In the case of the liquid-vapor transition, the usual convexity

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<sup>†</sup> Precise data for  $H_2O$  can be found in ref. 53, for  $CO_2$  in ref. 54, and for  $Xe$  in refs. 55 and 56.

conditions on  $f(v, T)$ :

$$\left(\frac{\partial^2 f}{\partial v^2}\right)_T = -\left(\frac{\partial p}{\partial v}\right)_T = \frac{\rho}{k_T} > 0, \quad (\text{B1a})$$

$$\left(\frac{\partial^2 f}{\partial T^2}\right)_v = -\left(\frac{\partial s}{\partial T}\right)_v = -\frac{c_v}{T} < 0, \quad (\text{B1b})$$

(which simply express the positivity of the isothermal compressibility and the isochoric specific heat) suffice to ensure the stability of the fluid everywhere except in the immediate vicinity of the critical point. The difficulty here is that both the slope and the curvature of the critical isotherm vanish at this point, so that stability along the isotherms just above  $T_c$  depends upon the sign of  $\partial^2 p / \partial \rho \partial T$  for  $\rho = \rho_c$  as  $T \rightarrow T_c$ . This derivative<sup>†</sup> (or its first nonvanishing partial derivative with respect to temperature) must be positive to make certain that the isotherms will slope upwards in the one-phase region. As a result, it is necessary to choose a representation for which a certain set of thermodynamic quantities, viz.:  $f$ ,  $s$ ,  $p$ ,  $\partial p / \partial \rho$ ,  $\partial^2 p / \partial \rho^2$ ,  $\partial^3 p / \partial \rho^3$ ,  $\partial p / \partial T$  and  $\partial^2 p / \partial \rho \partial T$  (though not necessarily any higher partials), are finite in the neighborhood of the critical point.

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<sup>†</sup> **Contrary** to the conclusion of Landau and Lifshitz (ref. 8, § 80) about the character of the two thermodynamic inequalities at the critical point, the simultaneous conversion of these to equalities is possible precisely because  $c_v \rightarrow \infty$  there. It therefore becomes necessary to consider still higher-order terms in the Taylor series expansion of the energy to discern the type of extremum associated with this point. The result is that not only must  $(\partial p / \partial \rho)_T$  and  $(\partial^2 p / \partial \rho^2)_T$  vanish at this point, but we must also have  $(\partial^3 p / \partial \rho^3)_T > 0$  and  $(\partial^2 p / \partial \rho \partial T) > 0$ . The latter is, in fact, implied (even though not explicitly stated) in the analysis of stability near the critical point presented in § 81 of their text.

After a number of futile attempts to attain this objective in a single stage, it became apparent that a preliminary step should be to find a satisfactory representation along the critical isochore, where temperature is the single independent variable, and only then attempt to generalize it for other densities. Our major premise is that each of the dependent thermodynamic variables can be resolved into an anomalous (or singular) part, hereinafter indicated by an asterisk, and a regular (or nonsingular) part, to the representation of which the main part of this report is devoted. The validity of such an assumption in relation to specific-heat anomalies in solids at various temperatures has been recognized for a long time (see ref. 5, § 8.3 or ref. 16, Chap. I).

Therefore, we begin with an approximation for  $c_v^*$  which, on the basis of experience, should be valid in the range<sup>†</sup>  $\tau_h < \tau < .003$

$$-c_v^*/T = \partial^2 f^*/\partial T^2 \simeq (2R/T_c) \alpha \log \frac{\tau}{\beta}. \quad (\text{B2})$$

By twice integrating this with respect to  $T$ , noting that  $T_c(\partial/\partial T) = \partial/\partial \tau$ , we obtain

$$f^* \simeq RT_c \alpha \left( \tau^2 \log \frac{\tau}{\beta} - \frac{3}{2} \tau^2 + c_1^* \tau + c_0^* \right), \quad (\text{B3})$$

where  $c_1^*$  and  $c_0^*$  are constants of integration and  $\alpha$  and  $\beta$  are parameters to be adjusted to fit the specific-heat data within the indicated temperature range. On a semilogarithmic plot,  $\alpha$  is proportional to the (negative) slope of the rectilinear portion of the curve, and  $\beta$  corresponds to the intercept of the straight-line portion extended to meet the horizontal axis, provided that the nonsingular part

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<sup>†</sup> The value assigned to  $\tau_h$  depends to a certain extent on the ingenuity of the techniques employed in obtaining the data. Ultimately, a lower bound on  $\tau_h$  is fixed by the ratio of the difference in gravitational potential energy (over the height of the calorimeter cell) to the average kinetic energy of the molecules at the critical temperature of the fluid in question, as pointed out in ref. 43.

of  $c_v$  has been subtracted from the measurements. Although this quantity is not immediately known, it can presumably be treated as constant over so small a temperature interval with little error; its effect will merely be a vertical displacement of the corresponding graph of  $c_v$ . Hence, a definite physical significance can be attributed to  $\alpha$  and  $\beta$ , the former measuring the "strength" of the anomaly and the latter, its range of influence.

In actuality, the specific-heat data exhibit a moderate leveling off for  $\tau > .003$ , suggesting that the anomaly is fading away. Accordingly, to extend the interval of approximation, it would be desirable for the argument of the logarithm in equation (B2) to approach unity as  $\tau$  becomes indefinitely large. One such form is

$$c_v^*/T \simeq -(2R/T_c) \alpha \log \left[ \frac{\tau}{\beta} (1 - e^{-\beta/\tau}) \right]. \quad (B4)$$

Near the critical temperature, this may be expressed as

$$c_v^*/T \simeq -(2R/T_c) \alpha \left( \log \frac{\tau}{\beta} - e^{-\beta/\tau} - \dots \right), \quad \tau \ll \beta \quad (B4a)$$

and the contribution due to the factor  $1 - e^{-\beta/\tau}$  in the argument is seen to be negligible there. The integrations of equation (B4) to obtain the free energy cannot now be carried out in closed form (in terms of elementary functions), but by analogy with the result obtained in equation (B3), we find that  $f^*$  must include a term of the form

$$RT_c \alpha \tau^2 \log \left[ \frac{\tau}{\beta} (1 - e^{-\beta/\tau}) \right] = -RT_c \alpha \beta^2 \frac{1}{x^2} \log \frac{x}{1 - e^{-x}}, \quad (B5)$$

where  $x = \beta/\tau$ . The behavior of this expression is decidedly singular at the critical temperature ( $x \rightarrow \infty$ ), whereas it is perfectly regular for any finite  $x$ .

To determine what additional terms are required to ensure proper asymptotic behavior for indefinitely large  $\tau$ , we expand the logarithmic factor of equation (B5) in a Taylor series about the point  $x = 0$ ,

$$\begin{aligned}
\log \frac{x}{1-e^{-x}} &= \log \left[ \frac{1}{2}x (1 + \coth \frac{1}{2}x) \right] \\
&= \log \left( 1 + \frac{1}{2}x + \frac{1}{12}x^2 + 0x^3 - \frac{1}{720}x^4 + \dots \right) \\
&= \frac{1}{2}x - \frac{1}{24}x^2 + 0x^3 + \frac{1}{2880}x^4 - \dots \dots
\end{aligned} \tag{B6}$$

Hence,

$$\frac{1}{x} \log \frac{x}{1-e^{-x}} = \frac{1}{2x} - \frac{1}{24} + \frac{1}{2880}x^2 - \dots \tag{B7}$$

Although the first two terms ( $= \tau/2\beta - 1/24$ ) contribute nothing to  $c_v^*$ , they are such as to prevent  $s^*$  and  $f^*$  from vanishing in the limit as  $x \rightarrow 0$ . We therefore subtract them from equation (B7), and thus arrive at the following expression for the free-energy anomaly:

$$f^* \simeq -RT_c \alpha \beta^2 \left[ \frac{1}{x} \log \frac{x}{1-e^{-x}} - \frac{1}{2x} + \frac{1}{24} \right] \tag{B8}$$

$$= -RT_c \alpha \beta^2 \left[ \frac{1}{2880}x^2 - \dots \right], \quad x \ll 1. \tag{B8a}$$

