Thermodynamics at work: The pressure derivative of the specific heat

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Thermodynamics relates measurable quantities such as thermal coefficients and specific heats. The first law, which implies that the enthalpy is a function of state, yields a relation for the pressure derivative of the specific heat c_P. The second law gives a simpler and well-known relation for this pressure derivative. We compare the values of the pressure derivative of c_P obtained from the first and second laws to the values obtained from measurements for water at different pressures. The comparison illustrates the scope and methodology of thermodynamics. © *1999 American Association of Physics Teachers.*

I. INTRODUCTION

Thermodynamics is based on a small number of principles and provides a formalism which relates the various thermal coefficients and specific heats for any substance in equilibrium.[1] Examples of typical thermodynamic relations are the reciprocity theorem, arising from the zeroth law, Reech's relation, arising from the first law, and Mayer's relation, arising from the second law. These relations can be summarized as follows.

From the zeroth law, the reciprocity theorem for a PVT (pressure, volume, and temperature) system states that

$$\beta=\frac{\alpha}{\kappa_T P} \quad \text{(reciprocity theorem)}, \tag{1}$$

where $\beta\equiv(1/P)(\partial P/\partial T)_V$ is the relative pressure coefficient, $\alpha\equiv(1/v)(\partial v/\partial T)_P$ is the (cubic) thermal expansion coefficient, v is the specific volume, and $\kappa_T\equiv-(1/v)\times(\partial v/\partial P)_T$ is the isothermal compressibility. Equation (1) follows readily from the existence of a thermal equation of state, because

$$\left(\frac{\partial v}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial v}\right)_P=-1. \tag{2}$$

It is interesting to show the validity of Eq. (1) using only experimental data. A pedagogical example using a rubber strip (a tension, length, and temperature system) is discussed in Ref. 2. If Eq. (2) were not experimentally fulfilled, the system would not be in equilibrium.[3] Equation (1) can be used to obtain a coefficient such as β, which is difficult to measure, from α and κ_T, which are easier to measure. (It is difficult in practice to keep the volume constant when the temperature is being changed by heating.)

We can derive Reech's relation from the first law,[4] which can be expressed as $du=\delta q-P\,dv$, where u is the specific internal energy and q is the (specific) heat transfer. Reech's relation[5] states that

$$c_V=c_P\frac{\kappa_s}{\kappa_T} \quad \text{(Reech's relation)}, \tag{3}$$

where $c_V\equiv(\delta q/\partial T)_V=(\partial u/\partial T)_V$ and $c_P\equiv(\delta q/\partial T)_P=(\partial h/\partial T)_P$ are the specific heats at constant volume and pressure, respectively, the (specific) enthalpy $h=u+Pv$, and $\kappa_s\equiv-(1/v)(\partial v/\partial P)_s$ is the adiabatic compressibility.[6] Equation (3) implies that the ratio of the specific heats at constant pressure and at constant volume[7,8] equals the ratio of the isothermal and adiabatic compressibilities.[9] If these quantities are measured independently, we could verify the first law. Equation (3) can be used to determine the specific heat, c_V, which is difficult to measure because of the difficulty of keeping the volume constant.

Mayer's relation follows from the second and first laws and can be expressed as:[10]

$$c_V=c_P-\frac{T\alpha^2 v}{\kappa_T} \quad \text{(Mayer's relation)}. \tag{4}$$

Equation (4) is one of the most important relations of thermodynamics.[11] The independent measurement of the coefficients appearing in Eq. (4) allows us to verify the first and second laws of thermodynamics. We may also use Eq. (4), instead of Eq. (3) to obtain c_V.

Equations (1), (3), and (4) imply that among the thermal coefficients α, κ_T, κ_s, and β, and the specific heats c_P and c_V, only three can be considered independent. For example, if we choose κ_T, α, and c_P, then c_V could be obtained from Eq. (4) and β and κ_s can be obtained from Eqs. (1) and (3).

It is difficult to verify any of the relations, Eqs. (1), (3), or (4) directly, because at least one of the quantities in each relation is difficult to measure. However, we can test experimental data for thermodynamic consistency by considering equations for $(\partial c_P/\partial P)_T$. In this paper, we show how to obtain $(\partial c_P/\partial P)_T$ using only the first law. We will arrive at the relation

$$\left(\frac{\partial c_P}{\partial P}\right)_T=\alpha v-\left[(c_P-c_V)\frac{\kappa_T}{\alpha}\right]', \tag{5}$$

where the prime denotes differentiation with respect to temperature at constant pressure. If we substitute Eq. (4) in Eq. (5), we obtain another relation

$$\left(\frac{\partial c_P}{\partial P}\right)_T=-Tv(\alpha'+\alpha^2). \tag{6}$$

Equation (6) is well-known, but Eq. (5) is not. Note that the latter relation provides an experimental check of the first law. We emphasize that the first law can be verified independently of the second. Thus, we may imagine a hypothetical reversible world where the first law holds but not the second.

