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AN EQUATION OF STATE FOR SODIUM

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A revised equation of state for sodium is presented. Changes in reference data and improvements in computational technique to those previously used are described.

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## 1. Introduction

The equation of state (EOS) <sup>49</sup> for sodium which has been employed in assessments of hypothetical accidents in liquid metal cooled fast breeder nuclear reactors has been in use for some years in the British programme. During this time some important experimental reference data, upon which the EOS is based, have been revised. The purpose of this report is primarily to update the sodium EOS by incorporating these revised data. In addition, a number of improvements have been made in the calculational technique used in deriving properties in the single phase. These refinements, which have indicated numerical errors in the earlier EOS output, have improved the precision of the reported data.

## 2. The Equation of State

### A brief résumé

As in Alderson's original report, the P-V surface (Fig. 1) is divided into four regions:

- (i) The compressed or subcooled liquid
- (ii) The expanded or superheated gas
- (iii) The two phase coexistence region
- (iv) The supercritical region.

Evaluation of thermodynamic properties within each of these regions is based upon a quantification of the envelope denoting the boundary between the two-phase coexistence region and the single phase regions.

The equilibrium envelope is effectively characterised once all the equilibrium properties, shown in Table I, are defined as a function of temperature. With respect to the determination of the position of the equilibrium envelope, the thermodynamic properties within the coexistence region are evaluated by application of the lever rule.

The properties in the compressed liquid and the expanded gas regions are evaluated on the basis that the thermal pressure coefficient,  $\gamma_v = \left(\frac{\partial P}{\partial T}\right)_v$  (see Appendix 1), is known throughout these regions. As no data are available on the behaviour of  $\gamma_v$  in the single phase, the assumption employed in both this and earlier work is that  $\gamma_v$  is only a function of volume. Consequently, provided it can be evaluated at one volume, that value can then be applied at the same volume for any other temperature.

In general, the evaluation of data for the subcritical single phase region involves integration of the relevant quantity between the point of interest and the appropriate point on the saturation envelope. Since, above the critical temperature, the saturation envelope is undefined, a further assumption needs to be employed in order to characterise the supercritical region. The assumption is that, at supercritical temperatures ( $T_{sup}$ ), the internal energy on the critical isochore  $V_c$ , is directly proportional to the temperature difference ( $T_{sup} - T_c$ ). The constant of proportionality is based on an averaging of the internal energies on the critical isochore for some small temperature range

directly below  $T_c$  and therefore generating an effective specific heat  $\bar{C}_v(V_c)$ .\*

In the absence of any supercritical data for sodium this treatment does at least allow the supercritical region to be quantified, but the method cannot be rigorously justified. This second assumption effectively establishes the critical isochore as a reference curve in the same sense as the coexistence envelope. A future development which would obviate the use of a critical isochore reference line would be to establish the position of a shock Hugoniot within the compressed liquid. This would provide an experimental reference line from which extrapolations could be made with greater confidence.

The above description summarises the approach which has been used to obtain an EOS code used for sodium. The techniques used are exactly those employed by Alderson<sup>(1)</sup>. As the new EOS is generated in exactly the same way there is no detailed description of the determination of the reference curves or of the evaluation of the thermodynamic properties, but simply the equations used are presented. It has been left to the reader to consult the original work of Alderson for a full description. The sections which follow describe the revisions which have been made to that original treatment.

### 3. The Revised Critical Data

Accurate knowledge of the critical temperature, volume and pressure is crucial to a confident construction of the equilibrium envelope. The measurements of Bhisra<sup>(2)</sup> have, for some time, been accepted as the most reliable<sup>(3)</sup> values for the critical constants of sodium. These are shown in Table II, along with those previously used in Alderson's equation of state.

The adoption of a new set of critical constants alters many of the equations describing the equilibrium properties on the coexistence envelope. In this treatment of the sodium EOS, Alderson's original equations are used up to 1640K.\*\* Above this temperature equations of exactly the same form are used except that, in order to accommodate the new critical constants, the coefficients of the equations necessarily change.

In general, the coefficients of an equation representing a given property above 1640K can be determined with a knowledge of the critical point values themselves, and by the continuity constraints at 1640K, e.g. the three coefficients of the expression for the vapour pressure,  $P_{sat}$ :

$$P_{sat} (T > 1640K) = Ae^{-B/T} T^{-C} \quad (1)$$

are fixed by a knowledge of the critical pressure, the pressure at 1640K and the slope of the vapour pressure with respect to temperature at 1640K, these last two values being obtained from the vapour pressure equations at lower temperatures. Occasionally a continuity constraint has no thermodynamic significance, but is purely a mathematical

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\* The variation of internal energy with temperature along  $V_c$  and below  $T_c$  is determined by application of the lever rule to the internal energies of liquid and vapour. From the resulting internal energies, an 'average' slope  $\bar{C}_v(V_c)$  can be established, which is then used at temperatures above  $T_c$ .

\*\* As distinct from 1644.28K which has no significance apart from being equivalent to 2500°F.

convenience. In the case of the vapour pressure, however, the slope  $dP/dT$  is related to the heat of vaporisation. This must vary smoothly across the 1640K boundary as there is no phase change for condensed sodium at this temperature.

The revised equations, which replace those of Alderson in the new code, are given in Appendix 2.

#### 4. Improvements in the Precision of Calculations

An improvement in the accuracy of characterising the equilibrium envelope must result from an improvement in an estimate of the critical constants. The precision with which the thermodynamic properties are determined away from this reference envelope is, however, also dependent, to various extents, upon the mathematical techniques involved in their evaluation. In applying the equations of Appendix 2 to the determination of single phase properties it becomes apparent that both numerical integration and numerical differentiation are unavoidable.

The eventual formulation of the equations of Appendix 2 into an EOS for sodium was achieved independently from the code used by Alderson. In this way the new EOS provided a useful test of the precision of the Alderson code.

Comparison of the results from the two codes revealed differences in the prediction of certain parameters at low temperatures ( $T < 700K$ ) which, by virtue of being described by the same equations, should not have existed. Investigation of both codes revealed that the numerical differentiation technique used by Alderson was inadequate at low temperatures. This is discussed fully in Appendix 3; at this point it is sufficient to say that the values of  $C_p$  and  $C_v$  used by Alderson for the equilibrium vapour below 700K are approximately twice those given in this EOS. This has important consequences, as will be seen in Section 5.

