Lecture T3 **DRAFT**

Equations of State, Maxwell Relations, and Response Functions

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Unit T2 built the thermodynamic potentials and read off their *first* derivatives: temperature, pressure, entropy, volume, chemical potential. The quantities an instrument reports are not these. A calorimeter returns a heat capacity, a dilatometer an expansion coefficient, an acoustic cell a compressibility, and each is a *second* derivative of a potential. This lecture develops the relations among those second derivatives, uses them to reconstruct entropy and energy from laboratory data, and ends with an acoustic measurement predicted from data containing no acoustics. Notation follows T2: E is the internal energy, N a particle number rather than a number of moles, and k_B appears explicitly.

Contents

1 What a Calorimeter Cannot Measure

Suppose we want the heat capacity of copper at room temperature. A solid-state calculation predicts C_V, the heat capacity at fixed volume, because the theory works with a fixed set of normal modes in a fixed box. A calorimeter measures C_P, for a sample at atmospheric pressure and free to expand.

The experiment cannot simply be redone at fixed volume. Holding copper's volume fixed while heating it means squeezing hard enough to cancel its thermal expansion, and Section 4 will show that this takes about 67 bar per kelvin — some 7000 bar over a 100 K rise. Yet reference tables list C_V for copper. White and Collocott [1] give, at 300 K,

$$C_P = 24.45 \text{ J mol}^{-1}\text{ K}^{-1}, \qquad C_V = 23.74 \text{ J mol}^{-1}\text{ K}^{-1}.$$

Only the first is measured. The second is computed from it using a thermodynamic identity together with the measured expansion and bulk modulus.

The same difficulty appears in a more basic form: compress a fluid, and ask how much its entropy changed. There is no entropy meter. We can measure T, P, V, and the heat delivered along a controlled path, and from those the answer must follow — or thermodynamics would have nothing to say about any real experiment.

Both problems have one structure and one solution. Laboratory instruments report derivatives of the first derivatives of a potential, and second derivatives of a smooth function are not independent: the mixed partials commute. Applied to each potential in turn, that single fact relates derivatives of the entropy, which we cannot measure, to derivatives of pressure and volume, which we can.

Two Standing Conventions

Fixed composition. Every derivative here is taken at fixed particle number for a single component. The subscript N is written in defining equations and boxed results and suppressed in intermediate algebra. Where composition matters — the frozen internal degrees of freedom of Section 8.3 — we say so.

Extensive basis. General identities are written for *total* quantities. Since α, κ_T and κ_S are intensive, each identity holds verbatim for molar or specific quantities provided the heat capacity and the volume are put on the *same* basis. Each worked example states its basis.

Symbol	Meaning	Units	Definition or note
E	internal energy	J	written U in many texts
S	entropy	$\mathrm{J\,K^{-1}}$	physical entropy, not S/k_B
N	particle number	—	particles, not moles; $R = N_A k_B$
C_V	heat capacity at fixed volume	$\mathrm{J\,K^{-1}}$	$T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \left(\frac{\partial E}{\partial T}\right)_{V,N}$
C_P	heat capacity at fixed pressure	$\mathrm{J\,K^{-1}}$	$T\left(\frac{\partial S}{\partial T}\right)_{P,N} = \left(\frac{\partial H}{\partial T}\right)_{P,N}$
α	thermal expansion coefficient	$\mathrm{K^{-1}}$	$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N}$; may be negative
$\kappa_T,\ \kappa_S$	isothermal, adiabatic compressibility	$\mathrm{Pa^{-1}}$	$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N},\ -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,N}$
γ	heat-capacity ratio	—	C_P/C_V

Table 1: Notation for unit T3. The heat capacities are defined as entropy derivatives rather than as heat per degree, so that they are properties of the state and not of a process. "Adiabatic" and "isentropic" are used interchangeably, which is legitimate only for the reversible changes considered throughout.

2 Integrability and the Maxwell Relations

Smoothness and Single Phase

We assume that on the region of state space under consideration the fundamental relation is twice continuously differentiable in its natural variables, and that the region is a single homogeneous phase at fixed N. Then mixed second partial derivatives commute, for E and for each of H, F, G. Across a first-order phase boundary the volume is discontinuous and κ_T diverges on a spinodal; neither commutation nor differentiability can be assumed there, and unit T6 treats coexistence with the appropriate machinery.

The recipe is mechanical. For a potential with $d\Phi = X\,dx + Y\,dy$ at fixed N, equality of mixed partials gives $(\partial X/\partial y)_x = (\partial Y/\partial x)_y$. Applied to the four potentials of T2:

Potential	Differential	Maxwell relation
E	$dE = T\,dS - P\,dV$	$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$
$H = E + PV$	$dH = T\,dS + V\,dP$	$\left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,N}$
$F = E - TS$	$dF = -S\,dT - P\,dV$	$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$
$G = E - TS + PV$	$dG = -S\,dT + V\,dP$	$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}$

All four are correct, but they are not equally useful. The first two hold the entropy fixed while varying something else, which requires knowing what value of S we are holding. The last two have entropy as the dependent quantity, and those are the two we will use.

The Two Working Maxwell Relations

For a single-phase one-component system at fixed N in a region where the fundamental relation is twice continuously differentiable,

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}, \tag{1}$$

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N} = -V\alpha. \tag{2}$$

Each expresses a derivative of the entropy, which no instrument reads, through quantities obtainable from an equation of state $P(T, V, N)$.