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Table I. Experimental data for water at $P_0 = 101.3$ kPa and temperatures ranging from the ice point to the boiling point (Ref. 15). The first six columns are direct experimental data and the last three columns are determined indirectly. The specific heat in column 8 was obtained from the relation $c_V = c_P \kappa_S / \kappa_T$ and the specific heat in column 9 was calculated by using $c_V = c_P - T\alpha^2 v / k_T$.

T °C	$v \times 10^3$ $m^3\,kg^{-1}$	$\alpha \times 10^6$ K^{-1}	$\kappa_T \times 10^{10}$ Pa^{-1}	$\kappa_S \times 10^{10}$ Pa^{-1}	c_P $J\,kg^{-1}\,K^{-1}$	β [Eq. (1)] K^{-1}	c_V [Eq. (3)] $J\,kg^{-1}\,K^{-1}$	c_V [Eq. (4)] $J\,kg^{-1}\,K^{-1}$
0	1.000 16	−67.89	5.0885	5.0855	4217.6	−1.3171	4215.1	4215.1
10	1.000 30	87.96	4.7810	4.7758	4192.1	1.8162	4187.5	4187.5
20	1.001 79	206.80	4.5891	4.5591	4181.8	4.4485	4154.5	4154.5
30	1.004 37	303.23	4.4770	4.4100	4178.4	6.6861	4115.9	4115.9
40	1.007 84	385.30	4.4240	4.3119	4178.5	8.5975	4072.6	4072.6
50	1.012 11	457.60	4.4174	4.2536	4180.6	10.226	4025.6	4025.6
60	1.017 09	523.07	4.4496	4.2281	4184.3	11.605	3976.0	3976.0
70	1.022 72	583.74	4.5161	4.2307	4189.5	12.760	3924.7	3924.7
80	1.029 00	641.11	4.6143	4.2584	4196.3	13.716	3872.6	3872.6
90	1.035 89	696.24	4.7430	4.3093	4205.0	14.491	3820.5	3820.5
100	1.043 41	750.30	4.9018	4.3819	4215.9	15.110	3768.7	3768.8

In Sec. II we derive these two results, and in Sec. III we compare them using experimental data for liquid water. Some conclusions and suggested problems are given in Sec. IV.

II. THERMODYNAMIC RELATIONS

The first law asserts that measurements of the variations of the internal energy in an isolated thermal system can be reduced to a pure mechanical problem.[12] This statement assumes the existence of adiabatic walls. Furthermore, these variations are independent of the process from the initial to the final state, and thus the internal energy is a function of state.

In practice, the most convenient independent variables are the intensive quantities T and P.[13] For this reason, the enthalpy should be used instead of internal energy. From the first law, we find the following expression relating the derivatives of the enthalpy:

$$\left(\frac{\partial h}{\partial T}\right)_v = c_V + v\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial h}{\partial T}\right)_P + \left(\frac{\partial h}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_v. \tag{7}$$

Using the definitions of c_P and β and Eq. (1), we obtain

$$c_P - c_V = \frac{\alpha}{\kappa_T}\left[v - \left(\frac{\partial h}{\partial P}\right)_T\right], \tag{8}$$

which may be written as:

$$\left(\frac{\partial h}{\partial P}\right)_T = v - (c_P - c_V)\frac{\kappa_T}{\alpha}. \tag{9}$$

Taking the derivative of this expression with respect to the temperature and applying Schwartz's theorem (the value of mixed derivatives is independent of the order in which the derivatives are taken) to the enthalpy leads directly to

$$\frac{\partial^2 h}{\partial T\,\partial P} = \alpha v - \left[(c_P - c_V)\frac{\kappa_T}{\alpha}\right]' = \frac{\partial^2 h}{\partial P\,\partial T} = \left(\frac{\partial c_P}{\partial P}\right)_T, \tag{10}$$

which is the same as Eq. (5). This result was given in a different form by Max Planck in his classical monograph.[14] In Appendix A, we derive Planck's result and show its equivalence to Eq. (5).

