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at E. For this potential (16) yields

$$T_{\min}(E) = L[2m(E - V_0)^{-1}]^{\frac{1}{2}}. \qquad (25)$$

Then

$$(\Delta E)_{\max} = (h/L)[(E - V_0)(2m)^{-1}]^{\frac{1}{2}}. \qquad (26)$$

The maximum fractional level spacing is

$$E^{-1}(\Delta E)_{\max} = (h/LE)[(E - V_0)(2m)^{-1}]^{\frac{1}{2}}$$
$$\sim h/L(2mE)^{\frac{1}{2}}. \qquad (27)$$

From Eq. (27) we see that the maximum fractional level spacing, which is attained for the square well, decreases like $1/\sqrt{E}$ for large E. For any other potential the width L in Eq. (27) increases with E so the fractional level spacing decreases faster than $1/\sqrt{E}$. Therefore we have proved that for any potential the level spacing divided by the energy decreases to zero with increasing energy. This apparently explains why quantization is not observed at high energies.

Strange Carnot Cycles; Thermodynamics of a System with a Density Extremum

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Sommerfeld has given an apparent case of a perpetual motion machine of the second kind. This consists of a Carnot engine employing liquid water and operating between the normal and anomalous regions of thermal expansion. His explanation of the paradox is shown to be incomplete when the temperature of maximum density is pressure-dependent. To analyze this case a simple thermodynamic model for a substance with a density extremum is given; this model yields a reasonable approximation to the data for water. Standard thermodynamic properties of the system are computed and useful approximate forms given. Various Carnot cycles and a non-trivial "two-process" cycle are then shown in the p-T, T-s, and p-v planes. Sommerfeld's paradox is resolved by showing that a Carnot cycle qualitatively similar to that in his problem involves *expansions* for *both* isothermal processes. Theoretical implications of the analysis and applications to sound waves and shock waves are briefly discussed.

A. INTRODUCTION

1. Sommerfeld Problem

IN his thermodynamics text, Sommerfeld[1] has posed the following instructive problem:

Imagine a Carnot cycle with water as the working substance operating between 2° and 6°C so that at 6°C there is isothermal expansion and isothermal compression at 2°C. It is seen that heat is added during both processes, if the pressure is low enough, and so heat is converted completely into work in violation of the second law. How is it possible to resolve this contradiction?

Sommerfeld resolves the paradox by showing that the 4°C isothermal is also an isentropic. This

may be seen from the second $T ds$ equation[2]

$$T ds = c_p dT - \beta T v dp. \qquad (1)$$

If $\beta \equiv (1/v)(\partial v/\partial T)_p$ vanishes for all pressures at 4°C, then the last term vanishes at this temperature; integration at constant temperature yields constant entropy. Hence no isentropics can *cross* the 4°C isothermal; the isentropics implicitly assumed in the problem statement do not exist. (It is interesting to compare the resolution of this paradox with the logical point raised by Mrs. Boas on the existence of certain postulated processes at absolute zero.[3])

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[1] A. Sommerfeld, *Thermodynamics and Statistical Mechanics* (Academic Press, Inc., New York, 1956), pp. 347, 359 (Problem I.6).

[2] See, for example, J. F. Lee and F. W. Sears, *Thermodynamics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1955), p. 194.

[3] M. L. Boas, Am. J. Phys. **28**, 675 (1960).

2. Generalization of Problem

However, precise data show that the temperature at which maximum density of water occurs varies slightly with pressure. (For example, at 100 atm it is roughly 2°C.) Hence an isentropic curve will have a horizontal tangent in the T,p plane at the point of maximum density [i.e., where $(\partial v/\partial T)_p$ vanishes], but will not be isothermal. Thus Sommerfeld's explanation is inadequate for the realistic case. How then is this paradox to be resolved?

The answer to this question involves an analysis of the entropy of water (or, more generally, any fluid) in the neighborhood of its density extremum. An indication of its anomalous behavior is shown in the tables of Keenan and Keyes.[4] At 0°C (32°F) the entropy increases with pressure up to about 3500 lb/in.[2] and then begins to decrease, whereas for other temperatures tabulated it decreases monotonically. These values come primarily from an earlier paper by Keenan.[5] Qualitatively similar results were found by Koch[6] and Schlegel,[7] whose results are tabulated in Dorsey's[8] comprehensive reference book on the properties of water. However, none of these sources put special emphasis on the peculiarities of isentropics near 4°C. This is not surprising; entropy changes in the anomalous region are extremely small and are of minor importance in power applications.