Read (1) physically. The right side is the thermal pressure coefficient: heat a fluid in a rigid container and watch the pressure climb. The left side asks how fast the entropy grows under isothermal expansion. The identity says these are one number, because both are the mixed second derivative of F approached from different directions.

Equation (2) is the one we use most, since $V\alpha$ comes straight from a dilatometer. Its sign tracks α: for most substances isothermal compression lowers the entropy, but liquid water below 4 °C has $\alpha < 0$, and there compressing it isothermally raises the entropy. The identity covers both cases without caring which we are in.

A first use. For an ideal gas, $(\partial P/\partial T)_V = Nk_B/V$, so (1) gives $(\partial S/\partial V)_T = Nk_B/V$, reproducing the volume dependence T2 obtained by counting states, by a route that never mentions microstates. For a van der Waals fluid,

$$P = \frac{Nk_BT}{V - Nb} - \frac{aN^2}{V^2}, \tag{3}$$

we get $(\partial S/\partial V)_T = Nk_B/(V - Nb)$. The attractive parameter drops out, because it enters P without a factor of T. Section 6.2 shows that this one observation determines the entire energy of a van der Waals fluid.

3 Jacobians as a Change-of-Variable Tool

The identities we want require converting between derivatives taken with different variables held fixed. Doing that with the chain rule alone produces long calculations in which a sign is easy to lose. Jacobian notation is bookkeeping, not new physics, but it keeps the manipulations short enough to check. We introduce only what the derivations need; the general statement and its proof are in Appendix A, which can be skipped.

For functions u, w of variables x, y,

$$\frac{\partial(u, w)}{\partial(x, y)} \equiv \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial w}{\partial y}\right)_x - \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial w}{\partial x}\right)_y, \tag{4}$$

the determinant of the matrix of partial derivatives. Three properties follow at once, and one identification connects the notation to ordinary derivatives.

1. **Antisymmetry.** $\frac{\partial(u,w)}{\partial(x,y)} = -\frac{\partial(w,u)}{\partial(x,y)} = -\frac{\partial(u,w)}{\partial(y,x)}$.

2. **Chain rule.** $\dfrac{\partial(u,w)}{\partial(x,y)} = \dfrac{\partial(u,w)}{\partial(r,s)}\,\dfrac{\partial(r,s)}{\partial(x,y)}$ for any intermediate pair.
3. **Reciprocal.** $\dfrac{\partial(u,w)}{\partial(x,y)} = \left[\dfrac{\partial(x,y)}{\partial(u,w)}\right]^{-1}$.
4. **The identification.** Setting $w = y$ in (4), $\dfrac{\partial(u,y)}{\partial(x,y)} = \left(\dfrac{\partial u}{\partial x}\right)_y$.

Property 4 is what makes the notation useful: the held-fixed variable is no longer a decoration on the symbol but an entry the algebra can move.

Two consequences recur. Putting $u = x$, $w = y$ in the chain rule gives the reciprocal rule $(\partial x/\partial y)_z = [(\partial y/\partial x)_z]^{-1}$, valid provided the same variable is held fixed on both sides. The second is less intuitive:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial(P,V)}{\partial(T,V)} = \frac{\partial(P,V)}{\partial(P,T)}\,\frac{\partial(P,T)}{\partial(T,V)} = \left(\frac{\partial V}{\partial T}\right)_P \cdot \left(-\left(\frac{\partial P}{\partial V}\right)_T\right),$$

the minus sign coming from the single exchange in $\frac{\partial(P,T)}{\partial(T,V)} = -(\partial P/\partial V)_T$. Rearranged, this is the cyclic rule

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1, \tag{5}$$

whose minus sign is not a slip: P, V and T are tied by an equation of state, and travelling around the constraint surface must return us to the starting point. In response functions,

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = \frac{\alpha}{\kappa_T}. \tag{6}$$

This already earns its keep. It says the pressure rise of a fluid heated in a rigid container is the ratio of its expansivity to its compressibility, which is the origin of the copper estimate quoted in Section 1, and it converts the awkward right side of (1) into two separately tabulated quantities.

A worked conversion. Take a derivative we return to in Section 9: the temperature change of a fluid compressed adiabatically and reversibly. Entropy is held fixed, so this is not something to attack directly. In Jacobians,

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\partial(T,S)}{\partial(P,S)} = \frac{\partial(T,S)}{\partial(T,P)}\,\frac{\partial(T,P)}{\partial(P,S)} = -\left(\frac{\partial S}{\partial P}\right)_T \left[\left(\frac{\partial S}{\partial T}\right)_P\right]^{-1},$$

and using (2) and $C_P = T(\partial S/\partial T)_P$,

$$\left(\frac{\partial T}{\partial P}\right)_{S,N} = \frac{TV\alpha}{C_P}. \tag{7}$$

Every symbol on the right is measurable. Adiabatic compression warms a substance with $\alpha > 0$ and cools one with $\alpha < 0$: compress cold water just above freezing and its temperature drops.

4 Response Functions and the Two Central Identities

Definitions and Sign Conventions

$$C_V \equiv T\left(\frac{\partial S}{\partial T}\right)_{V,N}, \qquad C_P \equiv T\left(\frac{\partial S}{\partial T}\right)_{P,N}, \qquad \alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N},$$

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}, \qquad \kappa_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,N}.$$

The minus signs make the compressibilities positive for ordinary matter, which contracts under pressure; the expansivity carries no such sign, and $\alpha < 0$ occurs. The factors $1/V$ make α, κ_T, κ_S intensive.