A further comparison of the two codes showed a disagreement in the high specific volume values of internal energy ( $U$ ) and enthalpy ( $H$ ) along isotherms near and above  $T_c$ . This is again discussed in Appendix 3 but essentially the rapid change of  $U$  and  $H$  at high volume is a consequence of an inefficient numerical integration technique used by Alderson. The internal energies and enthalpies ought, in fact, to tend to their equivalent perfect gas limits at high volumes for a given temperature, not diverge as shown in Alderson's tables.

#### 5. Results and Discussion

The equations employed in this EOS are given in Appendix 2. The EOS itself is given in microfiche form contained within this report. The structure of the EOS is in the same format as the original<sup>(1)</sup>. Appendix 4 lists the data contained within the microfiche.

Some comment is required on whether or not this reassessed EOS for sodium represents an improvement on Alderson's EOS both from a purely thermodynamic consideration and for the analysis of hypothetical accidents. A more accurate set of critical constants must improve the confidence placed upon the description of sodium liquid/vapour equilibrium. The low temperature specific heats of the vapour are greatly improved by the implementation of a more efficient calculational technique. In this sense, when equilibrium data are required in hypothetical accident analysis the results of such an analysis must be improved.

When single phase data are required for analysis of hypothetical accidents the concern over the precision of the extrapolative technique is the same as for the former EOS.

Some attempt to quantify the precision of such predictions can, however, be made, depending upon the extent into the single phase regions to which the extrapolations are applied. Calculations in the low temperature expanded gas region are obviously quite adequate. Below 1400K the vapour is virtually ideal.\* For an ideal gas the  $\gamma_V$  extrapolation is no longer an approximation, it is exact. Consequently, below 1400K the expanded gas extrapolations are as accurate as the equilibrium vapour reference line upon which they are based.

Above 1400K, up to ca. 1800K, the "ideality factor"  $\left(\frac{PV}{RT}\right)$  is still greater than ca. 0.7. As is later demonstrated in Appendix 1,  $\gamma_V$  for the vapour is evaluated from a van der Waals type treatment. At ca. 1800K the specific volume of the vapour is still sufficiently large to allow a van der Waals type description of the onset of non-ideality. Consequently, the extrapolations into the expanded gas between 1400K and 1800K are a fair approximation to reality.

The use of the  $\gamma_V$  extrapolation in the compressed liquid region does not benefit from a limiting comparison, as does the expanded gas  $\rightarrow$  perfect gas. The temperature insensitivity of  $\gamma_V$  (constant along an isochore) is an observed feature<sup>(4)</sup> for some materials. A strong indication that the same constraint is valid for sodium is demonstrated by comparing the  $\gamma_V$  extrapolation with one based on the so-called Gruneisen extrapolation. This asserts that the Gruneisen parameter  $\Gamma_V = (1/V) \left(\frac{\partial P}{\partial E}\right)_V$  is also constant along an isochore. If both extrapolations give rise to the same, or very similar, extrapolated results, our confidence will increase. Furthermore, if the equilibrium  $C_V$  (for both phases) can be shown to be reasonably insensitive to temperature (see Appendix 5), then the extrapolation must be considered reasonable. Alderson demonstrated this to be the case for sodium except for the low temperature vapour. As was mentioned in Section 4, Alderson's values for  $C_V$  for his low temperature vapour were over-estimated. Fig. 3 shows that the  $C_V$  agreement is improved over that of the previous work.

The values of  $C_V(\text{liq})$  and  $C_V(\text{vap})$ , whilst being ca. 15% different, do exhibit the same trends over the range  $600 < T < 2300\text{K}$ . Fig. 5 gives an indication of the agreement between the  $\gamma_V$  and  $\Gamma_V$  extrapolations. From this we can infer that up to 2300K the techniques predict virtually the same results.

For  $2300 < T(\text{K}) < T_c$ , the variation of  $\gamma_V$  with temperature no longer benefits from comparison with either a perfect gas limit, or a constancy in  $C_V$ . Justification for continuing with a constant  $\gamma_V$  at these temperatures rests purely with observation of the invariance of  $\gamma_V$  with temperature for other materials. Above  $T_c$  the extrapolations, as mentioned in Section 2, are based upon the assumption of a constant  $C_V^{**}$  on the critical

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\*  $PV/RT \geq 0.85$  for  $T \leq 1400\text{K}$ .

\*\*  $C_V$  is not a constant on an isochore for subcritical temperatures.

isochore above  $T_c$  (not exactly at  $T_c$  as  $C_v = \infty$ ). This constraint is perhaps the least easily defended in the quantification of this type of EOS. The constancy of  $C_v$  along the critical isochore is consistent with a  $\gamma_v$  description. However,  $T_c$  is a point of singularity with respect of  $C_v$ . The adoption of a  $C_v(T > T_c)$  having a value equal to the average value obtained by applying the lever rule on the critical isochore below  $T_c$  is an intuitive assignment in the absence of any experimental guidance, and therefore represents a best approximation at this time.

In conclusion, the reported EOS is considered an improvement over Alderson's original tables and its adoption will improve the thermodynamic description of sodium.

#### References

1. ALDERSON, M.A.H.G., An EOS for use with sodium, UKAEA Report SRD, R50, 1975.
2. BHISA, V.S., Experimental critical point and high temperature vapour pressure and derived thermodynamic properties of sodium, Columbia Univ. Eng. Sci. D., 1977.
3. Equation of State of Materials of Relevance to the Analysis of Hypothetical Fast Breeder Reactor Accidents, IWGFR/26, Vienna, 1978. (P.E. Potter, P. Browning, M.J. Gillan, E.A. Khodarev)
4. ROWLINSON, J.S., Liquids and liquid mixtures, 2nd ed., Plenum Press, New York, 1969.

TABLE I

Equilibrium Properties Needed to Characterise Fully  
the Saturation Envelope

The following equilibrium quantities, as functions of temperature up to  $T_c$ , are sufficient to characterise fully the EOS of sodium.