The present paper deals specifically with this anomalous region. Necessary thermodynamic data for water are first plotted and approximated by simple analytical expressions. From these relations the equation for the isentropics is derived. Next a fundamental equation for the system is obtained, and other thermodynamic quantities, including internal energy, are computed. Approximate forms of these equations are then given, which are appropriate to the particular case of water. Finally the results are applied to analyze Carnot cycles in this region and to resolve the paradox presented above.

[4] J. H. Keenan and F. G. Keyes, *Thermodynamic Properties of Steam* (John Wiley & Sons, Inc., New York, 1936), Table 4, pp. 74–5.
[5] J. H. Keenan, Mech. Eng. **53**, 127 (1931).
[6] W. Koch, Z. Ver. deut. Ingr. **78**, 1110 (1934).
[7] E. Schlegel, Z. tech. Physik **14**, 105 (1933).
[8] N. E. Dorsey, *Properties of Ordinary Water-Substance* (Reinhold Publishing Corporation, New York, 1940), Table 123, p. 267.
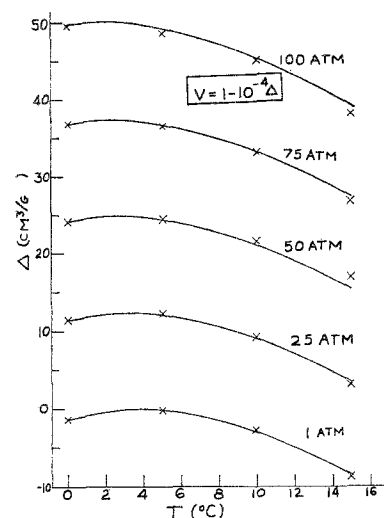
FIG. 1. p-v-T plot for water near temperature of maximum density. Experimental points are obtained from Amagat data; curves represent Eqs. (2) and (3). Note that $v=1-10^{-4}\Delta$, where v is in cm³/g.

B. THERMODYNAMIC MODEL

1. Properties of Compressed Water

Figure 1 shows the specific volume of compressed water in the anomalous temperature region and the pressure range 1–100 atm, using the data of Amagat[9] as tabulated in Dorsey.[10] Each of the isobaric curves in the figure may be approximated by the same parabola, provided that the vertex is properly translated. Furthermore the vertices lie very nearly on a straight line. Hence the specific volume may be represented, to a good approximation, by the relation

$$v = v_0[1+\lambda(T-T_0+ap)^2-k_0p], \qquad (2)$$

where v is in cm³/gm, T is in °K, and p is in dynes/cm², and

$$v_0 = 1.000\ 08\ \text{cm}^3/\text{g},$$
$$\lambda = 8 \times 10^{-6}\ (°\text{K})^{-2},$$
$$T_0 = 277°\text{K}, \qquad (3)$$
$$a = 2.0 \times 10^{-8}\ °\text{K-cm}^2/\text{dyne},$$
$$k_0 = 5.0 \times 10^{-11}\ \text{cm}^2/\text{dyne}.$$

Some additional input data are necessary to calculate the various thermodynamic properties.

[9] M. E. H. Amagat, Ann. chim. et phys. **29**, 68, 505 (1893).
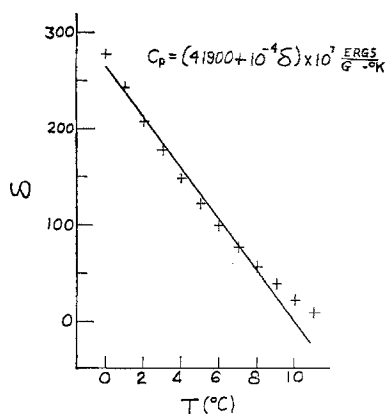[10] See reference 8, Table 95.I., pp. 207–9.