That the compressibilities *are* positive is a stability statement, not a definition, and nothing in this lecture establishes it. It follows from requiring equilibrium to be a maximum of the entropy rather than a stationary point, which is unit T5. We use $\kappa_T > 0$ and $C_V > 0$ where needed and flag each use.

4.1. The Difference of the Heat Capacities

The two heat capacities differ because a sample heated at constant pressure also expands, and the expansion both does work on the surroundings and changes the internal energy. Write the entropy in the variables the experiments control. Taking $S = S(T, V)$ at fixed N and using (1),

$$T\,dS = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_{V,N} dV. \tag{8}$$

This is an identity among state functions, not a statement about heat flow; it becomes a heat only along a reversible path. Dividing by dT at constant P,

$$C_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_{V,N}\left(\frac{\partial V}{\partial T}\right)_{P,N}.$$

The conceptual work is done. The second derivative is $V\alpha$ by definition and the first is α/κ_T by (6), so:

Difference of the Heat Capacities

For a single-phase one-component system at fixed composition,

$$C_P - C_V = \frac{TV\alpha^2}{\kappa_T}. \tag{9}$$

Both heat capacities and the volume must be on the same basis. Since α enters squared and $\kappa_T > 0$ by stability, $C_P \geq C_V$ always, with equality only where $\alpha = 0$.

Three checks. *Dimensions:* $\mathrm{K}\cdot\mathrm{m}^3\cdot\mathrm{K}^{-2}\cdot\mathrm{Pa} = \mathrm{J\,K}^{-1}$. *Ideal-gas limit:* with $\alpha = 1/T$ and $\kappa_T = 1/P$ the right side is $PV/T = Nk_B$, which is Mayer's relation, recovered rather than assumed. *Copper:* with the molar volume $7.09\ \mathrm{cm}^3\,\mathrm{mol}^{-1}$ quoted by White and Collocott, $\alpha = 4.95\times10^{-5}\ \mathrm{K}^{-1}$

and an isothermal bulk modulus of 136 GPa,

$$C_{P,m} - C_{V,m} = \frac{(300)(7.09\times10^{-6})(4.95\times10^{-5})^2}{7.4\times10^{-12}} = 0.71\ \mathrm{J\,mol^{-1}\,K^{-1}},$$

the difference between the two tabulated columns of Section 1. The inputs are known to a percent or two, so agreement in the second decimal is better than the data deserve; the useful conclusion is the size of the effect. The correction is 3% of C_P, ten times the stated accuracy of C_P itself. It is small, and it cannot be ignored. Equation (6) also supplies the estimate promised earlier: $\alpha/\kappa_T = 6.7\times10^{6}\ \mathrm{Pa\,K^{-1}}$, about 67 bar per kelvin.

4.2. The Ratio of the Heat Capacities

Jacobians earn their place here, since the direct route is not four lines. Cancelling the common $-1/V$ and inserting an intermediate pair,

$$\frac{\kappa_T}{\kappa_S} = \frac{(\partial V/\partial P)_T}{(\partial V/\partial P)_S} = \frac{\partial(V,T)}{\partial(P,T)}\,\frac{\partial(P,S)}{\partial(V,S)} = \left[\frac{\partial(V,T)}{\partial(V,S)}\,\frac{\partial(V,S)}{\partial(P,S)}\,\frac{\partial(P,S)}{\partial(P,T)}\right]\frac{\partial(P,S)}{\partial(V,S)}.$$

The second and fourth factors are reciprocals and cancel, leaving $\frac{\partial(V,T)}{\partial(V,S)}\frac{\partial(P,S)}{\partial(P,T)} = (\partial T/\partial S)_V(\partial S/\partial T)_P$.

Ratio of the Heat Capacities

Under the same conditions as (9),

$$\gamma \equiv \frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S}, \qquad \text{and hence} \qquad \kappa_T - \kappa_S = \frac{TV\alpha^2}{C_P}, \tag{10}$$

so the adiabatic compressibility is never larger than the isothermal one. The second form is the useful one, since C_P rather than C_V is what a calorimeter reports.

Why is a substance stiffer when compressed adiabatically? Figure 1 shows the two curves through one state. Compress isothermally and the heat of compression is carried away, so the pressure rises only as far as the isotherm requires. Compress adiabatically and that heat stays put; the temperature rises, and for $\alpha > 0$ the resulting thermal expansion opposes the compression we are imposing. More pressure is needed for the same volume change. The argument survives the sign change: for water below 4 °C adiabatic compression cools the sample, negative expansivity turns cooling into expansion, and the effect again opposes the compression — which is why α appears squared in (10). The two compressibilities coincide only at the temperature of maximum density, where α vanishes.

4.3. How Many Are Independent?

Unit T2 ended by asking how many response functions of a simple fluid are genuinely independent. Of the five quantities C_P, C_V, α, κ_T, κ_S, the identities (9) and (10) leave three — and the count is tighter still, because an equation of state delivers α and κ_T together by differentiation.