- Vapour pressure
- Liquid and vapour densities
- Liquid and vapour enthalpies
- Liquid and vapour adiabatic compressibilities
- Vapour thermal pressure coefficient

Those quantities not mentioned in this list are directly calculable from the above quantities.

TABLE II

The Old and Revised Critical Constants for Sodium

| Source   | Ref. | $T_c$ (K) | $P_c$ (MPa) | $V_c$ ( $m^3/kg$ )     |
|----------|------|-----------|-------------|------------------------|
| Alderson | 1    | 2733      | 41.36       | $5.501 \times 10^{-3}$ |
| Bhisa    | 2    | 2503      | 25.98       | $4.685 \times 10^{-3}$ |

## APPENDIX 1

### The Evaluation of Single Phase Properties

The thermal pressure coefficient,  $\gamma_v$ , is defined as

$$\gamma_v = \left( \frac{\partial P}{\partial T} \right)_v$$

From the considerations of Section 2 the pressure in the single phase (sp) region is directly obtained from

$$P_{sp} = P_{sat} + \gamma_v(T_{sp} - T_{sat}) \quad (1.1)$$

where  $\gamma_v$  is evaluated at  $T_{sat}$  on the two phase envelope. As is discussed later in this appendix, the behaviour of the thermal pressure coefficient determines all the single phase thermodynamic properties. The calculation of  $\gamma_v$  is therefore crucial.

Evaluation of  $\gamma_v$  along the liquid saturation line is described in Reference 1. The approximation that  $\gamma_v$  is only a function of volume, thereby allowing extrapolative calculations to be performed, is based on observation. No further comment on the extrapolation of  $\gamma_v$  (sat.liq.) will be made here. The extrapolation of  $\gamma_v$  (sat.vap.) does benefit from comparison of  $\gamma_v$  for both a perfect gas and a slightly "imperfect" gas. The expression used to evaluate  $\gamma_v$  (sat.vap.) in this work is of the form:

$$\gamma_v(\text{sat.vap.}) = \frac{A}{V_{\text{sat.vap.}} - B} \quad (1.2)$$

where A and B are constant.

If we consider the perfect gas equation

$$PV = RT \quad (1.3)$$

then: 
$$\gamma_v = \left( \frac{\partial P}{\partial T} \right)_v = \frac{R}{V} \quad (1.4)$$

Comparing (1.2) and (1.4) we see that for high volumes the general form of (1.2) tends towards (1.4) (i.e. B can eventually be neglected). Thus for (1.2) to be a reasonable equation to use the coefficient A must be close to the gas constant, R. The value is shown in Appendix 2 and is indeed seen to be close to R. Thus the limiting form of (1.2) is correct. As V decreases then B can no longer be ignored. The origin of B can be demonstrated using van der Waals' equation:

$$\left( P + \frac{a}{V^2} \right) \cdot (V - b) = RT \quad (1.5)$$

for small departures from ideality (1.5) reduces to

$$P(V - \beta) = RT$$

$$\gamma_v = \left( \frac{\partial P}{\partial T} \right)_v = \frac{R}{V - \beta} \quad (1.6)$$

Comparing (1.6) with (1.2) we again see that A can be associated with R, and B with  $\beta$ , in the van der Waals equation.

The van der Waals equation is most useful as a qualitative description of the onset of non-ideality in a gas. In practice it has little quantitative application except at very high volumes. The choice of this type of expression to describe  $\gamma_v$  (sat.vap.), right up to  $T_c$ , lies with Alderson<sup>(1)</sup>. The author was aware of the inherent inadequacies and chose to allow both A and B (eqn. (1.2)) to vary from their high volume values, to afford a better description near  $T_c$ , rather than use a more appropriate expression.

For the purpose of this EOS, evaluation of single phase properties reduces to that of obtaining values for the internal energy and entropy. As mentioned in Section 2, this involves integration of the appropriate function with respect to a point on the reference curve ( $T_0, V_0$ ). The energy in the condensed liquid region is evaluated using

$$U(T_0, V_1) = U(T_0, V_0) + \int_{V_0}^{V_1} (T\gamma_v - P)_{\text{sat}} dV \quad (1.7)$$

Equation (1.7) is best illustrated by reference to Fig. 3. The integration in (1.7) is evaluated numerically by evaluating  $(T\gamma_v - P)_{\text{sat}}$  at an adequate number of points along the two phase envelope between, and including,  $V_0$  and  $V_1$ . The entropy at the same point is evaluated using

$$S(T_0, V_1) = S(T_0, V_0) + \int_{V_0}^{V_1} (\gamma_v)_{\text{sat}} dV \quad (1.8)$$

where the quantities in (1.8) are entropy equivalents of the energies in (1.7).

The evaluation of these quantities in the expanded gas is achieved in exactly the same fashion. Up to the critical isotherm, the energy and entropy are evaluated in the above manner. Once into the supercritical region they are extended using  $\bar{C}_v(V_c)$ , introduced in section 2. Fig. 4 illustrates the technique for evaluating supercritical energies; entropies are evaluated in an analogous manner, the entropy along the critical isochore being evaluated by

$$S(T_0, V_c) = S(T_c, V_c) + \bar{C}_v(V_c) \ln \left( \frac{T_0}{T_c} \right) \quad (1.9)$$

and the energy by

$$U(T_0, V_c) = U(T_c, V_c) + \bar{C}_v(V_c) \cdot (T_0 - T_c) \quad (1.10)$$

APPENDIX 2

Updated Equations for Na for  $T_c = T = 1640K$

Critical Constants:

$$\begin{aligned} T_c &= 2505K \\ P_c &= 25.98 \text{ MPa} \\ V_c &= 4.685 \times 10^{-5} \text{ m}^3/\text{kg} \end{aligned}$$

Saturated Vapour Pressure:

$$\begin{aligned} P_s(T) &= A e^{-B/T} T^{-C} \quad (\text{MPa}) \\ A &= 486.714 \\ B &= 11419.68 \\ C &= -0.2085587 \end{aligned}$$

Saturated Liquid Volume:

$$\begin{aligned} V_s(T) &= \frac{V_c}{1 + A(1 - BT)^C} \quad (\text{m}^3/\text{kg}) \\ A &= 5.25112 \\ B &= 3.995205755 \times 10^{-4} \\ C &= 0.489129 \end{aligned}$$

Saturated Vapour Volume:

$$V_{sv}(T) = V_{sl}(T) + \frac{\Delta H_{vap}}{(P_s(0.2085587 + 11419.68 T))} \quad (\text{m}^3/\text{kg})$$

$\Delta H_{vap}$  is the enthalpy of vaporisation and is given below.