Given the definitions:  $\tau = (T-T_c)/T_c$  and  $x = \beta/\tau$ , there follows the relation

$$\frac{\partial}{\partial T} = \frac{1}{T_c} \frac{\partial}{\partial \tau} = -\frac{1}{T_c \beta} x^2 \frac{\partial}{\partial x},$$

by means of which we derive the corresponding expressions for the entropy and specific-heat anomalies:

$$s^* = -\frac{\partial f^*}{\partial T} \simeq R \alpha \beta \left[ \frac{2}{x} \log w - \frac{1}{x} (1 - we^{-x}) - \frac{1}{2} \right] \tag{B9}$$

$$= -R \alpha \beta \left[ \frac{1}{1440}x^3 - \dots \right], \quad x \ll 1; \tag{B9a}$$

$$c_v^*/T = \frac{\partial s^*}{\partial T} \simeq (R/T_c)\alpha [2 \log w - 3 + (2+w)we^{-x}] \quad (\text{B10})$$

$$= (R/T_c)\alpha \left[ \frac{1}{480} x^4 - \dots \right], \quad x \ll 1; \quad (\text{B10a})$$

where  $w = x/(1 - e^{-x})$ .

The question now arises as to whether a specific-heat anomaly described by the formula of equation (B10) is positive for all  $T > T_c$  and decreases monotonically as  $x \rightarrow 0$ . It is clearly positive for sufficiently small  $x$ , as shown by equation (B10a), and it is likewise positive near the critical temperature (i. e., as  $x \rightarrow \infty$ ), since  $e^{-x}$  then vanishes and equation (B10) reduces to<sup>†</sup>

$$c_v^*/T \simeq (R/T_c)\alpha(2 \log x - 3) = -(2R/T_c)\alpha \left[ \log \frac{\tau}{\beta} + \frac{3}{2} \right], \quad \tau \ll \beta. \quad (\text{B11})$$

The behavior between these extremes can be inferred from a knowledge of the slope and curvature of the function defined in equation (B10). However, to obviate the occurrence of unbounded derivatives at the critical point, we differentiate with respect to the variable  $\log \tau$ , using the relation

$$\frac{\partial}{\partial \log \tau} = \tau \frac{\partial}{\partial \tau} = -x \frac{\partial}{\partial x}.$$

The results are:

$$\frac{\partial}{\partial \log \tau} (c_v^*/T) = -(R/T_c)\alpha [2 - w^3 e^{-x} (1 + e^{-x})]; \quad (\text{B12})$$

<sup>†</sup> It should be noted that the parameter  $\beta$  acquires a slightly different interpretation here than it had in equation (B2). The value of  $\tau$  for which equation (B11) vanishes, say  $\tau_0$ , now corresponds to  $\beta e^{-3/2}$  instead of  $\beta$ . Thus, after deducting the nonsingular part of  $c_v$  and extending the linear section of the graph to its intercept with the horizontal axis, we would have as an estimate  $\beta \simeq e^{3/2} \tau_0 = 4.4817 \tau_0$ .



$$\frac{\partial^2}{\partial(\log \tau)^2} (c_v^*/T) = (R/T_c)\alpha w^3 e^{-x} [w(1+4e^{-x}+e^{-2x})-3(1+e^{-x})]. \quad (\text{B13})$$

It can be shown that the first of these expressions increases monotonically from the value  $-(2R/T_c)\alpha$  near the critical point to zero as  $\log \tau \rightarrow \infty$ ; while the second expression (which remains positive throughout this range) has a maximum at  $x = 4.9584$  and approaches zero at both extremes. However, since the value of  $c_v^*/T$  is zero at  $x = 0$  according to equation (B10a), a demonstration of its positivity and monotonic decay over the interval  $0 < \tau < \infty$  will only require us to prove that its derivative, given by equation (B12), is negative for all  $x > 0$ .

To simplify the analysis, we introduce a new independent variable,

$$t = 1 - e^{-x} \quad (\text{B14})$$

which maps the region of interest onto the unit interval. Also, for the expression within the brackets of equation (B12), we define

$$y = 2 - w^3 e^{-x}(1 + e^{-x}) = 2 - w^3(2 - 3t + t^2) \quad (\text{B15})$$

where we now have

$$\begin{aligned} w &= x/t, \\ x &= -\log(1-t), \end{aligned}$$

and the conditions on  $y(t)$  are that it should be positive and should increase monotonically in the interval  $0 < t < 1$ . Again, since  $y(0) = 0$ , it will suffice to show that  $y'(t)$  is positive everywhere within the unit interval; i. e.,

$$y' = w^2 [w(3-2t) - 3w'(2-3t+t^2)] > 0, \quad 0 < t < 1. \quad (\text{B16})$$

The proof makes use of the following Taylor series:

$$\begin{aligned} w(t) &= -t^{-1} \log(1-t) \\ &= 1 + \frac{1}{2}t + \frac{1}{3}t^2 + \dots + \frac{1}{n+1}t^n + \dots \end{aligned} \quad (\text{B17})$$

$$w'(t) = \frac{1}{2} + \frac{2}{3}t + \frac{3}{4}t^2 + \dots + \frac{n+1}{n+2}t^n + \dots \quad (\text{B18})$$

Thus, we find

$$(3-2t)w(t) = 3 + \sum_{n=1}^{\infty} \frac{n-2}{n(n+1)} t^n \quad (\text{B19})$$

$$3(2-3t+t^2)w'(t) = 3 + \sum_{n=1}^{\infty} \frac{3(n-2)}{n(n+1)(n+2)} t^n \quad (\text{B20})$$

which, after substitution in equation (B16), yield the result

$$\begin{aligned} y'(t) &= w^2 \sum_{n=1}^{\infty} \frac{(n-1)(n-2)}{n(n+1)(n+2)} t^n > 0, \quad 0 < t < 1 \\ &= w^2 \left( \frac{1}{30}t^3 + \frac{1}{20}t^4 + \frac{2}{35}t^5 + \dots \right). \end{aligned} \quad (\text{B21})$$

The first two coefficients vanish, while all subsequent ones are positive, ultimately approaching the value  $1/n$  as  $n$  increases without limit. Consequently, the series converges to a value which is positive at every point within the unit interval. Since the function  $w(t)$  also remains finite in the same interval, we conclude that the required conditions are satisfied. Hence, a specific-heat anomaly of the form given in equation (B10) will remain positive while the corresponding entropy, equation (B9), and free energy, equation (B8), will be negative, the magnitudes of all three quantities decreasing monotonically toward zero with increasing temperature.

To help appraise this more comprehensive formulation and understand some of its implications, we rewrite equation (B8) in terms of the variable  $\tau$ ,

$$f^* \simeq RT_c \alpha \left\{ \tau^2 \log \left[ \frac{\tau}{\beta} (1 - e^{-\beta/\tau}) \right] + \frac{1}{2} \beta \tau - \frac{1}{24} \beta^2 \right\}. \quad (\text{B22})$$

Comparing this equation with the initial approximation, equation (B3), we notice that the superfluous quadratic term is absent and the two integration

constants are now given explicitly in terms of the parameter  $\beta$ . The elimination of an undetermined function of temperature along the critical isochore is a consequence of the vanishing stipulations placed on  $f^*$  and  $s^*$  as  $\tau \rightarrow \infty$ . The last two terms of equation (B22) also serve a purpose with regard to  $f^*$  and  $s^*$  when  $\tau \rightarrow 0$ : both these quantities will assume finite, negative values at the critical point. For, in the limit as  $x \rightarrow \infty$ , equations (B8) and (B9) reduce to

$$f_c^* = -RT_c \alpha \beta^2 / 24 \quad (\text{B23})$$

$$s_c^* = -R\alpha \beta / 2 . \quad (\text{B24})$$

This result is consistent with the theory that behavior of substances near the critical point is characterized by a cooperative phenomenon (see ref. 5, §3.2 or ref. 15, Chap. XXI) accompanied by a decrease in entropy to reflect the more ordered state of matter under such circumstances. Moreover, the peculiar nature of the singularity introduced in equation (B4) in order to accomplish the first part of our objective tends to reinforce Zimm's conjecture (ref. 35) that there must be an essential singularity (in the function-theoretic sense) at the critical point. In the quantum-mechanical frame of reference, it corresponds to an accumulation point where the possible energy states become infinitesimally close to one another (see ref. 5, §3.6.2).