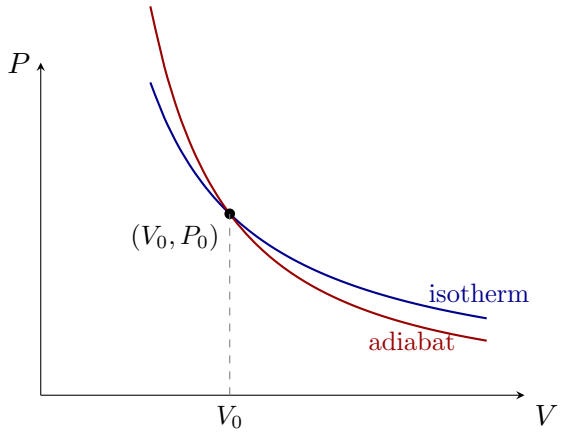

Figure 1: An isotherm and a reversible adiabat through the same state of a fluid with $\alpha > 0$, drawn for an ideal gas with $\gamma = 1.4$ so that the effect is visible. The slopes at (V_0, P_0) are $-1/(V_0\kappa_T)$ and $-1/(V_0\kappa_S)$, in the ratio γ. Suppressing heat flow makes the fluid harder to compress.

Key Point

For a single-phase one-component fluid at fixed N, the equation of state $P(T, V, N)$ together with $C_V(T, V_0)$ along a single isochore determines every response function at every state. Sections 6 and 7 show that it also determines all entropy and energy differences, and identify the constraints an equation of state must satisfy for that determination to be consistent.

Table 2 gives room-temperature values for three substances spanning the range of behaviour. Note that κ_T for water is smaller than for air by five orders of magnitude and for copper by two more — this is what "condensed matter" means quantitatively — and that γ is near 1 for the condensed phases and appreciably larger for the gas. Section 8 shows that this last difference decides whether the distinction between isothermal and adiabatic compression matters at all.

	α (K^{-1})	κ_T (Pa^{-1})	$\gamma = C_P/C_V$	basis
Air (ideal-gas model, 293 K, 1 bar)	3.4×10^{-3}	1.0×10^{-5}	1.40	—
Liquid water (298.15 K, 0.1 MPa)	2.57×10^{-4}	4.52×10^{-10}	1.011	specific
Copper (300 K)	4.95×10^{-5}	7.4×10^{-12}	1.030	molar

Table 2: Response functions at room temperature. The water entries are computed in Section 8.4 from the reference correlation of Pátek et al. [2]; the copper values are from White and Collocott [1], with α three times the linear expansivity and κ_T the reciprocal of the isothermal bulk modulus. The air row uses $\alpha = 1/T$ and $\kappa_T = 1/P$ exactly, which is the model rather than a measurement.

5 Other Kinds of Work

Nothing so far depended on the work being mechanical. If a system exchanges energy reversibly another way — a magnetic moment in a field, a wire under tension — the same construction runs with the new conjugate pair in place of $(-P, V)$. The sign errors live in the work convention, so we do two cases explicitly.

The General Pattern

Let the reversible work done *on* the system be $đW = X\,dx$, with X the generalised force and x the displacement. Then $dE = T\,dS + X\,dx$, and every relation above carries over under $-P \to X$, $V \to x$. With $\Phi \equiv E - TS - Xx$ giving $d\Phi = -S\,dT - x\,dX$,

$$\left(\frac{\partial S}{\partial X}\right)_T = \left(\frac{\partial x}{\partial T}\right)_X, \qquad \left(\frac{\partial T}{\partial X}\right)_S = -\frac{T}{C_X}\left(\frac{\partial x}{\partial T}\right)_X,$$

$$C_X - C_x = \frac{T}{(\partial x/\partial X)_T}\left[\left(\frac{\partial x}{\partial T}\right)_X\right]^2.$$

The pressure case carries an extra minus sign relative to these, because P is defined as the force conjugate to V *with* a minus sign. This is the commonest source of error in transcribing results between one kind of work and another.

Magnetic response. Magnetic work admits several conventions, and results from different sources cannot be combined without checking which is in use. Let $B_0 = \mu_0 H_0$ be the uniform applied field in tesla and m the component of the sample's magnetic moment along it, in $\mathrm{A\,m^2}$. We take $đW = B_0\,dm$, which *excludes* the vacuum field energy and the work done by the sources, so that $dE = T\,dS + B_0\,dm$ at fixed volume. The isothermal susceptibility is $\chi_T \equiv \mu_0(\partial M/\partial B_0)_T = (\partial M/\partial H_0)_T$ with $M = m/V$, dimensionless in SI. The pattern then gives

$$\left(\frac{\partial S}{\partial B_0}\right)_T = \left(\frac{\partial m}{\partial T}\right)_{B_0}, \qquad \left(\frac{\partial T}{\partial B_0}\right)_S = -\frac{T}{C_{B_0}}\left(\frac{\partial m}{\partial T}\right)_{B_0}. \tag{11}$$

The second is the magnetocaloric effect. For a paramagnet obeying Curie's law $m = \mathcal{C}B_0/T$, the moment falls as temperature rises, so $(\partial T/\partial B_0)_S > 0$: magnetising adiabatically warms the sample and demagnetising cools it. Unit T9 builds a cooling cycle on this.

One caution, since the analogy with κ_T invites an unwarranted conclusion. *Nothing here fixes the sign of χ_T.* Paramagnets have $\chi_T > 0$; diamagnets have $\chi_T < 0$, and that violates none of these relations. Whether stability forbids $\chi_T < 0$ depends on which energy is assigned to the system — our convention leaves out the vacuum field energy and the source work — and on whether the sample's demagnetising field has been accounted for. That question belongs with the other stability criteria in T5. What is safe here is narrower: whatever the sign of χ_T, relations (11) hold.