Saturated Liquid Entropy:

$$S_{sl}(T) = S_{sl}(1640K) + \int_{1640}^T \frac{C_{sl}(T) dT}{T} \quad (\text{kJ/kg.K})$$

where

$$C_{sl}(T) = \left( \frac{dH_{sl}(T)}{dT} - V_{sl} \left( \frac{dP}{dT} \right)_{sl} \right) \times 10^5 \quad (\text{kJ/kg.K})$$

where

$$\frac{dH_{sl}(T)}{dT} = \frac{A \cdot B \cdot C (1 - T/T_c)^C}{2 \cdot (T_c - T)} \quad (\text{MJ/kg.K})$$

$$A = 8.51525 \times 10^{-4}$$

$$B = 1.9152 \times 10^{-5}$$

$$C = 0.53699$$

and

$$\left(\frac{dP}{dT}\right)_{s1} = Ae^{-B/T} \left( C \cdot T^{(-C-1)} + T^{-C} \frac{B}{T^2} \right) \quad (\text{MPa} \cdot \text{K}^{-1})$$

where

$$\begin{aligned} A &= 486.714 \\ B &= 11419.68 \\ C &= -0.2085587 \end{aligned}$$

Saturated Liquid Enthalpy:

$$H_{s1}(T) = A + BT - \frac{1}{2} \Delta H_{\text{vap}} \quad (\text{MJ/kg})$$

where

$$\begin{aligned} A &= 2.4423 \\ B &= 8.5125 \times 10^{-4} \end{aligned}$$

Enthalpy of Vaporisation:

$$\Delta H_{\text{vap}} = A T_c \left(1 - T/T_c\right)^B \quad (\text{MJ/kg})$$

where

$$\begin{aligned} A &= 1.9152 \times 10^{-3} \\ B &= 0.33699 \end{aligned}$$

Saturated Vapour Thermal Pressure Coefficient:

$$\gamma_v(T) = \frac{A}{V_{sv} \times 10^3 - B} \quad (\text{MPa/K})$$

where

$$\begin{aligned} A &= .382268 \\ B &= 0.02959 \end{aligned}$$

(Note: the gas content  $R = 0.361637 \text{ MPa} \cdot \text{m}^3/\text{kg} \cdot \text{K}^{-1}$ )

Saturated Liquid Adiabatic Compressibility:

$$\beta_s = A \left( \frac{T - B}{C(T_c - T)} \right) \quad (\text{MPa}^{-1})$$

where

$$\begin{aligned} A &= 1.985 \times 10^{-4} \\ B &= 5252.0 \\ C &= 3.0751 \end{aligned}$$

Saturated Liquid Thermal Expansion Coefficient:

$$\alpha_{s1} = \frac{1}{V_{s1}} \frac{dV_{s1}}{dT} \quad (\text{K}^{-1})$$

where  $V_{s1}$  is given above, and

$$\frac{dV_{sl}}{dT} = \frac{ABC(1 - BT)^{C-1}}{1 + A(1 - BT)^C} \quad (\text{m}^3/\text{kg}\cdot\text{K})$$

where

$$A = 3.23112$$

$$B = 3.995205 \times 10^{-4}$$

$$C = 0.489129$$

All other thermodynamic quantities evaluated in this EOS are calculable given the above equations. The reader is referred to Reference 1 for these additional equations.

## APPENDIX 5

### Improvements in Computational Technique

Two parts of the data given in Reference 1 are in error. These are the low temperature specific heat,  $C_v$ , of the saturated vapour, and the high volume internal energies in the single phase expanded gas.

It is necessary, in calculating  $C_v$  for both the liquid and vapour, to evaluate the saturated expansion coefficients,  $\alpha_s$ , for both phases

$$\alpha_{s\sigma} = \frac{1}{V_{s\sigma}} \frac{dV_{s\sigma}}{dT} \quad (5.1)$$

where  $\sigma$  represents either liquid, l, or vapour, v. For the liquid this may be done analytically using the equation given in Appendix 2. For the vapour, owing to the procedure involved in evaluating  $V_{sv}$  it is much easier to calculate  $\alpha_{sv}$  numerically. In fact, the evaluation of  $\alpha_{sl}$  is also done numerically for convenience, no significant loss of accuracy being incurred. In the evaluation of this numerical differential it is necessary to choose a suitable step length in T. Alderson chose a 5K step length. This is adequate for most calculations, however, at temperatures below 700°C the specific volume of the vapour increases rapidly with decreasing temperature. A step length of 5K is too large for a reliable estimate of  $\alpha_{sv}$  in this region. The consequence of this was to over estimate  $C_v$  by ca. 100% at 600K. In Section 4 it was stated that this had important consequences regarding the general applicability of the EOS. It will be seen in Appendix 5 that one of the arguments supporting the adoption of a  $\gamma_v$  which is only a function of volume is the 'invariance' of  $C_v$  with temperature, for both liquid and vapour. In his original work Alderson concluded that " $C_v$  is approximately constant up to about 2500K apart from the low temperature vapour." Fig. 2 shows  $C_v$  for both phases, evaluated from this work and the agreement at low temperatures is improved, compared with the original work. In consequence, confidence in the  $\gamma_v$  extrapolation technique is increased.

The second area of Alderson's tabulation in which errors occur is the high volume expanded gas internal energy (and consequently the enthalpy), near and above  $T_c$ . For a given temperature, the internal energy of a single phase gas tends towards that of a perfect gas as the volume increases. The internal energy of a perfect gas is only a function of temperature and consequently the high volume internal energy given in Alderson's isothermal tabulation should tend to the perfect gas limit and not diverge as is evident from the tabulation.