FIG. 2. Specific heat c_p for water at 1 atm. Experimental points are obtained from Osborne, Stimson, and Ginnings; straight line represents Eqs. (4) and (5).

The simplest, and probably most accurate, additional item is the constant pressure specific heat at atmospheric pressure. This data[11] has been obtained from Osborne, Stimson, and Ginnings and is plotted in Fig. 2. To rather high accuracy it may be represented by

$$(c_p)_{1\text{atm}} = c_0 - b(T - T_0), \qquad (4)$$

where c_p is in ergs/g-°K and

$$c_0 = 4.2057 \times 10^7 \text{ ergs/g-°K},$$
$$b = 0.0026 \times 10^7 \text{ ergs/g-(°K)}^2. \qquad (5)$$

2. Model and Discussion

The above relations were used as a guide to form a simple thermodynamic model, which includes the essential features of the problem under consideration. The system will be defined by Eq. (2) and a slight simplification of Eq. (4), viz.,

$$c_p(0,T) = c_0 - b(T - T_0), \qquad (6)$$

i.e., the specific heat at zero pressure is assumed as known. Since the pressure variation of c_p for a liquid is extremely small, even for a change of 100 atm, the constants given in Eq. (5) may be used without appreciable error.

This model should give a reasonable approximation to the thermodynamic behavior of any liquid (or solid under hydrostatic pressure) in

[11] N. S. Osborne, H. F. Stimson, and D. C. Ginnings, J. Research Natl. Bur. Standards **23**, 238 (1939).

the region of a density extremum, regardless of whether it is a maximum or a minimum and regardless of the sign of the pressure coefficient a. In the case of water both λ and a are positive constants. A more accurate fit to the experimental data may be obtained by adding a function of pressure alone (e.g., $v_0 k_1 p^2$) to Eq. (2) and adding a function of temperature alone to Eq. (6); these modifications will not affect the qualitative nature of the results below.

Two limitations should be emphasized: (1) As already stated, Eqs. (2) and (6) give only an approximate representation of the properties of a real fluid; (2) the model has no physical reality for pressures below those on the vaporization curve since the substance is then in the gaseous phase with totally different properties. For the case of water the saturation pressure is of the order of 0.01 atm in the region of interest.

C. THERMODYNAMIC CALCULATIONS

1. Calculation of Entropy

It is convenient to calculate first the value of c_p at all pressures. This is easily obtained from the relation[2]

$$(\partial c_p/\partial p)_T = -T(\partial^2 v/\partial T^2)_p. \qquad (7)$$

With the help of Eq. (2) it follows that

$$c_p(p,T) = c_p(0,T) - T \int_0^p (2\lambda v_0)dp. \qquad (8)$$

Substitution of Eq. (6) now gives

$$c_p(p,T) = c_0 - b(T - T_0) - 2\lambda v_0 pT. \qquad (9)$$

Entropy may now be calculated from the second Tds equation[2]:

$$Tds = c_p dT - T(\partial v/\partial T)_p dp. \qquad (10)$$

Insertion of Eqs. (2) and (9) in this expression yields

$$Tds = (c_0 - bT + bT_0)dT - 2\lambda v_0$$
$$\times [pTdT + T(T - T_0)dp] - 2\lambda v_0 Tapdp. \qquad (11)$$

Integrating and taking the entropy as zero in the reference state $(0,T_0)$ gives

$$s(p,T) = (c_0 + bT_0) \ln(T/T_0)$$
$$- b(T - T_0) - 2\lambda v_0 p(T - T_0) - \lambda v_0 ap^2. \qquad (12)$$

Isentropic curves of T vs p may now be obtained by setting s constant. Typical examples are plotted in Fig. 3; they are best understood from the approximate form of Eq. (12) which will be developed in Sec. C5. It is clear that the curves show a normal behavior [i.e., $(\partial T/\partial p)_s > 0$] where the coefficient of thermal expansion is positive, and an anomalous behavior where it is negative. As previously emphasized, these curves have no physical significance at zero pressure, but only down to the vaporization curve.

It is now possible to pass on to Sec. D and resolve the Carnot cycle paradox, with perhaps a brief reference first to the approximation in Sec. C5. However, for completeness, a fuller treatment of the thermodynamic properties of the system is given below.