Although Eq. (6) can be obtained by substituting Eq. (4) into Eq. (5), another way of deriving Eq. (6) is the following. If we combine the second and the first laws, we have

$$ds = \frac{1}{T}dh - \frac{v}{T}dP = \frac{1}{T}\left[\left(\frac{\partial h}{\partial P}\right)_T - v\right]dP + \frac{c_P}{T}dT. \tag{11}$$

Applying Schwartz's theorem to the entropy, we obtain

$$\frac{1}{T}\left(\frac{\partial c_P}{\partial P}\right)_T = -\frac{1}{T^2}\left[\left(\frac{\partial h}{\partial P}\right)_T - v\right] + \frac{1}{T}\frac{\partial^2 h}{\partial T\,\partial P} - \frac{1}{T}\left(\frac{\partial v}{\partial T}\right)_P. \tag{12}$$

Using Eq. (10), we obtain

$$\left(\frac{\partial h}{\partial P}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_P = v(1 - T\alpha). \tag{13}$$

This important result may be called the compatibility condition because it equates two different kinds of quantities: a derivative of the enthalpy on the left-hand side and a function obtained directly from the equation of state on the right-hand side. Equation (6) is obtained by taking the temperature derivative of Eq. (13) at constant pressure.

III. ANALYSIS OF EXPERIMENTAL DATA

In the following we obtain the derivative $(\partial c_P/\partial P)_T$ for water using data for the thermal coefficients and specific heats and various thermodynamic relations. We have chosen water because accurate data are available for a wide range of temperatures and pressures. The data in Table I are for liquid water at 101.3 kPa (normal atmospheric pressure).[15] The data in Table II is for liquid water in the pressure range 50×10^5 Pa to 200×10^5 Pa.[16]

The specific volume, v, and the thermal expansion coefficient, α, given in Table I can be measured directly. To obtain κ_T, specific volumes at different pressures are needed (see Table II). The coefficient κ_s is measured from the speed of sound. The enthalpy, h, and the specific heat, c_P, are measured using an electric calorimeter.

On the other hand, β and c_V are difficult to measure directly, because the volume of water changes upon heating. It is convenient, therefore, to use, respectively, the reciprocity theorem, Eq. (1) and Eq. (3) to obtain them. Table I shows the resulting values for β and c_V. In the last column of Table I we show the values of c_V as calculated from Eq. (4). The values of c_V turn out to be the same (within 5 digits) using either relation.

Table II. Experimental specific volumes, $v \times 10^3$ (in $m^3\,kg^{-1}$), and enthalpies, $h \times 10^{-3}$ (in $J\,kg^{-1}$), for water at different pressures and temperatures (in °C) (Ref. 16).

	$P=5$ MPa		$P=10$ MPa		$P=15$ MPa		$P=20$ MPa	
T	v	h	v	h	v	h	v	h
0	0.9977	5.03	0.9952	10.04	0.9928	15.04	0.9904	20.00
20	0.9995	88.65	0.9972	93.33	0.9950	97.99	0.9928	102.58
40	1.0056	171.98	1.0034	176.38	1.0013	180.78	0.9992	185.15
60	1.0149	255.30	1.0127	259.49	1.0105	263.67	1.0084	267.85
80	1.0268	338.85	1.0245	342.84	1.0222	346.81	1.0199	350.80
100	1.0410	422.81	1.0385	426.51	1.0361	430.28	1.0337	434.06

To obtain $(\partial c_P/\partial P)_T$ from experimental results at different pressures, we first consider the enthalpies given in Table II. We used a five point algorithm for numerical derivatives (see Appendix B) to compute $c_P=(\partial h/\partial T)_P$ for each T and P of Table II. For the range of pressures considered, c_P is a linear function of P for each T. To reduce the numerical error in $(\partial c_P/\partial P)_T$, we made linear fits to $c_P(P)$ (see Appendix B) for each T. The values of c_P at atmospheric pressure in Table I are included in these fits. The result is shown in Table III. The values of $(\partial c_P/\partial P)_T$ are negative, independent of the pressure. They are displayed in the second column of Table IV, which includes interpolated values for intermediate temperatures.

To compute $(\partial c_P/\partial P)_T$ at atmospheric pressure using Eq. (5), the derivative on the right-hand side with respect to T at constant P may be evaluated from the data of Table I using the same five points algorithm. The numerical derivative on the right-hand side of Eq. (5), with c_V given by Eq. (3), was taken after the expression in brackets was evaluated. The result appears in the third column of Table IV.