The proposed approximation for  $c_v^*$  cannot be satisfactorily tested without a reasonably good representation of the nonsingular part of  $c_v$ . However, use of the formulation proposed in the main part of this report is encumbered by the necessity to fit the data as a function of density as well as of temperature. A much simpler expression is needed for a check along the critical isochore, where relatively few reliable data are available. From a rather limited study, it was found that the specific heat could be fairly accurately approximated by the formula

$$c_v^{\text{reg}}/R = A\theta^{-j} + B, \quad [\theta = T/T_c = 1 + \tau] \quad (\text{B25})$$

provided that the data within the critical range are omitted. Hence, combining equations (B25) and (B10), we obtain

$$c_v/R = A\theta^{-j} + B + \alpha\theta [2 \log w - 3 + (2+w)we^{-x}] \quad (\text{B26})$$

where, as before,

$$w = x/(1-e^{-x}), \quad x = \beta/(\theta-1).$$

A least-squares fit of the isochoric specific-heat data for steam (ref. 38) over the range  $1 < \theta < 1.12$  and for nitrogen (ref. 40) over the range  $1 < \theta < 1.32$  yielded the following values for the parameters, with  $j$  restricted to an integer and  $T_c$  fixed at its generally accepted value:

	H <sub>2</sub> O	N <sub>2</sub>
T <sub>c</sub>	647.3 K	126.197 K
j	7	16
A	3.862	2.271
B	5.294	2.958
α	1.213	0.831
β	0.0354	0.0328

The experimental data as well as the curves calculated from equation (B26) are shown in Figures 1 and 2. It is apparent that the curves conform quite well to the trend of the data, and this strengthens the notion that  $\alpha$  and  $\beta$  are physically significant parameters. It might be argued that the number of adjustable constants is conducive to a good fit anyway, but it should be noted that the data extend far beyond the critical region, which is more or less confined to the interval  $0 < \tau < \beta$ .