2. Fundamental Equation

All thermodynamic information on the system may be expressed in a single *fundamental equation*. (See, for example, Wilson.[12]) With p and T as independent variables, the fundamental equation is the Gibbs function $g(p,T)$. Since $dg = -sdT + vdp$ is an exact differential, it may be computed along any convenient path. Let the reference state again be $(0,T_0)$ with $g_0 = 0$, and choose an isobaric path to $(0,T)$ and an isothermal path to (p,T). It follows that

$$g(p,T) = -\int_{T_0}^{T} s(0,T')dT' + \int_{0}^{p} v(p',T)dp', \quad (13)$$

where T' and p' are dummy variables of integration.

The integrand $s(0,T')$ may be obtained by setting $p=0$ in Eq. (12) or computed directly from Eq. (6) by taking

$$\int_{T_0}^{T'} [c_p(0,T'')/T'']dT'';$$

[12] A. H. Wilson, *Thermodynamics and Statistical Mechanics* (University Press, Cambridge, England, 1957), pp. 44–52.
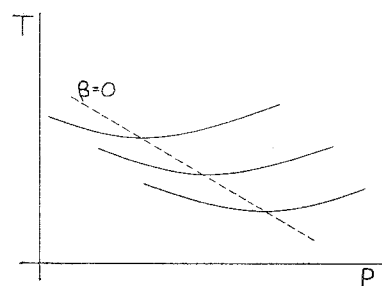

FIG. 3. Isentropic curves for water in T-p plane near temperature of maximum density, which is given by straight line T-$T_0 + ap = 0$.

$v(p',T)$ is given by Eq. (2). The result is

$$
\begin{aligned}
g(p,T) = &- (c_0 + bT_0)T \ln(T/T_0) \\
&+ (c_0 + bT_0)(T - T_0) \\
&+ \tfrac{1}{2}b(T - T_0)^2 + v_0[p - \tfrac{1}{2}k_0 p^2] \\
&+ \lambda v_0 p[(T - T_0)^2 + ap(T - T_0) + \tfrac{1}{3}a^2 p^2]. \quad (14)
\end{aligned}
$$

This result may now be checked by calculating $s = -(\partial g/\partial T)_p$ and $v = (\partial g/\partial p)_T$.

3. Other Thermodynamic Quantities

With the expressions for v, c_p, s, and g in Eqs. (2), (9), (12), and (14), other thermodynamic quantities may now be obtained in terms of p and T. The other three thermodynamic potentials are

$$
\begin{aligned}
f \equiv g - pv = &- (c_0 + bT_0)T \ln(T/T_0) \\
&+ (c_0 + bT_0)(T - T_0) + \tfrac{1}{2}b(T - T_0)^2 + \tfrac{1}{2}v_0 k_0 p^2 \\
&- \lambda v_0 p[ap(T - T_0) + \tfrac{2}{3}a^2 p^2], \quad (15)
\end{aligned}
$$

$$
\begin{aligned}
h \equiv g + Ts = &\ c_0(T - T_0) \\
&- \tfrac{1}{2}b(T - T_0)^2 + v_0(p - \tfrac{1}{2}k_0 p^2) \\
&- \lambda v_0 p[T^2 - T_0^2 + apT_0 - \tfrac{1}{3}a^2 p^2], \quad (16)
\end{aligned}
$$

$$
\begin{aligned}
u \equiv h - pv = &\ c_0(T - T_0) - \tfrac{1}{2}b(T - T_0)^2 \\
&+ \tfrac{1}{2}v_0 k_0 p^2 - 2\lambda v_0 p \\
&\times [T^2 - T(T_0 - ap) - \tfrac{1}{2}apT_0 + \tfrac{1}{3}a^2 p^2]. \quad (17)
\end{aligned}
$$