Because the experimental data in Table I satisfy Mayer's relation for c_V, we can also evaluate $(\partial c_P/\partial P)_T$ using Eq. (6). In this case we have to obtain α' numerically from α given in Table I. The result for $(\partial c_P/\partial P)_T$, using the five point algorithm, is the fourth column of Table IV. We take the latter result as the standard one because less numerical work is required (besides the empirical errors, only the numerical error of α' is present.) The maximum relative deviation of the results for Eq. (5) relative to Eq. (6) is 0.6%. However, the maximal deviation between the second and the fourth columns of Table IV is 16% and occurs at $T=0$ °C. These deviations are due to the inaccuracy in the derivatives of h with respect to the temperature (the error is bigger at the end points), in the linear fits to c_P, and in the linear interpolations of $(\partial c_P/\partial P)_T$ for intermediate temperatures. A further reason for relying more on the last column of Table IV than on the other columns is the fact that the enthalpy and its variations are more difficult to measure than the volume and the expansion coefficient.

Table III. Fits to $c_P(P)$ obtained from $c_P=(\partial h/\partial T)_P$ using the data given in Table II and the values of c_P at atmospheric pressure from Table I.

T °C	c_P $J\,kg^{-1}\,K^{-1}$
0	$4217.2-4.1714\times10^{-6}\,P$
20	$4183.4-2.7913\times10^{-6}\,P$
40	$4177.1-2.3982\times10^{-6}\,P$
60	$4182.7-2.1642\times10^{-6}\,P$
80	$4196.6-2.0930\times10^{-6}\,P$
100	$4218.0-2.3722\times10^{-6}\,P$

IV. CONCLUSIONS AND PROBLEMS

We have used experimental data for liquid water to obtain $(\partial c_P/\partial P)_T$ using the first and second laws and compared the indirect results to direct measurements done at different pressures. We argued that Eq. (6) arising from the second law requires less information and gives more accurate numerical results. The two thermodynamic predictions for $(\partial c_P/\partial P)_T$ agree very well with each other and reasonably well with the values extracted from experiments at different pressures.

We expect thermodynamic relations to be universal. Because water shows anomalous behavior,[17] testing thermodynamic relations using data on water provides a good test of thermodynamics. Similar data sets for other substances may also be used to check their thermodynamic consistency.

The questions studied here may help students better understand the formalism of thermodynamics. Students often become lost in the mathematical formalism and might not fully appreciate the physical content of the various thermodynamic relations. In contrast to engineering students, physics majors do not make much use of thermodynamic tables so that the connection of thermodynamics to experiment is limited. We think that it is educational to use empirical data and simple numerical methods to analyze it. To this end, we propose three problems for students.

Table IV. Comparison of values of $(\partial c_P/\partial P)_T\times10^6$ (in $J\,kg^{-1}\,K^{-1}\,Pa^{-1}$) for water at 101.3 kPa. The second column was obtained from the slopes of the equations in Table III. The third column is obtained using Eq. (5) (first law) taking numerical derivatives of data in Table I. The last column is obtained from Eq. (6) (second law) using the same table. In the second column, linear interpolation was used for the temperatures not given in Table III. The most accurate results are in the last column.

T °C	From Table III	From Eq. (5)	From Eq. (6)
0	−4.171	−4.935	−4.942
10	−3.481	−3.809	−3.808
20	−2.791	−3.127	−3.118
30	−2.595	−2.715	−2.713
40	−2.398	−2.462	−2.463
50	−2.281	−2.307	−2.308
60	−2.164	−2.219	−2.220
70	−2.129	−2.185	−2.184
80	−2.093	−2.190	−2.187
90	−2.233	−2.233	−2.228
100	−2.372	−2.306	−2.319

Table V. Experimental data of v and α for water at 101.3 kPa for temperatures close to 0 °C (to be used in Problem 1) (Ref. 18).