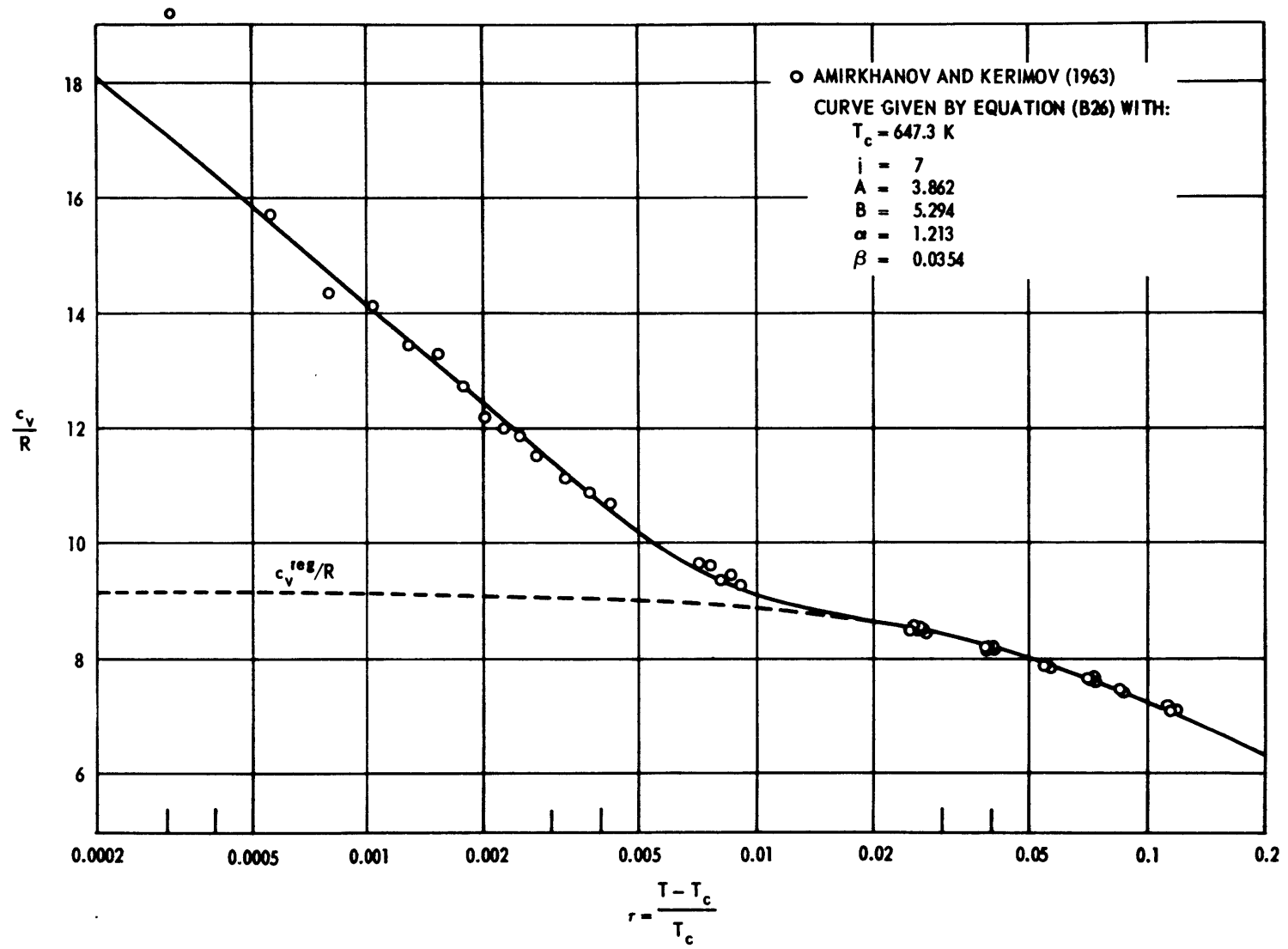


Figure 1 – Isochoric Specific Heat of Steam Along Critical Isochore

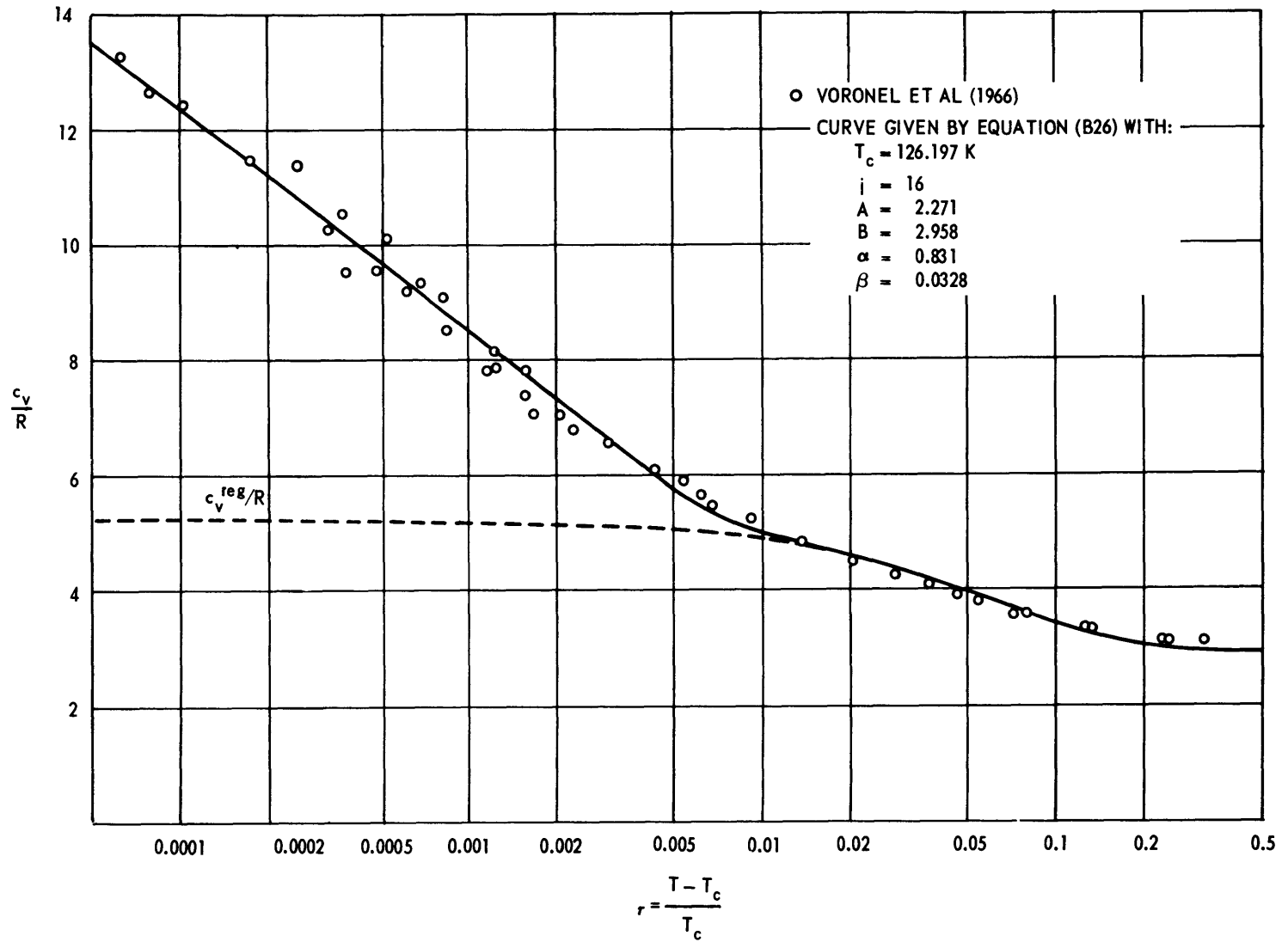


Figure 2 – Isochoric Specific Heat of Nitrogen Along Critical Isochore

An attempt to generalize formula (B22) must be based on a careful appraisal of the behavior of real fluids in the critical region. The occurrence of metastable states and the observed regularity (smooth behavior) of various thermodynamic quantities on approaching the coexistence curve would seem to preclude singularities in the free energy on this curve<sup>†</sup> except at the critical point. It does appear, however, that there must exist some other locus along which the free energy is singular (see ref. 50, sec. V).

Measurements along a number of isochores both above and below the critical density are likely to provide the most significant data. As indicated previously, the specific-heat curves along such paths have similar forms, rising ever more steeply with falling temperature until the coexistence curve is intersected. Except along the critical isochore, the values of  $c_v$  thus reached are finite, but their common trend conveys the impression of an approach toward a line of singular points — presumably lying entirely within the area bounded by the coexistence curve.

The existence of such a locus in the density-temperature plane has long been suspected (ref. 8, §79) although its true nature remains unknown. Nevertheless, one can assign certain plausible attributes to it. First a reasonable supposition is that it is convex upwards and attains its maximum ordinate at the critical point, where it must have a common tangent with the coexistence curve, as illustrated in Figure 3. A second assumption is that it cuts the density axis in two different places and that the area bounded by this line of singular points and the segment of the axis between the two points of intersection lies within the region in which the existence of a pure substance in a homogeneous state is not physically possible. We further assume that one of these

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<sup>†</sup> Widom (ref. 24) and Griffiths (ref. 49) do not necessarily make such a definite assumption about the coexistence curve.

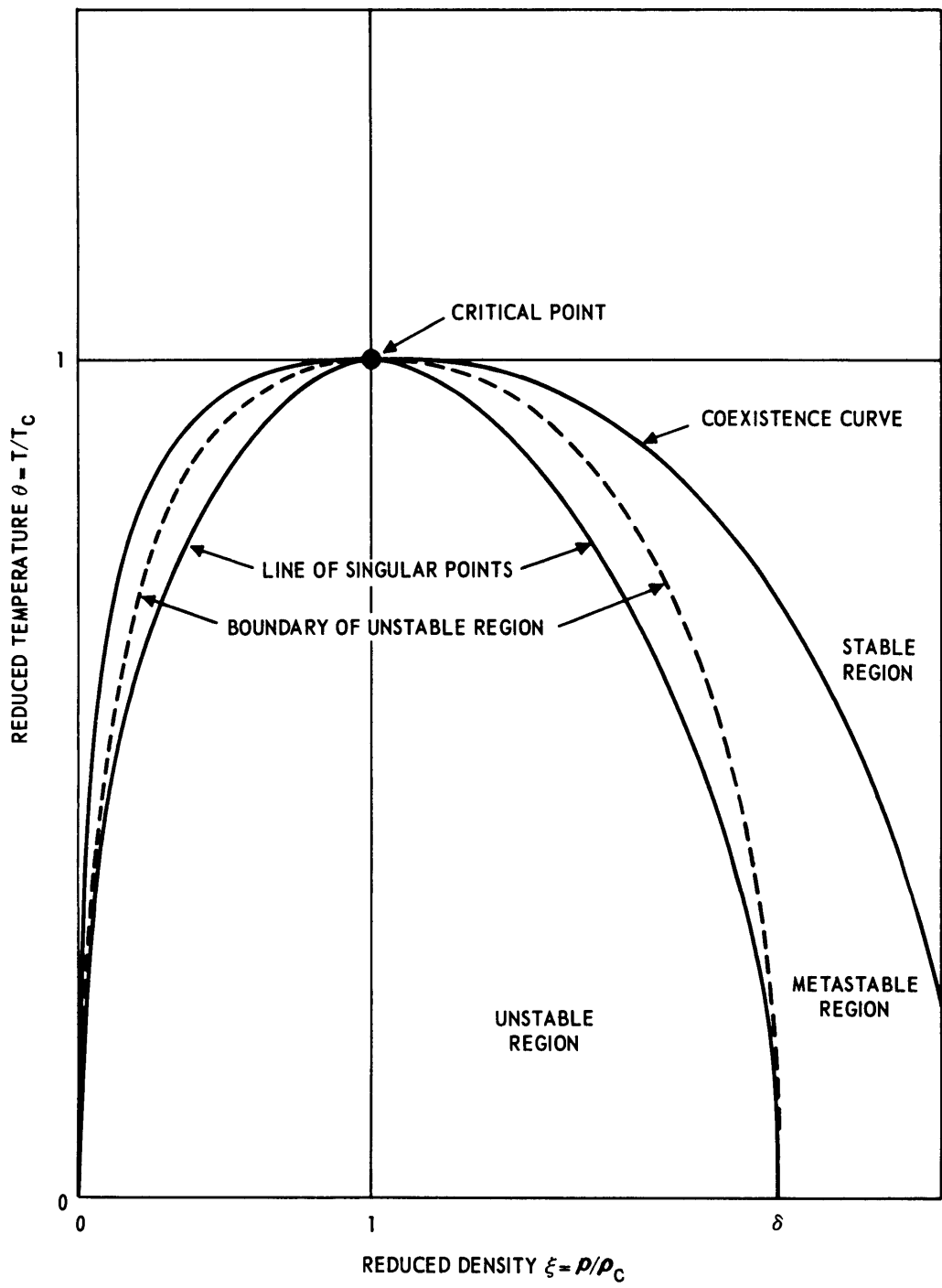


Figure 3 – State Diagram for a Typical Fluid



intersections lies at the origin, where both  $\rho$  and  $T$  vanish. This point is surely singular in any case: every point on the temperature axis, excluding the origin, corresponds to an ideal gas at some finite temperature, a state which is thermodynamically stable; whereas along the density axis, where  $T = 0$ , neither stable nor metastable states can be observed until a point, say  $\delta$ , well beyond the critical value is reached. Accordingly, the respective loci that separate the regions of differing states of stability will all meet at the origin.