Elastic response. A wire of length L under tension f takes $đW = f\,dL$, so f plays the role of X with no hidden minus sign. With the linear expansivity at constant tension $\alpha_L = L^{-1}(\partial L/\partial T)_f$ and the isothermal Young's modulus $Y_T = (L/A)(\partial f/\partial L)_T$, the pattern gives $(\partial S/\partial f)_T = (\partial L/\partial T)_f$ and

$$C_f - C_L = TV\alpha_L^2\,Y_T, \qquad V = AL. \tag{12}$$

Compare (9): same form, but a *modulus* where the fluid version has the reciprocal of a compressibility, and intermediate expressions differing in sign exactly as the general pattern warned. Both differences are non-negative, as they must be.

The instructive case is rubber. An elastomer heated at constant tension *contracts*, so $\alpha_L < 0$ where a metal wire has $\alpha_L > 0$. Since $(\partial S/\partial L)_T = -(\partial f/\partial T)_L$ and $(\partial f/\partial T)_L > 0$ for rubber, stretching it isothermally lowers its entropy and stretching it adiabatically warms it. Both signs are opposite to the intuition built on metal springs, and both follow from one identity; Problem 2

works the case out from an explicit equation of state. Equation (12) is untroubled by the sign of α_L, for the same reason (9) was.

6 Reconstructing the Entropy and the Energy

The relations so far are exact but local. To get a number — ΔS between two states — we must integrate them along a path.

Taking $S = S(T, P)$ and using (2),

$$dS = \frac{C_P}{T}\,dT - V\alpha\,dP, \tag{13}$$

and from $dE = T\,dS - P\,dV$ with (8),

$$dE = C_V\,dT + \left[\frac{T\alpha}{\kappa_T} - P\right] dV. \tag{14}$$

Look at what (13) needs. The second term needs $V\alpha$ at every state along the path, which is the full equation of state. The first needs C_P only where we choose to integrate it — so if the temperature leg always runs along one fixed isobar, calorimetry on that isobar alone suffices.

What Determines the Entropy and Energy

For a single-phase one-component fluid at fixed N, all entropy and energy *differences* are determined by an equation of state $V(T, P)$ over the region of interest together with the heat capacity $C_P(T, P_0)$ along a single isobar. No calorimetry away from P_0 is needed. The absolute values of S and E are not determined: (13) and (14) fix them only up to one additive constant each, and fixing the entropy constant is the business of the third law, in unit T9.

The integral must not depend on the route, or S would not be a function of state. That it does not is the integrability condition read in the other direction: writing $dS = M\,dT + N_P\,dP$, path independence requires $(\partial M/\partial P)_T = (\partial N_P/\partial T)_P$, that is,

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P. \tag{15}$$

So the calorimetric data and the equation of state are not independent: how C_P changes between isobars is already encoded in the curvature of the isobars in the V–T plane. Figure 2 shows the two natural routes.

6.1. An Ideal Gas

Take the model $PV = Nk_BT$ with $C_V = \frac{3}{2}Nk_B$, independent of T and V, and work in *molar* quantities. Then $V\alpha = R/P$ and $C_{P,m} = \frac{5}{2}R$, so (13) integrates to

$$\Delta S_m = \frac{5}{2}R\ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right), \tag{16}$$

both logarithms taking dimensionless arguments, the reference values having cancelled between the states. For one mole from (300 K, 1 bar) to (400 K, 3 bar),

$$\Delta S_m = 5.980 - 9.134 = -3.155\ \mathrm{J\,K^{-1}\,mol^{-1}}.$$

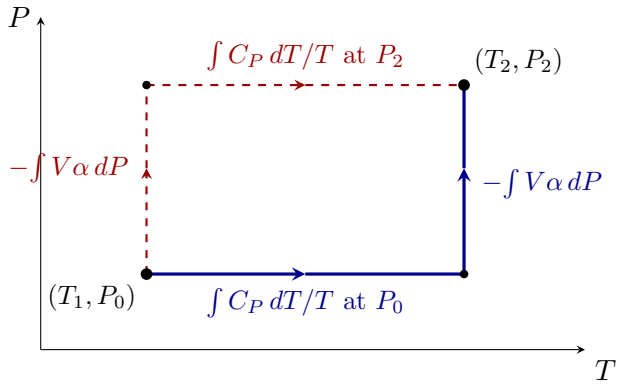

Figure 2: Two routes for integrating (13) between the same pair of states. The solid route heats along the reference isobar and then changes pressure isothermally, needing calorimetry only at P_0; the dashed route needs C_P at P_2 as well. They agree because (15) holds, which is a property of the substance and not a choice we make.

The two terms pull opposite ways and the compression wins. Heating at fixed pressure spreads the gas over a larger volume and a wider range of molecular speeds, raising the entropy; tripling the pressure confines it. Here the confinement outweighs the heating and the gas leaves with less entropy than it started with, which is permitted because it is not isolated. The energy change needs no path: $\Delta E_m = \frac{3}{2}R\,\Delta T = 1247\ \mathrm{J\,mol^{-1}}$, since E depends only on T for this model — for a reason given in Section 7, not by assumption.