The standard thermodynamic derivatives β, k, and c_v as well as the speed of sound $\mathfrak{v}$, are

computed as shown below:

$$\beta \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{2\lambda(T-T_0+ap)}{1+\lambda(T-T_0+ap)^2-k_0 p}, \tag{18}$$

$$k \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = \frac{k_0-2\lambda a(T-T_0+ap)}{1+\lambda(T-T_0+ap)^2-k_0 p}, \tag{19}$$

$$c_v = c_p - \frac{\beta^2 vT}{k} = c_0 - b(T-T_0) - 2\lambda v_0 pT - \frac{4\lambda^2 T v_0 (T-T_0+ap)^2}{k_0-2\lambda a(T-T_0+ap)}, \tag{20}$$

$$\mathcal{U} = \left(\frac{\partial p}{\partial \rho}\right)_s^{\frac{1}{2}} = \left[\frac{v}{k}\left(\frac{c_p}{c_v}\right)\right]^{\frac{1}{2}} = \frac{v_0^{\frac{1}{2}}[1+\lambda(T-T_0+ap)^2-k_0 p]}{[k_0-2\lambda a(T-T_0+ap)]^{\frac{1}{2}}}$$

$$\times\left\{1-\frac{4\lambda^2 v_0 T(T-T_0+ap)^2}{[c_0-b(T-T_0)-2\lambda v_0 pT][k_0-2\lambda a(T-T_0+ap)]}\right\}^{-\frac{1}{2}}. \tag{21}$$

4. Stability Criteria

A necessary and sufficient set of conditions for stability (see, for example, Wilson[13]) is $c_v > 0$ and $k > 0$. These conditions can now be checked by inserting numerical values in Eqs. (19) and (20).

In the case of water the criteria are, of course, satisfied by a wide margin in the region of interest. For example at low pressures $k > 0$ up to about 160°C, which is far outside the range of validity of the model.

5. Approximate Expressions

All expressions obtained thus far represent exact results for the thermodynamic model considered. It is useful to consider the quantitative values of the parameters for water, as given in Eqs. (3) and (5), and to derive some approximate forms. For this purpose it will be assumed here that $p \sim 10^8$ dynes/cm² (i.e., 10^2 atm) and $|T-T_0| \sim 5°K$, these figures being based on the range of validity of Eqs. (2) and (4).

In the expression for entropy, Eq. (12), the logarithm may be expanded as a Taylor series in $(T-T_0)/T_0$; all but the first two terms of the series are negligible compared with the remainder of Eq. (12). Hence it follows that

$$s(p,T) \approx \frac{c_0(T-T_0)}{T_0} - \frac{(c_0+bT_0)(T-T_0)^2}{2T_0^2}$$
$$-2\lambda v_0 p(T-T_0) - \lambda v_0 a p^2. \tag{22}$$

13 See reference 12, p. 60.

Each isentropic for the real liquid may be characterized by the temperature T_f at which it intersects the vaporization curve. In the anomalous region the saturation pressure is very small; hence the isentropics may be approximated by setting the above expression equal to $s_f \approx s(0,T_f)$. From the numerical values involved (or from the discussion in Sec. A1 for the case $\beta = 0$), it is clear that the isentropic curves are very nearly isothermal. Hence, to high accuracy, T may be replaced by T_f in all terms except the first. The resulting expression for an isentropic is

$$T-T_f \approx \frac{\lambda T_0 v_0}{c_0}[2(T_f-T_0)p+ap^2]. \tag{23}$$

Thus the isentropics are very nearly parabolic, as indicated in Fig. 3. For $T_f > T_0$, they are monotonically increasing while for $T_f < T_0$ they first decrease and then reach a minimum along the line $T-T_0+ap=0$.

The p-v relation for an isentropic process may be derived similarly. Expanding Eq. (2) as a Taylor series in temperature about T_f and retaining only the linear term gives

$$v \approx v_0[1+\lambda(T_f-T_0+ap)^2-k_0 p]$$
$$+2\lambda v_0(T_f-T_0+ap)(T-T_f). \tag{24}$$

Substituting Eq. (23) in the above now yields

$$v \approx v_0[1+\lambda(T_f-T_0+ap)^2-k_0 p]+\frac{2\lambda^2 v_0^2 T_0}{c_0}$$
$$\times(T_f-T_0+ap)[2(T_f-T_0)p+ap^2], \tag{25}$$

which is the desired result. The last term, which represents the volume difference between the isentropic and isothermal curves originating at saturation temperature T_f, is a cubic in p.