On the basis of the foregoing assumptions, we now postulate an equation  $z(\xi, \theta) = 0$  for the line of singular points, adopting the simplest form that proves to be acceptable: namely, a polynomial quadratic in density (to permit a maximum at the critical point) and linear in temperature raised to the third power (to ensure suitable behavior at low temperatures). As such, it will involve the terms  $1, \xi, \xi^2, \theta^3, \xi\theta^3$ , and  $\xi^2\theta^3$ , subject to four constraints:

$$z(0, 0) = 0; \quad z(\delta, 0) = 0; \quad z(1, 1) = 0; \quad \frac{\partial z}{\partial \xi}(1, 1) = 0. \quad (\text{B27})$$

The resulting polynomial may be written

$$z(\xi, \theta) = \gamma(\xi - 1)^2\theta^3 - \xi(\xi - \delta)(\theta^3 - 1), \quad (\text{B28})$$

in which  $\gamma$  and  $\delta$  are adjustable parameters. To examine the nature of this function near the critical point, we express it in terms of  $\sigma$  and  $\tau$ . Thus,

$$z(\sigma, \tau) = \gamma\sigma^2 + [(\gamma - 1)\sigma^2 + (\delta - 2)\sigma + \delta - 1](\tau^2 + 3\tau + 3)\tau \quad (\text{B29})$$

where, by definition,

$$\sigma = \xi - 1 = (\rho - \rho_c) / \rho_c,$$

$$\tau = \theta - 1 = (T - T_c) / T_c.$$

To a first approximation, we get

$$z(\sigma, \tau) = \gamma\sigma^2 + 3(\delta-1)\tau + \dots \quad (\text{B29a})$$

In order that the locus  $z = 0$  should be concave downward, we must therefore have

$$\gamma' = \gamma/3(\delta-1) > 0. \quad (\text{B30})$$

Further analysis discloses that if the locus is to have only a single branch in the first quadrant of the  $\xi, \theta$ -plane, one of the following conditions must hold:

$$\gamma > \delta^2/4(\delta-1) \quad \text{if } 1 < \delta < 2; \quad (\text{B31a})$$

$$\gamma \geq 1 \quad \text{if } \delta \geq 2. \quad (\text{B31b})$$

For the specific case  $\delta = 2$ , equation (B28) reduces to

$$z(\xi, \theta) = [(\gamma-1)\theta^3 + 1](\xi-1)^2 + \theta^3 - 1. \quad (\text{B32})$$

This is the only circumstance in which the locus is symmetrical about the critical isochore. However, for real gases, it is probably skewed toward higher densities in a manner similar to that of the coexistence curve, and the value of  $\delta$  should therefore be greater than 2.

The ground has now been laid for the first step in the generalization of equation (B8) to other densities. Let us extend the definition of the variable  $x$  in such a way as to preserve the desired asymptotic behavior of the anomaly away from the critical region, e. g. ,

$$x(\xi, \theta) = \frac{3\beta(\delta-1)\xi\theta}{z(\xi, \theta)} = \frac{3\beta(\delta-1)\xi\theta}{\gamma(\xi-1)^2\theta^3 - \xi(\xi-\delta)(\theta^3-1)}. \quad (\text{B33})$$

It is apparent that the function  $x(\xi, \theta)$  will vanish if either one of the independent variables is fixed at some finite value while the other approaches zero or infinity, or if both approach infinity together — provided that the conditions (B30) and (B31) are not violated. Moreover,

along the critical isochore, equation (B33) simplifies to

$$x(1, \theta) = \frac{3\beta\theta}{\theta^3 - 1} \quad (\text{B34})$$

$$\simeq \frac{\beta}{\theta - 1} = \frac{\beta}{\tau}, \quad \tau \ll 1, \quad (\text{B34a})$$

which, for temperatures near the critical value, agrees with the original definition of  $x$  used in equation (B5). In like manner along the critical isotherm, equation (B33) simplifies to

$$x(\xi, 1) = \frac{3\beta(\delta - 1)\xi}{\gamma(\xi - 1)^2} \quad (\text{B35})$$

$$\simeq \frac{3\beta(\delta - 1)}{\gamma\sigma^2} = \frac{\beta}{\gamma'\sigma^2}, \quad \sigma \ll 1. \quad (\text{B35a})$$

At this juncture, the inclination is to replace the quantity  $x$  in equation (B8) with the expression (B33). Such a step, however, leads to a logarithmic divergence of both  $\partial^3 f^*/\partial\rho^2\partial T$  and  $\partial^4 f^*/\partial\rho^4$  to negative infinity<sup>†</sup> at the critical point. That such behavior would be thermodynamically unstable can be shown by the following argument. In the immediate neighborhood of the critical point, we can write

$$x(\sigma, \tau) \simeq \frac{3\beta(\delta - 1)}{\gamma\sigma^2 + 3(\delta - 1)\tau} = \frac{\beta}{\gamma'\sigma^2 + \tau}. \quad (\text{B36})$$

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<sup>†</sup> It is this sort of "catastrophe" that must be avoided in the analysis of critical behavior. See ref. 49, equations (30) and (44b).

Substituting this expression in equation (B8) and neglecting the exponential term, we obtain

$$f^*(\sigma, \tau) \simeq RT_c \alpha [(\gamma' \sigma^2 + \tau)^2 \log \beta^{-1}(\gamma' \sigma^2 + \tau) + \frac{1}{2} \beta(\gamma' \sigma^2 + \tau) - \beta^2/24], \quad (\text{B37})$$

from which, by differentiation and substitution of the values  $\sigma = 0$  and  $\tau = 0$ , we find

$$\left(\frac{\partial p^*}{\partial \rho}\right)_c = \alpha \beta \gamma' RT_c, \quad \left(\frac{\partial^2 p^*}{\partial \rho^2}\right)_c = 2\alpha \beta \gamma' RT_c / \rho_c. \quad (\text{B38})$$

These nonzero values at the critical point derive from the second term within the brackets of equation (B37), and they could be made to vanish there simply by subtracting the quantity  $\frac{1}{2} \beta \gamma' \sigma^2$  from the second term. Nor would this affect either  $s^*$  or  $c_v^*$ . Even so, on differentiating  $\partial p^*/\partial \rho$  once more (this time with respect to temperature), we get

$$\frac{\partial^2 p^*}{\partial \rho \partial T} \simeq 2R\alpha \gamma' \left[ 2 \log \beta^{-1}(\gamma' \sigma^2 + \tau) + 4 \frac{\gamma' \sigma^2 (1 + \sigma)}{\gamma' \sigma^2 + \tau} + 3 + 2\sigma \right]. \quad (\text{B39})$$

Whereas the other terms remain finite, the logarithmic term diverges to negative infinity when both  $\sigma$  and  $\tau$  approach zero simultaneously.

Such behavior presents a fundamental difficulty: to ensure stability, the value of this partial derivative must be positive in the neighborhood of the critical point so that the pressure isotherms for temperatures just above  $T_c$  will slope upwards. However, it is still possible to realize an acceptable form through certain minor modifications of equation (B8). The logarithmic divergence is due to the presence of the quantity  $\sigma^2$  in the coefficient of the first term of equation (B37). It ought, therefore, to be omitted – although it can (and indeed must) be retained in the argument of the logarithm. It must also be removed from the second term, as noted above. These changes will not affect

the behavior along the critical isochore, where  $f$  is a function of temperature only.