The effect of these errors upon any conclusions of hypothetical accident analysis is not expected to be significant.

APPENDIX 4

Tabular Format of the Equation of State

|          |                          |  |                         |
|----------|--------------------------|--|-------------------------|
| Table 1. | Saturation temperature   |  |                         |
|          | listing:                 | specific volume<br>internal energies<br>enthalpies<br>entropies<br>pressure  | } for liquid and vapour |
| Table 2. | Saturation pressures     |  |                         |
|          | listing:                 | specific volumes<br>internal energies<br>enthalpies<br>entropies<br>temperatures   | } for liquid and vapour |
| Table 3. | Constant temperatures    |  |                         |
|          | listing:                 | pressure<br>condition<br>specific volume<br>internal energy<br>enthalpy<br>entropy   |                         |
| Table 4. | Constant entropy         |  |                         |
|          | listing:                 | pressure<br>specific volume<br>internal energy<br>enthalpy<br>temperature  |                         |
| Table 5. | Constant volumes         |  |                         |
|          | listing:                 | temperature<br>internal energy<br>enthalpy<br>entropy<br>pressure  |                         |
| Table 6. | Constant internal energy |  |                         |
|          | listing:                 | temperature<br>specific volume<br>enthalpy<br>entropy<br>pressure  |                         |
| Table 7. | Saturated properties     |  |                         |
|          | listing:                 | temperature<br>thermal expansion coefficient, $\alpha_p$<br>isothermal compressibility, $\beta_T$<br>thermal pressure coefficient, $\gamma_V$<br>constant pressure specific heat, $C_p$<br>constant volume specific heat, $C_v$<br>Gruneisen gamma, $\Gamma_V$ | } for liquid and vapour |

## APPENDIX 5

### The Comparison of a Gruneisen Extrapolation with One Based on the Thermal Pressure Coefficient, and the Implications for the Behaviour of $C_v$

In contrast to the thermal pressure coefficient technique, a Gruneisen extrapolation asserts that the Gruneisen parameter  $\Gamma_v$  is invariant with volume. It is defined as

$$\Gamma_v = v \left( \frac{\partial P}{\partial E} \right)_v \quad (5.1)$$

Comparing (5.1) with (1.1), we see that in using a  $\Gamma_v$  description we are formulating an equation of state in terms of (P,V,E) rather than (P,V,T). Different techniques have to be employed to develop such an equation of state; then, the two extrapolative techniques can be compared.

Calculations for both systems have been performed by extrapolating along isotherms away from the saturated liquid line into the compressed liquid. Fig. 5 shows isotherms for  $T \geq 2000\text{K}$ . Below this temperature, in fact up to ca. 2300K, the difference in the two techniques is very small over the range of pressures shown in Fig. 5. Beyond this pressure range the isotherms begin to diverge. Above 2300K the isotherms for the two techniques were clearly different, as can be seen.

The agreement between the  $\gamma_v$  and  $\Gamma_v$  techniques is illustrated by the following:-  
from (5.1) we can write

$$\Gamma_v = v \left( \frac{\partial P}{\partial T} \right)_v - \left( \frac{\partial T}{\partial E} \right)_v = \frac{v\gamma_v}{C_v} \quad (5.2)$$

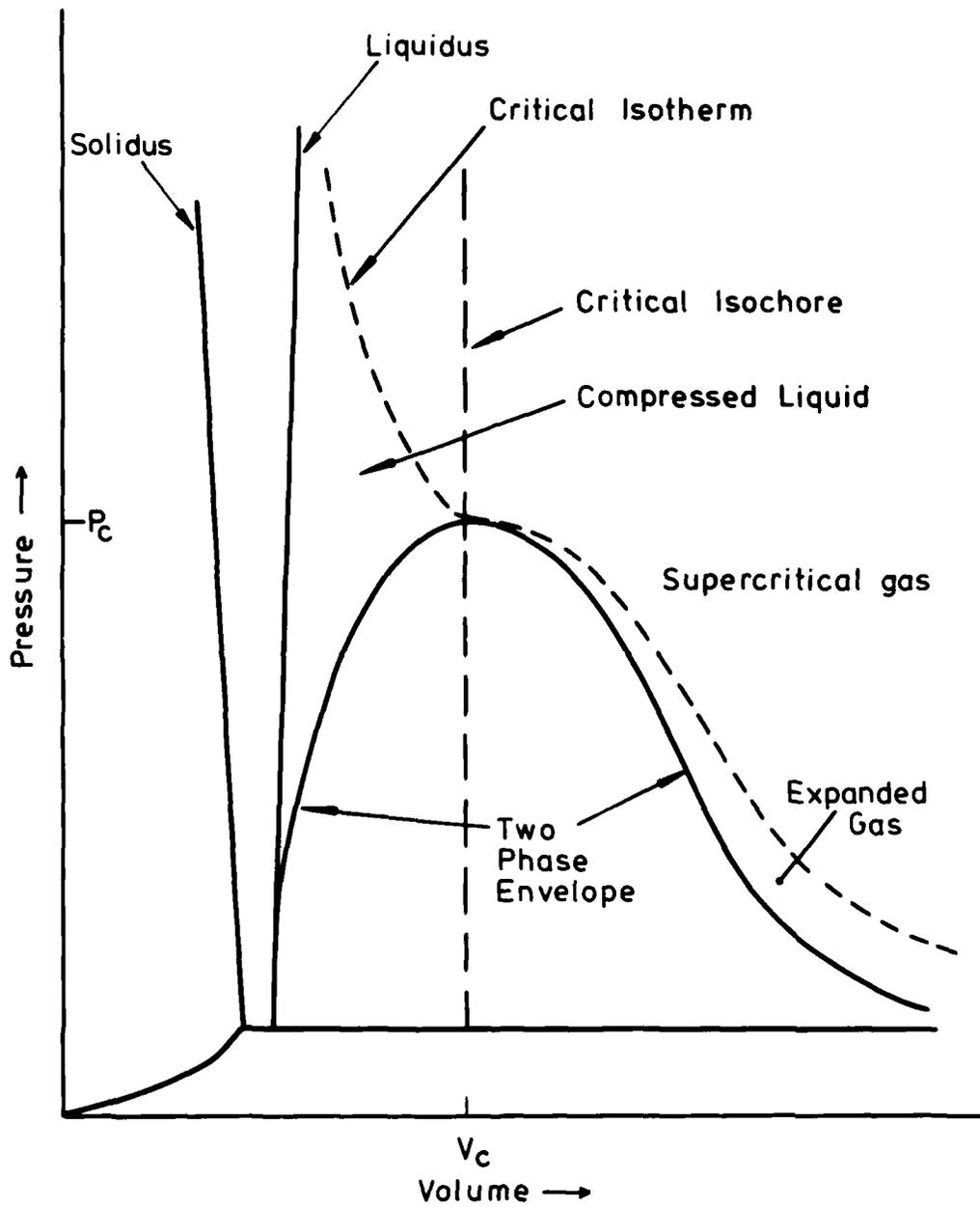
If  $\gamma_v$  and  $\Gamma_v$  are only functions of V, it follows from (5.2) that  $C_v$  must also only be a function of V. Employing the following relationship