Simplified expressions for enthalpy and internal energy may easily be obtained from Eqs. (16) and (17). While the terms in brackets may be neglected to a high approximation, this would omit all anomalous features of the problem (i.e., all terms in λ and a). Hence a more refined treatment will be used. These expressions will be expanded about the point $(0, T_0)$ and terms linear in p and $T - T_0$ retained. It follows that

$$h \approx c_0(T - T_0) - \tfrac{1}{2}b(T - T_0)^2 + v_0(p - \tfrac{1}{2}k_0 p^2)$$
$$- 2\lambda v_0 T_0 p(T - T_0 + \tfrac{1}{2}ap), \quad (26)$$

$$u \approx c_0(T - T_0) - \tfrac{1}{2}b(T - T_0)^2 + \tfrac{1}{2}v_0 k_0 p^2$$
$$- 2\lambda v_0 T_0 p(T - T_0 + \tfrac{1}{2}ap). \quad (27)$$

In the above results, the anomalous terms are small and produce no important qualitative effects.

Approximations for β, k, c_v, and $\mathfrak{v}$, Eqs. (18) to (21), are straightforward from consideration of the numerical values involved. The results are

$$\beta \approx 2\lambda(T - T_0 + ap), \quad (28)$$

$$k \approx k_0 - 2\lambda a(T - T_0 + ap), \quad (29)$$

$$c_v \approx c_0 - b(T - T_0) - 2\lambda v_0 p T$$
$$- (4\lambda^2 T v_0 / k_0)(T - T_0 + ap)^2, \quad (30)$$

$$\mathfrak{v} \approx (v/k)^{\frac{1}{2}} \approx (v_0/k_0)^{\frac{1}{2}}$$
$$\times [1 - k_0 p + (\lambda a / k_0)(T - T_0 + ap)]. \quad (31)$$

While the last term in Eq. (30) is extremely small, it is retained to show the distinction between c_p and c_v.

6. Comparison with Other Results

Keenan's paper[5] and the Keenan and Keyes steam tables[4] give isothermal property changes at 0°C (32°F). These values for volume and enthalpy changes agree with Eqs. (2) and (26) [using the numerical values given in Eqs. (3) and (5)] to within about 2%.

A more sensitive test is provided by entropy. Figure 4 shows a comparison of the Keenan[5] results with those given by Eq. (12); the latter has been extended beyond its expected range of validity. The qualitative form of the two curves
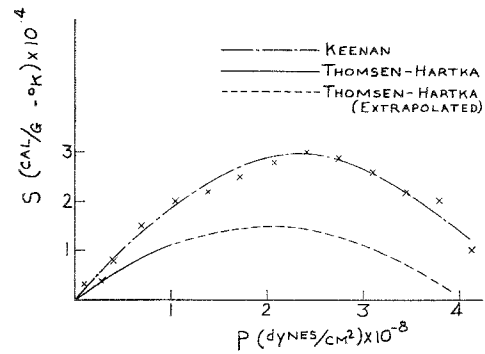

FIG. 4. Comparison of Keenan and Thomsen-Hartka entropy calculations at 0°C. Ordinate represents difference between entropy at pressure p and saturation value.

is the same, but the Keenan values are about twice as large. This discrepancy is presumably caused by slight differences in the specific volume data. Due to the small changes in volume, these calculations could be very sensitive to graphical corrections, methods of interpolation, etc. Keenan's paper is not sufficiently detailed on this point to draw further conclusions. In any event, the discrepancy is small compared to the entropy differences involved in most of Keenan's calculations and occurs in a region of minor interest for power applications, with which he was primarily concerned. Hence it seems possible that the simplified model used here is more accurate within its limited range of validity.

Since the Koch[6] and Schlegel[7] values for entropy are given to only one significant figure in this region, it seems pointless to make detailed numerical comparisons. They are in order of magnitude agreement with those in Fig. 4 and somewhat closer to Keenan's values.

The velocity of sound, as calculated from Eq. (31), agrees with the recent experimental values obtained by Wilson to within about 2%.[14] The predicted temperature dependence is excellent, but the predicted pressure variation is poor and sometimes even incorrect in sign. This seems to indicate the need for an additional term of the form $v_0 k_1 p^2$ in Eq. (2) to account for the variation in compressibility; such a refinement may easily be included and will not alter the expression for entropy. Wilson's paper may also be consulted for a discussion of possible inaccuracies in the Amagat data.