The proposed modification of equation (B8) is

$$f^* = -RT_c \alpha \beta^2 \nu^2 \left[ \frac{1}{x_1} \log \frac{x}{1-e^{-x}} - \frac{1}{2x_1} + \frac{1}{24} \right], \quad (\text{B40})$$

where  $x_1(\theta) = x(1, \theta) = \frac{3\beta\theta}{\theta^3 - 1}$  and  $\nu$  is a function, such as  $1-e^{-x}$  or  $(1-e^{-x})/(1+e^{-x}) = \tanh \frac{1}{2} x$ , that takes on the value unity in the critical region but elsewhere constrains  $f^*$  to vanish for extreme values of density and temperature<sup>†</sup>. Otherwise, in these limiting situations there would be contributions to the free energy and its derivatives of inappropriate mathematical form, a result of the nonvanishing behavior (except when  $\xi = 1$ ) of the expression within the brackets of equation (B40). Thus, we again encounter a need for a factor which involves an essential singularity in order to effect a proper transition from the critical realm to states far removed from it.

Just outside the line of singular points, the quantity  $1-e^{-x}$  has a seemingly negligible influence on the thermodynamic functions derived from equation (B40), since  $x$  becomes indefinitely large there in accordance with the definition (B33). Furthermore, the values of the functions will be real on both sides of this boundary because the signs of the numerator and denominator of the argument of the logarithm always agree. Hence, their quotient remains positive. Nevertheless, this line constitutes a natural boundary, and the functions cannot be analytically continued across it. Thus, as surmised by Landau and

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<sup>†</sup> For example, an analysis of equation (B40) shows that it will contribute a term of the form  $-\xi^2 \theta^{-5}$  at low temperatures and one of the form  $\xi^2 \theta^{-2}$  at high temperatures to the virial series expansion.

Lifshitz (ref. 8, §81), the Maxwell construction (or equal-area rule) along the pressure isotherms below the critical temperature does not really apply, nor is this necessary anyway. Temperley (ref. 5, §4.3) points out that a sufficient condition for the equilibrium of the two phases along the coexistence curve (which fixes its location) is that the chemical potential  $g = \partial(\rho f)/\partial\rho$  be represented by analytically the same function along both the liquid and vapor branches of the isotherm - with the same constants of integration for each branch.

We shall conclude the investigation of the critical-point anomaly with an analysis of the behavior of certain important derivatives of the free energy in the neighborhood of the singularity. To do so, we approximate  $v$  by 1,  $x$  by  $\beta/(\gamma'\sigma^2 + \tau)$  as before in equation (B36), and  $x_1$  by  $\beta/\tau$  as in equation (B34a). Thus, by substitution in equation (B40), we obtain

$$f^*(\sigma, \tau) \simeq RT_c \alpha \left[ \tau^2 \log \beta^{-1} (\gamma'\sigma^2 + \tau) + \frac{1}{2} \beta \tau - \beta^2/24 \right]. \quad (\text{B41})$$

It then follows that

$$s^* \simeq -R\alpha \left[ 2\tau \log \beta^{-1} (\gamma'\sigma^2 + \tau) + \frac{\tau^2}{\gamma'\sigma^2 + \tau} + \frac{1}{2}\beta \right], \quad (\text{B42})$$

$$c_v^*/\theta \simeq -R\alpha \left[ 2 \log \beta^{-1} (\gamma'\sigma^2 + \tau) + \frac{4\tau}{\gamma'\sigma^2 + \tau} - \left( \frac{\tau}{\gamma'\sigma^2 + \tau} \right)^2 \right]. \quad (\text{B43})$$

As well as a variable contribution along the critical isochore just above  $T_c$ , the first term of equation (B43) adds a constant amount  $2R\alpha \log \beta$  to  $c_v^*/\theta$  and the two rational terms, a total of  $-3R\alpha$ . Thus, the only singularity to appear along this path occurs at the critical point, where the specific heat diverges to positive infinity. The same singularity appears along the critical isotherm although the rational terms vanish along this path. Below  $T_c$  the contributions of the rational terms are both positive, and they increase more rapidly

as the line of singular points (given by  $\tau = -\gamma'\sigma^2$ ) is approached, where they have first- and second-order poles, respectively. With the exception of the critical point, of course, these divergences in  $c_v$  are beyond the reach of direct experimental investigation, because the density-temperature pairs at which they would occur lie within the region where the fluid is mechanically unstable (as will be shown subsequently). Such a mathematical representation is none the less reasonable, since it is in accord with the observation that, along other isochores on either side of the critical one, the value of  $c_v$  rises at an ever increasing rate as the temperature approaches the value corresponding to the ordinate of the coexistence curve.

Before proceeding with an analysis of the density derivatives, it is necessary to express the coefficient  $\alpha$  as a particular function of density, viz.,

$$\alpha(\xi) = \alpha_1 + \alpha_0/\xi, \quad (\text{B44})$$

so as to avoid constraining these derivatives in a possibly inappropriate way. From a consideration of the thermodynamic identity

$$\rho c_v/T = (\partial^2 p/\partial T^2)_v - \rho (\partial^2 g/\partial T^2)_v \quad (\text{B45})$$

it is clear that the second partial derivative of either the pressure or the chemical potential (or both) will exhibit the same singular behavior at the critical point as does the specific heat. Since it is not definitely known from physical measurements which of these alternatives is the correct one (see ref. 52, §3.2 or ref. 62), we shall write an expression for the anomalous free energy per unit volume in a form that embraces both of these possibilities, viz.,

$$a^* = \rho f^* \simeq RT_c \rho_c (\alpha_1 \xi + \alpha_0) \psi, \quad (\text{B46})$$

where  $\psi$  stands for the function within the brackets of equation (B41),

i. e. ,

$$\psi(\sigma, \tau) = \tau^2 \log \beta^{-1} (\gamma' \sigma^2 + \tau) + \frac{1}{2} \beta \tau - \beta^2 / 24 . \quad (\text{B47})$$

Then

$$g^* = \frac{\partial a^*}{\partial \rho} \simeq RT_c [(\alpha_1 \xi + \alpha_0) \frac{\partial \psi}{\partial \sigma} + \alpha_1 \psi] , \quad (\text{B48})$$

$$p^* = \rho g^* - a^* \simeq RT_c \rho_c [(\alpha_1 \xi + \alpha_0) \xi \frac{\partial \psi}{\partial \sigma} - \alpha_0 \psi] , \quad (\text{B49})$$

and, in particular,

$$g^* \simeq RT_c \alpha_0 \frac{\partial \psi}{\partial \sigma} \quad \text{if } \alpha_1 = 0, \alpha_0 \neq 0 ,$$

$$p^* \simeq RT_c \rho_c \alpha_1 \xi^2 \frac{\partial \psi}{\partial \sigma} \quad \text{if } \alpha_0 = 0, \alpha_1 \neq 0 .$$

Formulas for other thermodynamic derivatives in terms of  $\psi$  are obtained in a similar fashion, e. g. ,

$$\frac{\partial p^*}{\partial \rho} = \rho \frac{\partial g^*}{\partial \rho} \simeq RT_c \xi [(\alpha_1 \xi + \alpha_0) \frac{\partial^2 \psi}{\partial \sigma^2} + 2\alpha_1 \frac{\partial \psi}{\partial \sigma}] . \quad (\text{B50})$$

To verify that equation (B46) does not preclude a thermodynamically stable formulation of the Helmholtz free energy, expressions are given below for the set of partial derivatives of  $\psi$  that, with the exception of  $\partial^2 \psi / \partial \tau^2$ , must remain finite in the neighborhood of the critical point exterior to the coexistence curve. For a clear and compact display of the results, we introduce an auxiliary variable

$$\omega(\sigma, \tau) = \frac{\tau}{\gamma' \sigma^2 + \tau} \leq 1 \quad \text{when } \tau > -\gamma' \sigma^2 , \quad (\text{B51})$$

with derivatives

$$\frac{\partial \omega}{\partial \sigma} = - \frac{2\gamma' \sigma \omega^2}{\tau} = - \frac{2\omega(1-\omega)}{\sigma} ,$$



$$\frac{\partial \omega}{\partial \tau} = \frac{(1-\omega)^2}{\gamma' \sigma^2} = \frac{\omega(1-\omega)}{\tau} .$$