T °C	$v\times 10^3$ $m^3\,kg^{-1}$
0	1.000 160
1	1.000 100
2	1.000 060
3	1.000 036
4	1.000 028
5	1.000 036

(1) Water has a density maximum at 4 °C (Table V). Use the five points algorithm given in Appendix B to evaluate α and α' for the temperatures indicated in the table. Evaluate the right-hand side of Eq. (6) at 0 °C and compare the result with the corresponding ones in Table IV.
(2) From the data of Table II obtain $(\partial h/\partial P)_T$ by fitting values at the same temperature and different pressures. Then evaluate the same quantity at atmospheric pressure from Eq. (9) (first law) and from Eq. (13) (second law) using the data of Table I.
(3) Insert the compatibility condition, Eq. (13), in Eq. (11). Use a numerical integration algorithm,[19] to integrate Eq. (11) and construct a table for the entropy $s(T,P)$ from the data in Table II. Take $s(T=273.15\,\mathrm{K}, P=5.00\,\mathrm{MPa})=0.0001\,\mathrm{kJ\,kg^{-1}\,K^{-1}}$.[16]

APPENDIX A: PLANCK'S RESULT

Based on the first law only, Planck established the following relation between thermal coefficients and specific heat:[14]

$$(c_P-c_V)\frac{\partial^2 T}{\partial P\,\partial v}+\left(\frac{\partial c_P}{\partial P}\right)_v\left(\frac{\partial T}{\partial v}\right)_P-\left(\frac{\partial c_V}{\partial v}\right)_P\left(\frac{\partial T}{\partial P}\right)_v=1 \quad \text{(Planck's result)}. \tag{14}$$

Here we derive this result and show that it is equivalent to Eq. (5).

Taking the specific internal energy u as a function of the specific volume v and pressure P, we may write

$$\left(\frac{\partial u}{\partial P}\right)_v=c_V\left(\frac{\partial T}{\partial P}\right)_v. \tag{15}$$

From $du=\delta q-P\,dv$, we obtain

$$\left(\frac{\partial u}{\partial v}\right)_P=c_P\left(\frac{\partial T}{\partial v}\right)_P-P. \tag{16}$$

Taking derivatives of Eqs. (15) and (16) and applying Schwartz's theorem, we obtain

$$\left\{\frac{\partial}{\partial v}\left[c_V\left(\frac{\partial T}{\partial P}\right)_v\right]\right\}_P=\left\{\frac{\partial}{\partial P}\left[c_P\left(\frac{\partial T}{\partial v}\right)_P-P\right]\right\}_v, \tag{17}$$

or

$$\left(\frac{\partial c_V}{\partial v}\right)_P\left(\frac{\partial T}{\partial P}\right)_v+c_V\frac{\partial^2 T}{\partial v\,\partial P}=\left(\frac{\partial c_P}{\partial P}\right)_v\left(\frac{\partial T}{\partial v}\right)_P+c_P\frac{\partial^2 T}{\partial P\,\partial v}-1. \tag{18}$$

By applying Schwartz's theorem to $T=T(P,v)$, we obtain Planck's result (14).

Now we use T and P as independent variables to verify that Eq. (18) is equivalent to Eq. (5). From the definitions of α and κ_T and Eq. (1), we have

$$\left(\frac{\partial c_V}{\partial v}\right)_P\left(\frac{\partial T}{\partial P}\right)_v=\left(\frac{\partial c_V}{\partial T}\right)_P\left(\frac{\partial T}{\partial v}\right)_P\left(\frac{\partial T}{\partial P}\right)_v=\frac{c_v'\kappa_T}{\alpha^2 v}. \tag{19}$$

Moreover,

$$\frac{\partial^2 T}{\partial v\,\partial P}=\left[\frac{\partial}{\partial v}\left(\frac{\kappa_T}{\alpha}\right)\right]_P=\left[\frac{\partial}{\partial T}\left(\frac{\kappa_T}{\alpha}\right)\right]_P\left(\frac{\partial T}{\partial v}\right)_P=\frac{1}{\alpha v}\left(\frac{\kappa_T}{\alpha}\right)', \tag{20}$$

and the left-hand side of Eq. (18) becomes

$$c_V'\frac{\kappa_T}{\alpha^2 v}+\frac{c_V}{\alpha v}\left(\frac{\kappa_T}{\alpha}\right)'=\frac{1}{\alpha v}\left(\frac{c_V\kappa_T}{\alpha}\right)'. \tag{21}$$

On the other hand, we have

$$\left(\frac{\partial c_P}{\partial P}\right)_v\left(\frac{\partial T}{\partial v}\right)_P=\left[\left(\frac{\partial c_P}{\partial P}\right)_T+c_P'\frac{\kappa_T}{\alpha}\right]\frac{1}{\alpha v}, \tag{22}$$

and the right-hand side of Eq. (18) is

$$\frac{1}{\alpha v}\left[\left(\frac{\partial c_P}{\partial P}\right)_T+c_P'\frac{\kappa_T}{\alpha}\right]+\frac{c_P}{\alpha v}\left(\frac{\kappa_T}{\alpha}\right)'-1=\frac{1}{\alpha v}\left(\frac{c_P\kappa_T}{\alpha}\right)'+\frac{1}{\alpha v}\left(\frac{\partial c_P}{\partial P}\right)_T-1. \tag{23}$$

If we equate Eqs. (21) and (23) and reorder terms, we obtain Eq. (5).