$$\left( \frac{\partial C_v}{\partial V} \right)_T = T \left( \frac{\partial^2 P}{\partial T^2} \right)_v = T \left( \frac{\partial \gamma_v}{\partial T} \right)_v$$

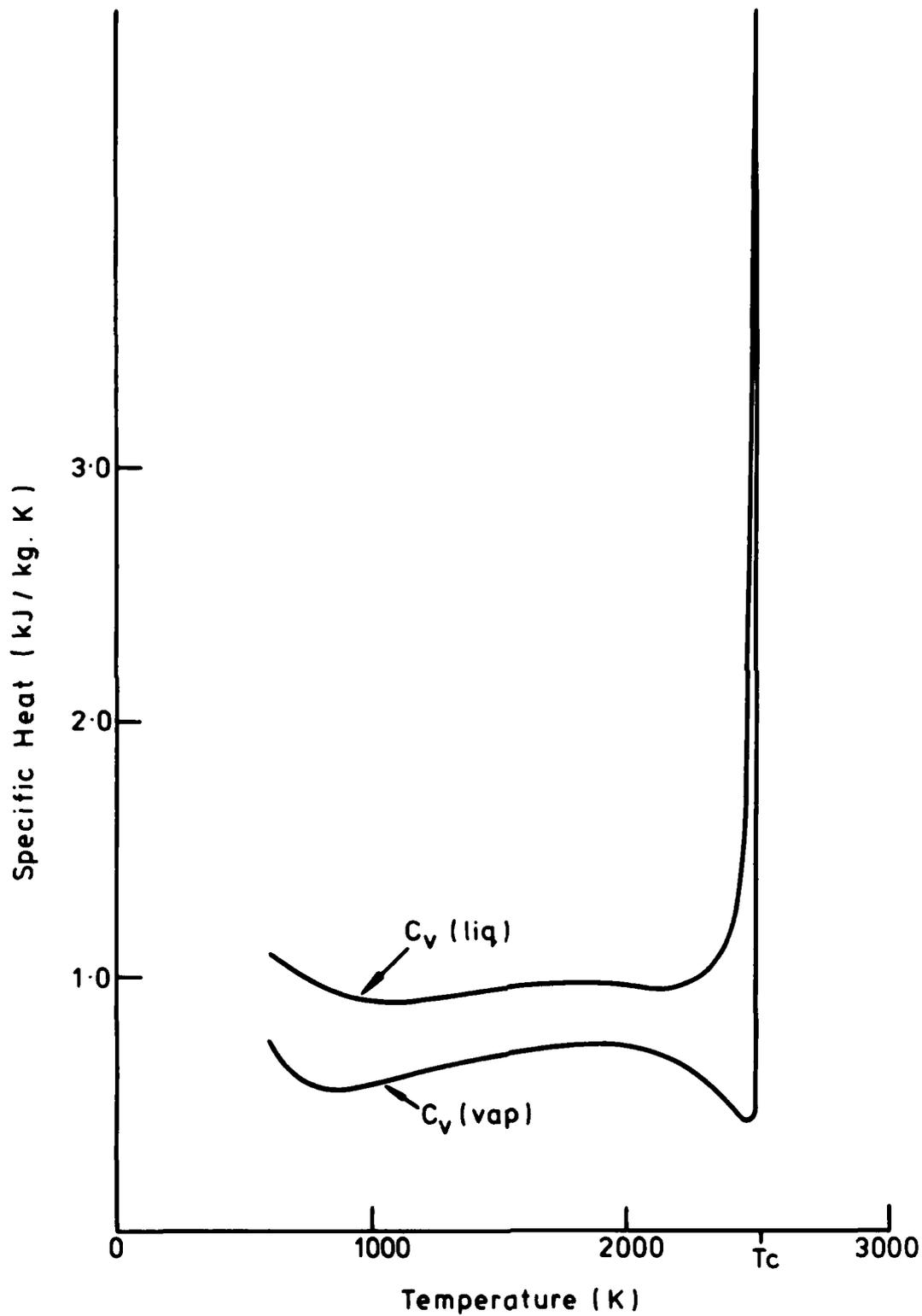
we see that the last term is zero as  $\gamma_v$  is only a function of volume; consequently