Thus, rewriting equation (B47) in terms of  $\omega$  (which takes on the value unity along the critical isochore, zero along the critical isotherm, and negative infinity along the line of singular points), we obtain:

$$\psi = \tau^2 \log(\tau/\beta \omega) + \frac{1}{2} \beta \tau - \beta^2/24 \quad (\text{B52})$$

$$\frac{\partial \psi}{\partial \tau} = 2\tau \log(\tau/\beta \omega) + \tau \omega + \frac{1}{2} \beta \quad (\text{B53})$$

$$\frac{\partial^2 \psi}{\partial \tau^2} = 2 \log(\tau/\beta \omega) + \omega(4-\omega) \quad (\text{B54})$$

$$\frac{\partial \psi}{\partial \sigma} = 2\gamma' \sigma \tau \omega \quad (\text{B55})$$

$$\frac{\partial^2 \psi}{\partial \sigma^2} = -2\gamma' \tau \omega(1-2\omega) \quad (\text{B56})$$

$$\frac{\partial^3 \psi}{\partial \sigma^3} = 4\gamma'^2 \sigma \omega^2(1-4\omega) \quad (\text{B57})$$

$$\frac{\partial^4 \psi}{\partial \sigma^4} = -12\gamma'^2 \omega^2 [1-8\omega(1-\omega)] \quad (\text{B58})$$

$$\frac{\partial^2 \psi}{\partial \sigma \partial \tau} = 2\gamma' \sigma \omega(2-\omega) \quad (\text{B59})$$

$$\frac{\partial^3 \psi}{\partial \sigma^2 \partial \tau} = -2\gamma' \omega(2-\omega)(1-2\omega) \quad (\text{B60})$$

These partial derivatives exist and remain bounded (except for  $\partial^2 \psi / \partial \tau^2$ ) as the singular point is approached from the upper half-plane ( $\tau > 0$ ). Thus, by assigning suitable values to the corresponding derivatives of the regular (nonsingular) part of the free energy at the critical point – so that, where necessary, they will dominate the contributions of the singular part – it is always possible to satisfy the stability criteria. We specifically note that  $\partial^4 \psi / \partial \sigma^4$  and  $\partial^3 \psi / \partial \sigma^2 \partial \tau$  yield constant values (rather than diverge) as the singular point is approached from above along the critical isochore. This is in contrast to the result derived from the analysis of equation (B37).

The higher partials also exist, but since their formulas involve negative powers of  $\sigma$  and/or  $\tau$ , they do not, in general, remain bounded as the singular point is approached from the upper half-plane<sup>†</sup>. Hence, the analytic character of the function  $\psi(\sigma, \tau)$  is such that it "just" meets the requirements for acceptable behavior in the immediate neighborhood of the critical point while concomitantly providing for a logarithmic singularity in  $c_v^*$ . Note that  $\partial \psi / \partial \sigma$  and its various partial derivatives, when multiplied by suitable powers of  $\sigma$  and/or  $\tau$ , all reduce to polynomials in  $\omega$ . This quantity thus becomes a "scaling" variable, in terms of which the values of certain thermodynamic quantities remain invariant along trajectories for which  $\omega$  is constant. Such a property does not, however, characterize  $\psi$  and its first two temperature derivatives (and therefore not  $c_v^*$ ) due to the presence of the logarithmic terms.

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<sup>†</sup> One of these, viz.,  $\partial^3 \psi / \partial \sigma \partial \tau^2 = 4(1-\omega)^3 / \sigma$ , which enters into the two quantities on the right-hand side of equation (B45), vanishes to the 5th degree in  $\sigma$  along the critical isochore. Thus  $g^*(0, \tau)$  or  $p^*(0, \tau)$ , but not both, may be free of the logarithmic singularity, should either  $\alpha_1$  or  $\alpha_0$  be zero.

A comparison of equation (B41) with equation (1) of ref. 61, or with the identical equation (4) of ref. 63, reveals a similar mathematical expression for  $f^*$  in the neighborhood of the critical point<sup>†</sup>. The argument of the logarithmic term is expressed in a form equivalent to  $\beta^{-1} [(\gamma'\sigma^2 + \tau)^2 + (\gamma''\sigma^2)^2]^{1/2}$ , which reduces to that of equation (B41) when  $\gamma'' = 0$ . However, unless this condition prevails, the argument can vanish only at the critical point, and the line of singular points will have complex coordinates, viz.,  $\tau = -(\gamma' \pm i\gamma'')\sigma^2$ . Also, since the additional quantity in the argument varies as  $\sigma^4$ , its influence will be negligible near the critical density. Thus, as is conceded, the value of the coefficient  $\gamma''$  cannot be readily ascertained from experimental data. Moreover, along other isochores the argument can decrease only to its minimum value  $(\gamma''/\beta)\sigma^2$ , which will occur when  $\tau = -\gamma'\sigma^2$ . Consequently, none of the partial derivatives of  $f^*$  can become infinite at any point along a subcritical isotherm, and there is then no assurance that the boundary between the metastable and unstable regions will constitute a well-defined locus. Finally, although it is recognized that supplementary terms are required in  $f^*$ , they are not explicitly formulated.

The closed form of equation (B41), with its simpler logarithmic term, affords a plausible interpretation of the observations associated with the critical region. It is instructive to analyze the behavior of the pressure along a subcritical isotherm ( $\tau < 0$ ) as the line of singular points is approached from both the vapor and liquid regions. First, we note that  $\omega$  has the same sign as  $\tau$ , according to the definition (B51). Therefore, the value of the quantity  $\partial^2\psi/\partial\sigma^2$  given

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<sup>†</sup> The present investigation was, in fact, strongly motivated by these previous results.

by equation (B56) will always be negative on the subcritical isotherms. Furthermore, this quantity will become the dominant element of the expression (B50) for  $\partial p^*/\partial \rho$  in the immediate neighborhood of the line of singular points because the magnitude of  $\omega$  becomes indefinitely great there. However, since the value of the regular part of  $\partial p/\partial \rho$  is, by definition, bounded everywhere, a point must be reached on each branch of these isotherms at which the regular and singular parts will exactly compensate (and beyond which the fluid would be mechanically unstable). The locus of such points defines the inner boundary of the metastable states, as illustrated in Figure 4. A corollary is that the value of  $c_v$  along this locus remains finite except at the critical point<sup>†</sup>.

Among other thermodynamic derivatives that exhibit peculiar properties near the critical point is the quantity  $\partial^2 p/\partial \rho \partial T$ . This quantity was investigated some time ago by Widom and Rice (ref. 64) with respect to the PVT data for xenon and carbon dioxide. They attempted to expand the pressure in a (pseudo-) Taylor series about the critical point, taking the first three density derivatives equal to zero there, but they were unable to assign any fixed set of values to the coefficients which would consistently describe the immediate neighborhood of the critical point as well as the region somewhat more distant. The data indicated that  $\partial^2 p/\partial \rho \partial T$  was positive (as it must be to preserve stability) but by no means constant in the critical region. For example, it appeared to change quite rapidly along the isotherms just above  $T_c$ , no doubt due in some degree to the influence of higher-order terms in the regular part of the expansion. However, the

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<sup>†</sup> Other than the origin, the critical point is the only point in the density-temperature plane that simultaneously borders on the stable, metastable, and unstable domains, and it corresponds to the only physically realizable state (at least in a limiting sense) for which the specific heat can approach infinity.