6.2. A Real Fluid

Now use van der Waals' equation in molar form, not because it is quantitatively accurate but because it is the simplest equation of state with both ingredients an ideal gas lacks: a finite molecular volume b and an attraction a. Fixing both from the measured critical point of carbon dioxide, $T_c = 304.13$ K and $P_c = 7.3773$ MPa [3], through $a = 27R^2T_c^2/(64P_c)$ and $b = RT_c/(8P_c)$, gives $a = 0.366\ \mathrm{Pa\,m^6\,mol^{-2}}$ and $b = 4.28 \times 10^{-5}\ \mathrm{m^3\,mol^{-1}}$.

Since $(\partial P/\partial T)_{V_m} = R/(V_m - b)$ is independent of T,

$$\left(\frac{\partial E_m}{\partial V_m}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_{V_m} - P = \frac{a}{V_m^2}, \qquad \left(\frac{\partial C_{V,m}}{\partial V_m}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_{V_m} = 0. \tag{17}$$

Both are informative. The energy rises as the fluid expands, by exactly the amount the attraction contributes to the pressure: pulling molecules apart against their attraction costs energy. And $C_{V,m}$ cannot depend on volume at all, so the single function measured in a dilute gas serves at every density the equation describes. Neither was assumed; the form of $P(T, V_m)$ forced both. Integrating along an isotherm,

$$\Delta E_m = a\left(\frac{1}{V_1} - \frac{1}{V_2}\right), \qquad \Delta S_m = R\ln\left(\frac{V_2 - b}{V_1 - b}\right).$$

For one mole expanding isothermally at 350 K from 1.0 to 10.0 litres — both single phase, since 350 K exceeds T_c, with the pressure falling from 26.8 to 2.89 bar — this gives $\Delta E_m = +329\ \mathrm{J\,mol^{-1}}$ and $\Delta S_m = 19.473\ \mathrm{J\,K^{-1}\,mol^{-1}}$, against 0 and $R\ln 10 = 19.145$ for an ideal gas. The energy change is the term that makes a real gas cool on free expansion. The entropy exceeds the ideal value by

1.7% because the accessible volume is $V_m - b$ rather than V_m, and the ratio of accessible volumes is the larger one.

What the Numbers Do and Do Not Establish

These are properties of the van der Waals model with parameters fitted to the critical point of CO_2, not measurements of carbon dioxide. The equation is qualitatively right and quantitatively mediocre, and poorest near the critical region the parameters came from. What the example establishes is structural: $P(T, V_m)$ alone fixes the volume dependence of both E_m and $C_{V,m}$, and the direction and rough size of both corrections. A quantitative treatment would use the reference equation of state of Span and Wagner [3], which is built as a fundamental relation for exactly this reason.

7 What an Equation of State Must Satisfy

The derivatives in (17) were not special to van der Waals.

Consistency Conditions on a Proposed Equation of State

For a single-phase one-component fluid, any $P(T, V, N)$ determines

$$\left(\frac{\partial E}{\partial V}\right)_{T,N} = T\left(\frac{\partial P}{\partial T}\right)_{V,N} - P \qquad \text{and} \qquad \left(\frac{\partial C_V}{\partial V}\right)_{T,N} = T\left(\frac{\partial^2 P}{\partial T^2}\right)_{V,N}. \tag{18}$$

A proposed pair $\{P(T, V), E(T, V)\}$ is therefore over-determined: unless it satisfies the first of these, no fundamental relation has both members, and the pair is not merely inaccurate but impossible.

The first condition says more than it appears to. An equation of state is an incomplete description, and unit T2 was right that $P(T, V, N)$ alone does not determine the fundamental relation. But it does not follow that a P–V–T relation is silent about the energy. Apply (18) to the ideal-gas law:

$$\left(\frac{\partial E}{\partial V}\right)_{T,N} = T \cdot \frac{Nk_B}{V} - \frac{Nk_BT}{V} = 0.$$

A fluid obeying $PV = Nk_BT$ over some region *must* have an energy independent of volume there. Joule's law is not an independent experimental input alongside the ideal-gas law; given the second law it is a consequence of it. What the ideal-gas law genuinely leaves free is the *temperature* dependence, which is why monatomic, diatomic and polyatomic ideal gases share one equation of state and have different heat capacities.

Key Point

An equation of state constrains more than the mechanical behaviour. It fixes the volume dependence of E and of C_V completely, leaving only their temperature dependence and two additive constants for calorimetry to supply. Proposing $P(T, V)$ and $E(T, V)$ independently is a way of writing down a substance that cannot exist.

8 The Speed of Sound

One symbol has not yet been connected to an observable. The adiabatic compressibility was defined along a reversible adiabat, which sounds like an idealisation no apparatus realises. In fact it is measured routinely, to five or six figures, by listening.

8.1. Which Derivative?

Linearise the equations of motion of a fluid about a uniform state at rest, neglecting viscosity and conduction. Mass and momentum conservation then give a wave equation with speed $c^2 = (\partial P/\partial \rho)_{\mathcal{X}}$, where $\mathcal{X}$ is whatever is held fixed as each element is alternately compressed and expanded. The mechanics does not say what $\mathcal{X}$ is. That is a thermodynamic question, and the whole difficulty lives in it.