$$\left( \frac{\partial C_v}{\partial V} \right)_T = 0$$

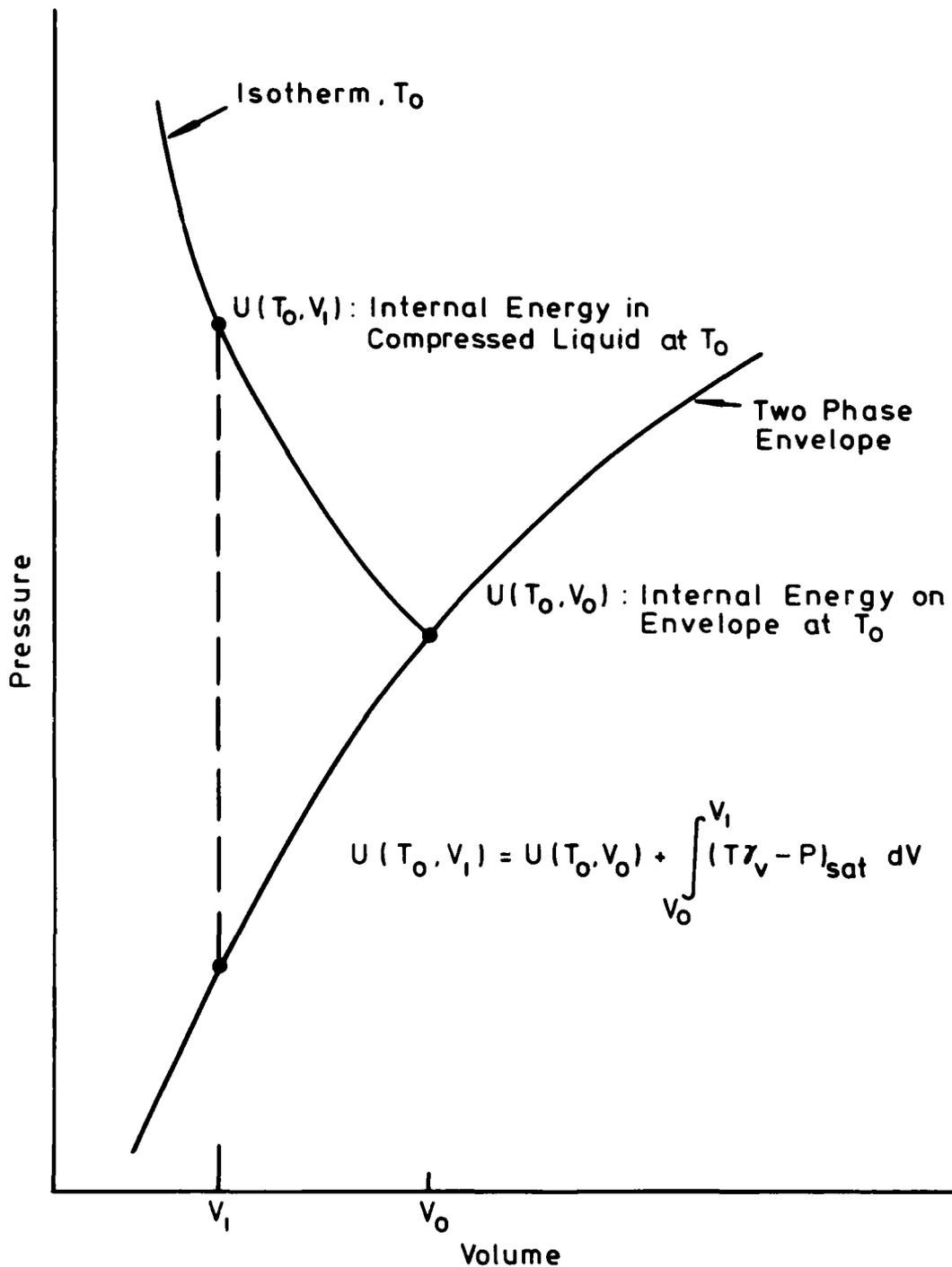
Thus  $C_v$  must be a constant if  $\gamma_v$  and  $\Gamma_v$  are functions of volume only. It has been previously demonstrated (Fig. 2) that  $C_v$ , for both liquid and vapour, is reasonably constant up to ca. 2300K. They can now be seen to be sufficiently constant as to introduce no significant difference in the  $\gamma_v$  and  $\Gamma_v$  techniques up to ca. 2300K. Above this temperature  $C_v$  for both phases rapidly increases, and a commensurate divergence in  $\gamma_v$ ,  $\Gamma_v$  extrapolations is observed.



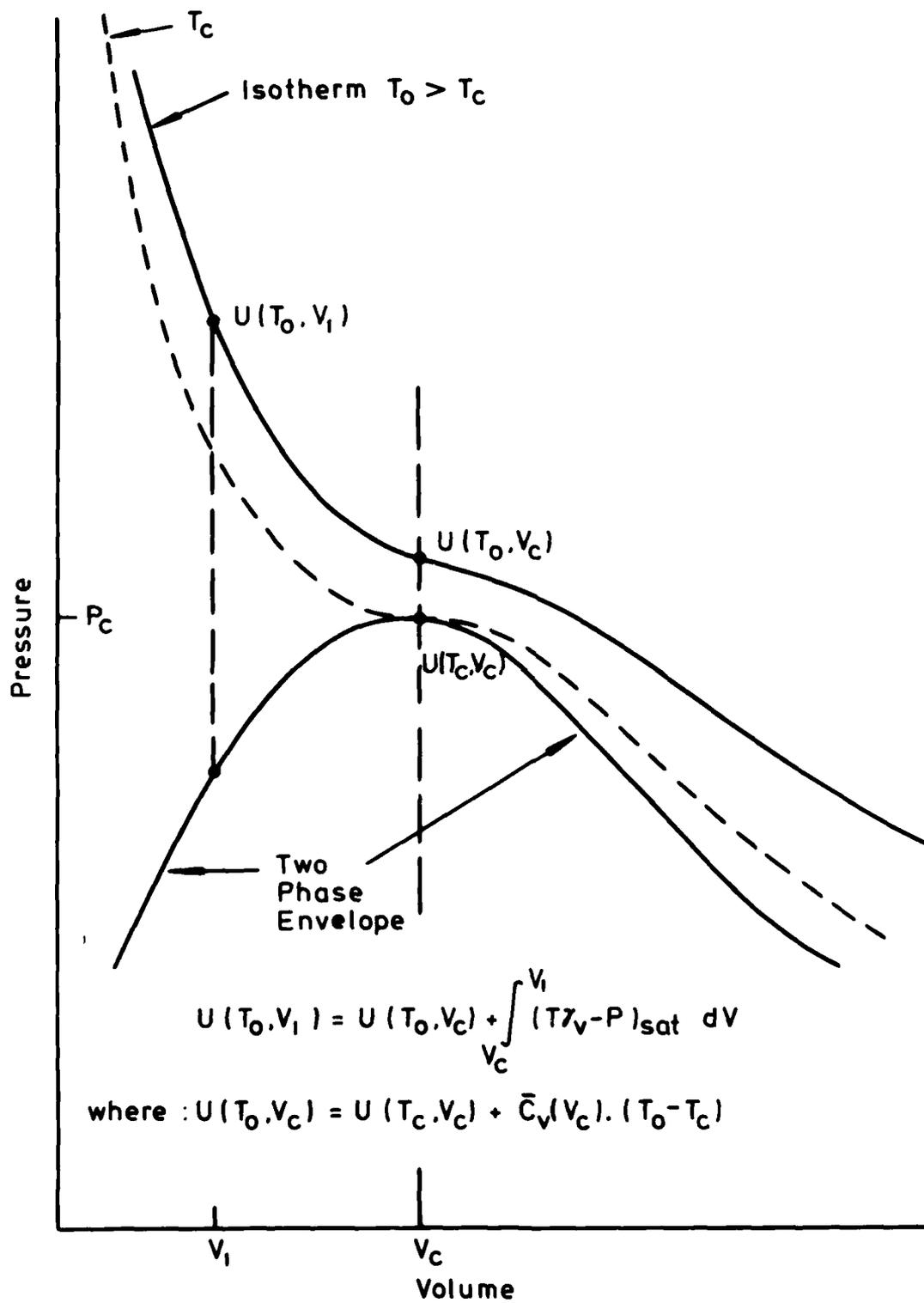
A.E.R.E. R9847. FIG. 1. THE GENERAL P-V SURFACE.