APPENDIX B: NUMERICAL METHODS

Given N data points for the quantity $y(x)$, the derivative dy/dx can be obtained numerically by using the five point algorithm:[20]

$$\left(\frac{dy}{dx}\right)_1=\frac{1}{24\Delta x}(-50y_1+96y_2-72y_3+32y_4-6y_5),$$

$$\left(\frac{dy}{dx}\right)_2=\frac{1}{24\Delta x}(-6y_1-20y_2+36y_3-12y_4+2y_5),$$

$$\left(\frac{dy}{dx}\right)_i=\frac{1}{24\Delta x}(2y_{i-2}-16y_{i-1}+16y_{i+1}-2y_{i+2}),$$

$$\left(\frac{dy}{dx}\right)_{N-1}=\frac{1}{24\Delta x}(-2y_{N-4}+12y_{N-3}-36y_{N-2}+20y_{N-1}+6y_N),$$

$$\left(\frac{dy}{dx}\right)_N=\frac{1}{24\Delta x}(6y_{N-4}-32y_{N-3}+72y_{N-2}-96y_{N-1}+50y_N).$$

The algorithm also applies to partial derivatives. This algorithm was implemented using Excel.

We used the analytical equation of state of Thomsen and Hartka[21] to estimate the error for α' at $T=0$ °C and $P=101.3$ kPa. For a temperature step of 10 °C, the result

$\alpha'(T=0\,°\mathrm{C})=16.0001\times10^{-6}\,\mathrm{K}^{-2}$ obtained with the five point algorithm is accurate to within $2\times10^{-10}\,\mathrm{K}^{-2}$.

Excel was also used to fit data for $c_P(P)$ to a straight line (linear regression). The use of spreadsheets is appropriate for the type of analysis presented in this paper and requires only modest knowledge of computer programming.

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[11]G. Weinreich, *Fundamental Thermodynamics* (Addison-Wesley, Reading, MA, 1968), notes that ''The fact that such a relation is mathematically an almost trivial identity should not blind us to the fact that there is nothing trivial physically about it or about other thermodynamic identities such as the Maxwell relations. The experiments which are used to obtain heat capacities are completely different from those that give the expansion coefficients. That the resulting numerical values consistently satisfy that relation must, accordingly, be viewed as the working of a deep physical law.''

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[13]Furthermore, for water at normal pressure and in the temperature range 0–8 °C, v and P cannot be independent variables because there are two values of T corresponding to the same v.

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[16]J. H. Keenan *et al.*, *Steam Tables. Thermodynamic Properties of Water Including Vapor, Liquid, and Solid Phases* (Wiley, New York, 1969), pp. 104–105. These data are transcribed in text books, such as A. Shavit and C. Gutfinger, *Thermodynamics. From Concepts to Applications* (Prentice–Hall, Europe, 1995), pp. 452–453. However, one must be aware of transcription errors. We found two in the latter book: one for $v(T=100\,°\mathrm{C}, P=5.00\,\mathrm{MPa})$ and the other for $v(T=20\,°\mathrm{C}, P=200\,\mathrm{MPa})$.

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[19]F. S. Acton, *Numerical Methods that Work* (The Mathematical Association of America, Washington, DC, 1990), Chap. 10.

[20]*Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1972), p. 914.

[21]J. S. Thomsen and T. J. Hartka, ''Strange Carnot cycles; Thermodynamics of a system with a density extremum,'' Am. J. Phys. **30**, 26–33 (1962).

IS QUANTUM THEORY ROTTEN?

I also told Wheeler that from the time that Bell began to study the quantum theory, he had conceptual problems with it, and that I had asked Bell if, at that time, he thought that the theory might simply be wrong—to which Bell had answered, ''I hesitated to think it might be wrong, but I *knew* that it was rotten.''

Jeremy Bernstein, ''John Wheeler: Retarded Learner,'' in *Quantum Profiles* (Princeton University Press, Princeton, 1991), p. 137.