Take constant entropy. With $\rho = m_{\mathrm{tot}}/V$ at fixed mass, $d\rho = -\rho\, dV/V$, so $(\partial P/\partial \rho)_S = -(V/\rho)(\partial P/\partial V)_S$ and

$$c = \frac{1}{\sqrt{\rho\, \kappa_S}} = \sqrt{\frac{\gamma}{\rho\, \kappa_T}}. \tag{19}$$

Dimensions: $[\rho\kappa_S]^{-1} = \mathrm{m^3\,kg^{-1}} \cdot \mathrm{Pa} = \mathrm{m^2\,s^{-2}}$. For an ideal gas $\kappa_S = 1/(\gamma P)$ and this reduces to $c = \sqrt{\gamma k_B T/\overline{m}}$, of the order of the thermal molecular speed — as it should be, since the molecules carry the disturbance.

The choice of $\mathcal{X}$ is not a detail. For air at $20\,^{\circ}\mathrm{C}$ the two candidates give $1/\sqrt{\rho\kappa_T} = 290\ \mathrm{m\,s^{-1}}$ and $1/\sqrt{\rho\kappa_S} = 343\ \mathrm{m\,s^{-1}}$, and the measured value is the second. Newton computed the first in the *Principia* — 979 feet per second in the second edition — and the discrepancy went unexplained for over a century, with Euler and Lagrange among those who failed to account for it [4]. Laplace identified the cause by 1802: the compressions are too rapid for the heat released to escape, so the local temperature rises and stiffens the fluid. By 1816 he had the correction in modern form, the Newtonian result times the square root of the ratio of specific heats, and in 1823 he used a measured ratio of 1.3748 to obtain 337.1 against a measured $340.9\ \mathrm{m\,s^{-1}}$ [4]. Two candidate answers differing in nothing but which variable is held fixed, and getting it wrong is a 15% error in a quantity already measurable to better than one percent.

8.2. When Is the Adiabatic Answer Right?

Laplace asserted the heat has no time to escape; his contemporaries were right to want a justification, and Stokes was still examining the question in the 1850s [4]. The criterion compares two lengths. In one period heat diffuses a distance of order $\sqrt{D_T \tau}$, with $D_T = k/(\rho c_P)$ the thermal diffusivity, while the temperature differences driving that diffusion are half a wavelength apart. Requiring the diffusion length to be much the shorter gives

$$\frac{\omega D_T}{c^2} \ll 1. \tag{20}$$

For air, $D_T = 2.1 \times 10^{-5}\ \mathrm{m^2\,s^{-1}}$ and $c = 343\ \mathrm{m\,s^{-1}}$ put the crossover near a gigahertz; at 20 kHz the left side is about 2×10^{-5}. The adiabatic assumption is not marginal. At very low frequencies the isothermal limit is recovered instead, which is why sound in a narrow tube with conducting walls behaves differently from sound in free air.

8.3. Which Variables Are Actually Frozen?

Constant entropy is the right constraint, but entropy of what? A polyatomic gas stores energy in translation, rotation and vibration, and a mixture stores it in the populations of distinct species. Each reservoir equilibrates on its own timescale τ_{int}, and the same comparison applies to each: a degree of freedom with $\omega\tau_{\mathrm{int}} \gg 1$ cannot exchange energy within a cycle and is *frozen*. It then contributes to neither heat capacity, and the effective γ exceeds the equilibrium one. This is not small in the atmosphere: the vibrational modes of N_2 and O_2 are partly frozen at audible frequencies, their relaxation is catalysed by water vapour, and the standard atmospheric absorption formulas are built on exactly these two processes [5]. So κ_S and γ are unambiguous only once we say which degrees of freedom are equilibrated on the timescale of the measurement. "Adiabatic" settles the heat conduction question; it does not settle the internal relaxation question.

8.4. A Closed Loop: Sound in Water

We can now predict an acoustic measurement from data containing no acoustics. Take liquid water at 298.15 K and 0.1 MPa. From the reference correlation of Pátek et al. [2], in *specific* form, densitometry and volumetric measurement give

$$\rho = 997.047\ \mathrm{kg\,m^{-3}}, \quad \alpha = 2.5729 \times 10^{-4}\ \mathrm{K^{-1}}, \quad \kappa_T = 4.5246 \times 10^{-10}\ \mathrm{Pa^{-1}},$$

and a calorimeter gives $c_P = 4181.45\ \mathrm{J\,kg^{-1}\,K^{-1}}$. Running the identities in order, with $v = 1/\rho$,

$$c_P - c_V = \frac{T v \alpha^2}{\kappa_T} = 43.75\ \mathrm{J\,kg^{-1}\,K^{-1}} \implies \gamma = 1.01057,$$

$$\kappa_S = \frac{\kappa_T}{\gamma} = 4.4773 \times 10^{-10}\ \mathrm{Pa^{-1}} \implies c = \frac{1}{\sqrt{\rho \kappa_S}} = 1496.70\ \mathrm{m\,s^{-1}}.$$

The tabulated speed of sound at that state is $1496.699\ \mathrm{m\,s^{-1}}$.

It is worth being careful about what the agreement demonstrates. The reference correlation obtains its speed of sound from precisely the identity we just used, so reproducing its number confirms our algebra, not the physics. The physical content lies one level down: that correlation reproduces the IAPWS-95 formulation, whose speed of sound is fitted to acoustic measurements with a stated uncertainty of 0.005%, while its density and heat capacity are fitted to independent volumetric and calorimetric data [2]. The identity ties three independent classes of experiment together and they agree, to about one part in 10^6. That is a test of thermodynamics.