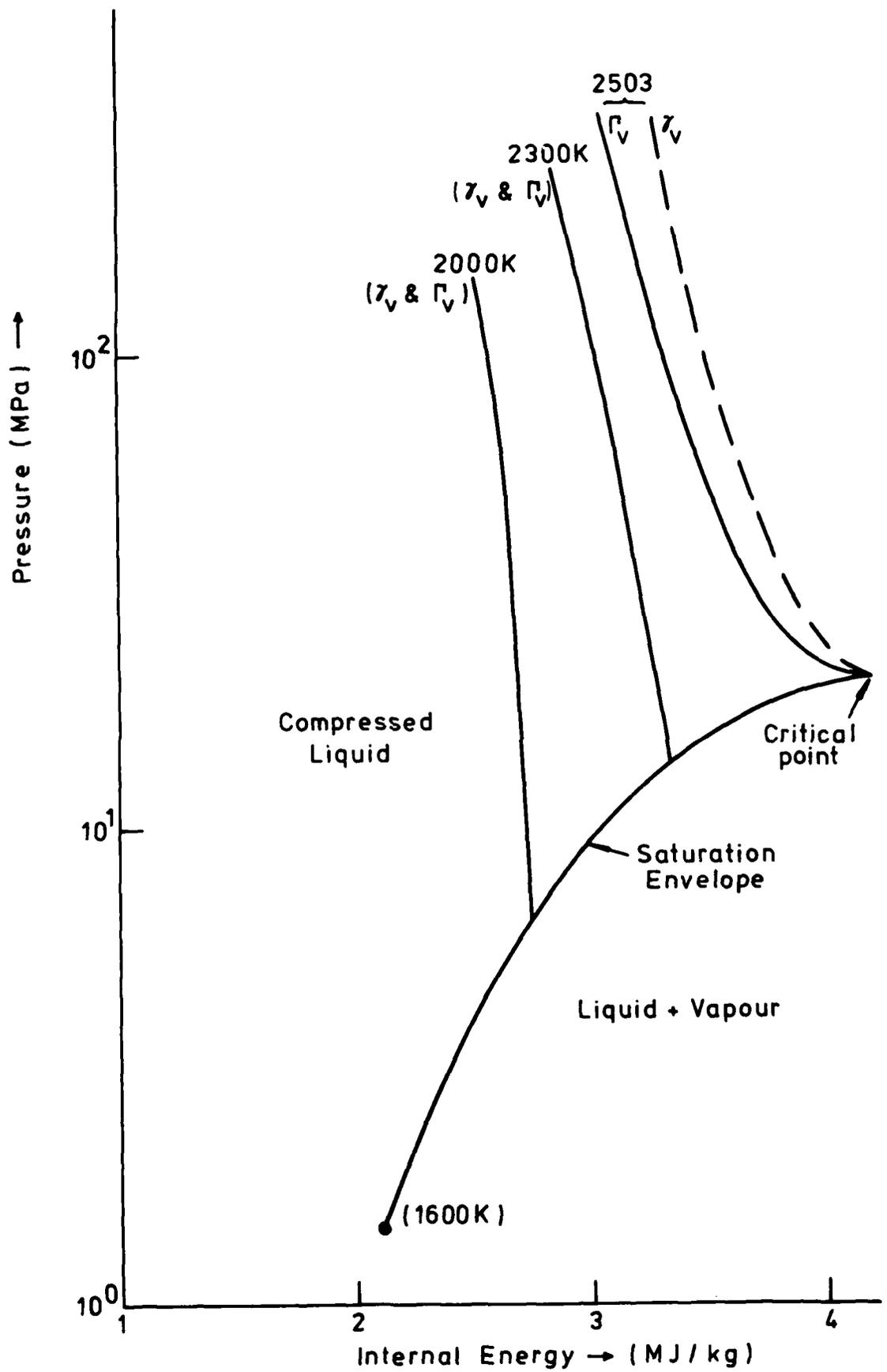
A.E.R.E. R9847. FIG. 2. THE BEHAVIOUR OF  $C_v(\text{liq})$  AND  $C_v(\text{vap})$  ALONG THE SATURATION ENVELOPE.



A.E.R.E. R9847. FIG. 3. EVALUATION OF THE INTERNAL ENERGY IN THE SUBCRITICAL COMPRESSED LIQUID



A.E.R.E. R9847. FIG. 4. EVALUATION OF THE INTERNAL ENERGY IN THE SUPERCRITICAL COMPRESSED LIQUID



A.E.R.E. R9847. FIG. 5. COMPARISON OF EXTRAPOLATIONS INTO THE COMPRESSED LIQUID USING THE GRUNEISEN ( $\Gamma_V$ ) AND THERMAL PRESSURE COEFFICIENT ( $\gamma_V$ ) TECHNIQUES