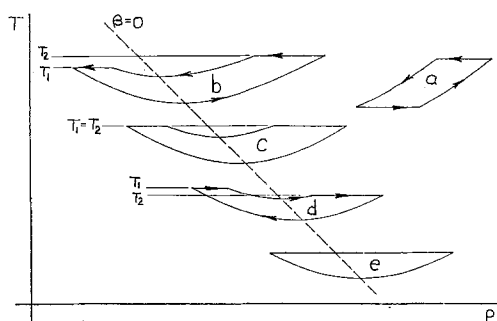[14] W. D. Wilson, J. Acoust. Soc. Am. **31**, 1067 (1959).

FIG. 5. (a)–(d). Various possible Carnot cycles in p-T plane; (e) "two-process cycle." Arrows in (a), (b), and (d) show direction for Carnot engine, i.e., $W>0$. In (c) and (e) $W=0$ in either direction. Dotted line represents T-T_0+ap $=0$, showing temperature of maximum density.

D. ANALYSIS OF CYCLES

1. p-T Representation

Various types of Carnot cycles may now be analyzed. (In the present context, this term denotes a reversible cycle consisting of two isentropic and two isothermal processes.) Initially it is simplest to consider the p-T representation since each point in this plane represents a unique state of the system. The appropriate isentropics may be plotted from Eq. (23).

Figure 5(a) represents a Carnot cycle in the normal region, where the coefficient of thermal expansion is positive. Figures 5(b), (c), and (d) show three examples of "strange Carnot cycles," which include both the normal and anomalous region. In these three respective cases the temperature of the isothermal in the normal region is respectively higher than, equal to, and lower than that in the anomalous region.

Figure 5(e) shows a still stranger case, a "two-process cycle," consisting of one isothermal and one isentropic. This cycle is, of course, non-existent for a normal fluid and is made possible only by the anomalous thermal expansion of the system.

In the case of water, the isentropic temperature changes possible within the range of validity of the model are of the order of 0.01°K. While these temperature variations are quite small, this does not alter the principles involved.

2. T-s Representation

Figure 6 shows the same five cycles in the T-s plane. In the last four cases the temperature range traversed includes values below that of the low-temperature reservoir. The cycles retrace

portions of their paths in the T-s plane. However, reference to the p-T plane shows that this is not a trivial case of returning along the original paths. Clearly, within a region of the T-s diagram each point corresponds to two distinct thermodynamic states. Hence these cycles are all nontrivial on a three-dimensional thermodynamic *surface*; but a false impression may be created by *projecting* them on the T-s *plane*.

3. p-v Representation

Equations (2) and (25) represent isothermal and isentropic processes in the p-v plane. Figures 7 and 8 correspond to the cycles (b) and (e) shown in Figs. 5 and 6. As in the T-s plane, each point within a certain region of the diagram represents two states. In Fig. 8 the net positive area enclosed is zero; this shows that, in accordance with the Kelvin-Planck statement of the second law,[15] the work done is zero even though the cycle is nontrivial. (This is also evident from the T-s plot.)

In Fig. 8 it will be noted that the isothermal and isentropic intersect in three points in the p-v projection. This appears to contradict the well-known result[16] that $k_s = (k/\gamma) \leq k$ so that $(\partial v/\partial p)_s$ $\leq (\partial v/\partial p)_T$, which would indicate that only one intersection is possible. The explanation is simple. Points 1 and 2 represent true intersections on the p-v-T surface, and the above relation is satisfied. Point X represents merely an intersection of the *projections* of the curves on the p-v plane; hence the above relation is inapplicable.

4. Resolution of Paradox

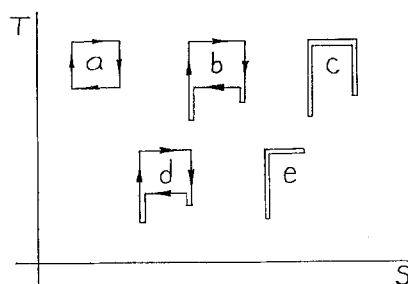The paradox described in Sec. A is now easily resolved. The cycle corresponding qualitatively

FIG. 6. T-s representation of the cycles in Fig. 5. Cycles (b)–(e) retrace portions of their paths; these portions are shown slightly separated for greater clarity.