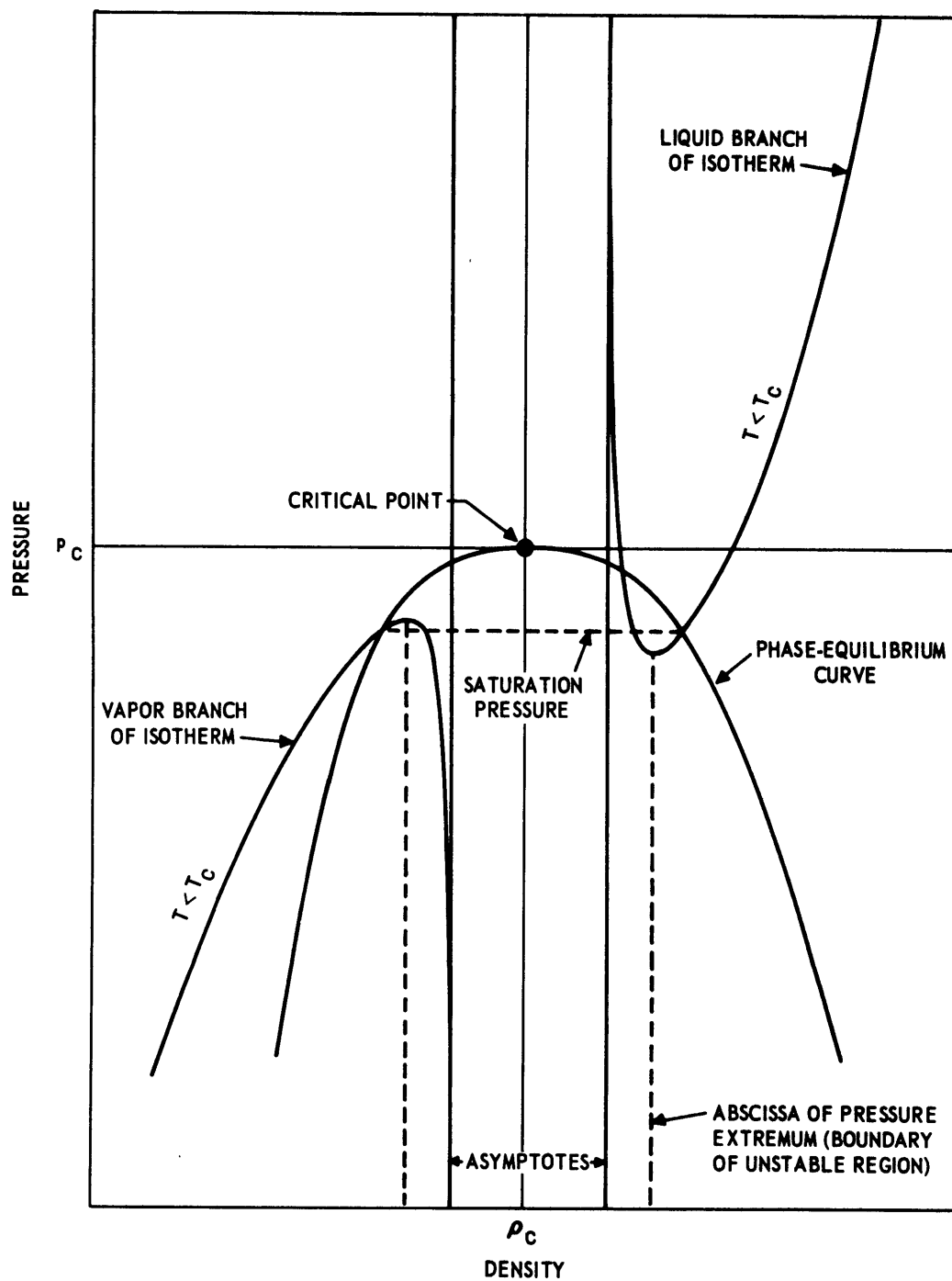


Figure 4 – Behavior of Subcritical Isotherm Near Pressure Extrema

singular part of this derivative, which involves the quantities  $\partial^2\psi/\partial\sigma\partial\tau$  and  $\partial^3\psi/\partial\sigma^2\partial\tau$  given by equations (B59) and (B60), is indeterminate at the critical point, its value shifting abruptly from zero along the critical isotherm to  $2\alpha\gamma^2R$  along the critical isochore. Its value depends, in general, on the way in which the singular point is approached, a property quite natural for a function that is not analytic at some point (cf. ref. 63).

A similar situation exists with regard to  $\partial^3p^*/\partial\rho^3$ . This quantity (like all the derivatives of  $p^*$  with respect to  $\rho$ ) vanishes along the critical isotherm, but along the critical isochore just above  $T_c$  it has the value  $-12\alpha\gamma^2RT_c/\rho_c^2$ . Since it is negative and virtually constant in the vicinity of this isochore where  $\omega \simeq 1$ , it must be fully compensated by a positive, nonsingular contribution in order to ensure thermodynamic stability just above the critical point. We therefore hypothesize that the conditions to be satisfied by the expansion of the pressure about the critical point (along the critical isotherm) are

$$\left(\frac{\partial p}{\partial \rho}\right)_c = 0, \quad (\text{B61})$$

$$\left(\frac{\partial^2 p}{\partial \rho^2}\right)_c = 0, \quad (\text{B62})$$

$$\left(\frac{\partial^3 p}{\partial \rho^3}\right)_c \geq 12\alpha\gamma^2RT_c/\rho_c^2 \quad (\text{B63})$$

If the equality sign holds, then  $\partial^3p/\partial\rho^3$  will vanish along the critical isochore just above  $T_c$ . Such a condition would be consistent with the experimentally observed flatness and near parallelism of the isotherms in this vicinity (ref. 31, §E, 1; see also refs. 54, 56, and 65). However,

the density interval over which such virtual compensation would prevail becomes shorter as  $\tau \rightarrow 0$ . In any event, the critical isotherm will be entirely free of any singular behavior, so that under the above conditions both the pressure and the chemical potential will have regular points of inflection with small (but positive) third derivatives at the critical point (unlike the isotherms which lie immediately above  $T_c$ ).

The main result of this supplemental investigation has been to show that a relatively simple mathematical form can be found for approximating the singular part of the free energy. It yields a logarithmic specific-heat anomaly without violating the conditions for thermodynamic stability in the neighborhood of the critical point, and it is evidently capable of representing the isochoric specific heat of real gases with considerable accuracy in this region. Since the presence of the singularity is manifested to the greatest degree in this particular property, it is surmised that the same formulation will also yield satisfactory values for the less sensitive thermodynamic properties. The substantiation of the hypotheses advanced in this study would be greatly facilitated if reliable data for  $c_v$  were available along the critical isotherm of some gas (such as carbon dioxide) for which the critical temperature has been determined with considerable accuracy.

In support of the objective originally set forth, we quote briefly from the closing paragraph of reference 52,

"Within the framework of the scaling laws as presently used, the most significant need, from a phenomenological point of view, is the formulation of the free energy as a function of density and temperature, since the knowledge of the equation of state [for the chemical potential in terms of density and temperature] by itself yields only a partial description of the critical region."

The formulation developed here is offered as a tentative resolution of the problem. In the final analysis, the adequacy of any scheme for representing observational data rests upon the precision of measurement attainable within the technological framework of a given time.



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13 ABSTRACT <p>This paper describes a new analytic formulation of the thermodynamic properties of a chemically homogeneous, stable molecular substance such as water or carbon dioxide. A mathematical expression for the Helmholtz free-energy function <math>f(v, T)</math> is derived by starting with a form that yields the laws for ideal gases and incorporating into it a series of terms and associated parameters suggested by statistical mechanics and quantum theory considerations. The anomalous behavior of pure substances near the liquid-vapor critical point is also taken into account. This leads to a more comprehensive equation of state applicable to the condensed phases in addition to the gaseous phase. Accordingly, it is adapted for smoothing as well as interpolating observational data over a wide range of variables.</p> <p>The final result may be regarded as a generalization of van der Waals' equation, modified so as to provide a more faithful representation of high-density measurements and to be consistent with Debye's theory at very low temperatures - and always of course, reducing to the ideal gas law as the density goes to zero. Values for the parameters which enter the approximation via the molecular partition function for the substance are fixed in advance. They are usually obtained with more than sufficient accuracy by analysis of spectroscopic measurements, and therefore need no further correction. All the remaining parameters - except for a few constants that must be estimated initially from physical considerations - occur linearly in the formulas, thus facilitating their determination by a least-squares adjustment.</p>			

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