[15] See, for example, reference 2, p. 121.
[16] See, for example, reference 2, p. 195.

to the Sommerfeld problem is that shown in Figs. 5(b), 6(b), and 7. Clearly this consists of one isentropic expansion, *two isothermal expansions*, and one isentropic compression. Heat is added during the isothermal expansion in the normal region and rejected during the *isothermal expansion* in the anomalous region. The fallacy in the paradox lies in the implicit assumption that in any Carnot cycle the low-temperature isothermal must represent a compression process.

E. DISCUSSION AND CONCLUSIONS

(1) A model has been set up to represent the qualitatively interesting features of a fluid (or a solid under hydrostatic pressure) with a density extremum and the principal thermodynamic properties derived. In general, the model applies to any density extremum, maximum, or minimum, and to either a positive or negative pressure coefficient. The numerical parameters obtained for water yield reasonably good quantitative results. Applications to solids may be of some practical interest since it may be possible to obtain a density extremum in a desired region by using an appropriate alloy.

(2) The paradox raised by the Sommerfeld problem has been completely resolved. The explanation illustrates the importance of existence questions (in this case, the existence of a Carnot cycle with an isothermal compression, under the assumed conditions). This is similar to the point recently raised by Mrs. Boas.[3] It also reinforces Kestin's[17] criticism of "proving" general thermodynamic statements by means of
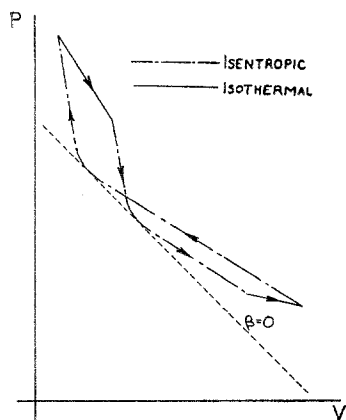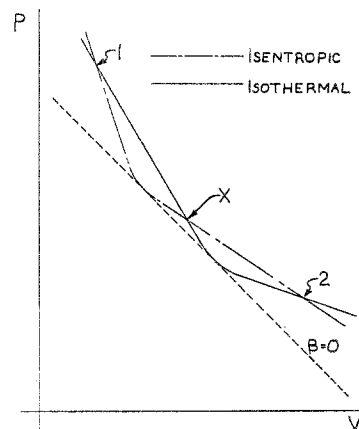

FIG. 8. *p-v* representation of the cycle shown in Figs. 5(e) and 6(e). On a *p-V-T* surface the curves intersect only at points 1 and 2.

p-v diagrams; curves whose projections intersect in this diagram need not really intersect at all.

(3) It may be noted that this system does not seem to meet the basic assumptions used in the Carathéodory approach.[18,19] The state of the system is not uniquely defined by the "deformation coordinate" v and a single mechanical "nondeformation coordinate"; his assumptions appear valid locally, but not globally. For those who feel that Carathéodory's formulation is the only rigorous approach to thermodynamics, this point would certainly seem to require further investigation.

(4) Fluids such as water should exhibit peculiarities in connection with sound waves. For example, in a sound wave through water at maximum density (i.e., satisfying $T - T_0 + ap = 0$) the temperature variation should be very nearly a pure second harmonic. However, the temperature amplitude will be so small that the sound wave will be almost isothermal; in fact this is one assumption used in approximating Eq. (21) by Eq. (31).

(5) Similarly there will be anomalous effects associated with shock waves. In particular, a shock wave can exist without any temperature change across the shock front. It is planned to treat this problem in a separate note.

ACKNOWLEDGMENTS

FIG. 7. *p-v* representation of the cycle shown in Figs. 5 (b) and 6 (b). Dotted line represents $T - T_0 + ap = 0$.

[17] J. Kestin, Am. J. Phys. **29**, 329 (1961).

[18] C. Carathéodory, Math. Ann. **67**, 355 (1909); Sitzber, preuss. Akad. Wiss., Physik-math. Kl. 39 (1925).
[19] See reference 12, Chap. 4.