Notice how differently the same question turns out for water and for air. The isothermal formula gives $1489\ \mathrm{m\,s^{-1}}$ for water, low by only 0.5%, where for air it was low by 15%. By (19) the ratio of the two candidates is $\sqrt{\gamma}$ and nothing else, so the whole question is settled by

$$\gamma - 1 = \frac{C_P - C_V}{C_V} = \frac{T V \alpha^2}{\kappa_T\, C_V}, \tag{21}$$

which is 0.400 for air and 0.0106 for water. No single factor accounts for the difference — water's expansivity and specific volume are far smaller, its compressibility smaller still, and the four enter with different powers and opposite signs — which is exactly why the formula is worth having. Whether the distinction between isothermal and adiabatic matters for a given substance is not a judgement about the apparatus; it is a number the equation of state and one calorimetric measurement deliver.

9 What We Have and the Next Question

Result	Statement	Conditions
Maxwell relations	$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$ $\left(\frac{\partial S}{\partial P}\right)_{T,N} = -V\alpha$	single phase; fundamental relation twice continuously differentiable; fixed N
Heat capacities	$C_P - C_V = TV\alpha^2/\kappa_T$ $C_P/C_V = \kappa_T/\kappa_S$	as above; all quantities on one basis; $C_P \geq C_V$ uses $\kappa_T > 0$, a stability condition from T5
Generalised work	$-P \to X$, $V \to x$ for $đW = X\,dx$	one conjugate pair at a time; convention stated explicitly; no sign of χ_T implied
Reconstruction	$dS = (C_P/T)dT - V\alpha\,dP$ $dE = C_V dT + [T\alpha/\kappa_T - P]dV$	as above; equation of state over the region plus C_P on one isobar; constants of integration undetermined
Consistency	$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ $\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$	as above; $P(T,V)$ fixes the volume dependence of E and C_V, not their temperature dependence
Speed of sound	$c = 1/\sqrt{\rho\kappa_S} = \sqrt{\gamma/(\rho\kappa_T)}$	small amplitude; viscosity and conduction neglected; $\omega D_T/c^2 \ll 1$; internal degrees of freedom either equilibrated or their frozen status stated

Table 3: Results of unit T3. The conditions in the third column are part of each statement rather than commentary on it.

This unit has been about states, not processes. Every identity relates properties at a single equilibrium state, and the integrations of Section 6 ran along paths chosen for convenience, with no claim that any apparatus follows them.

But the identities are built from exactly the derivatives that processes care about. We found that adiabatic compression changes the temperature at a rate $TV\alpha/C_P$. A closely related question decides whether a gas can be liquefied by throttling: what happens to the temperature when a fluid is forced through a porous plug, so that the enthalpy rather than the entropy is conserved? The derivative needed is $(\partial T/\partial P)_H$, and the machinery above reduces it to α, V and C_P in one line — Problem 4 does this. Its sign is not fixed: it changes where $T\alpha = 1$, and an ideal gas sits exactly on that boundary, which is why an ideal gas can never be cooled this way.

Those are the questions unit T4 takes up. Which processes actually cool a gas and which merely move energy around? How much work can a process deliver before entropy generation eats the difference, and what is the most useful work obtainable from a finite hot body? The response functions assembled here are the input to every one of those answers.

Appendix A: The Jacobian Chain Rule

This proves property 2 of Section 3. It is needed for no result in the main text and may be skipped.

Let u, w be differentiable functions of r, s, themselves differentiable functions of x, y. The ordinary chain rule gives $(\partial u/\partial x)_y = (\partial u/\partial r)_s (\partial r/\partial x)_y + (\partial u/\partial s)_r (\partial s/\partial x)_y$ and three similar expressions. In matrix form these four equations read

$$\begin{pmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial w}{\partial x}\right)_y & \left(\frac{\partial w}{\partial y}\right)_x \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial u}{\partial r}\right)_s & \left(\frac{\partial u}{\partial s}\right)_r \\ \left(\frac{\partial w}{\partial r}\right)_s & \left(\frac{\partial w}{\partial s}\right)_r \end{pmatrix} \begin{pmatrix} \left(\frac{\partial r}{\partial x}\right)_y & \left(\frac{\partial r}{\partial y}\right)_x \\ \left(\frac{\partial s}{\partial x}\right)_y & \left(\frac{\partial s}{\partial y}\right)_x \end{pmatrix}.$$

Taking determinants and using $\det(AB) = \det A \det B$ gives the chain rule as stated. Property 3 is the case $(r, s) = (u, w)$, where the left side is the determinant of the identity; property 1 is the antisymmetry of the determinant under exchange of rows or columns. The only hypothesis is differentiability, together with non-vanishing of the relevant Jacobian wherever a reciprocal is taken — the usual condition for the change of variables to be locally invertible. Physically, that condition fails where a response function diverges, as κ_T does at a critical point.

Appendix B: Problems

1. **What an equation of state constrains.** Derive both parts of (18) from (1), and evaluate them for the van der Waals fluid (3). Then consider a colleague's proposal that a gas obeys $P = Nk_BT/V$ while its energy is $E = \frac{3}{2}Nk_BT - cN^2/V$ with $c > 0$, on the grounds that attraction should lower the energy at small volume. Show that no fundamental relation has both properties, and identify what else would have to change.

2. **An elastomer.** A model rubber band of unstretched length L_0 obeys $f = aT(L/L_0 - L_0^2/L^2)$ with $a > 0$, for $L \geq L_0$. Find $(\partial S/\partial L)_T$ and show it is negative; show $\alpha_L < 0$; and find the sign of the temperature change when the band is stretched adiabatically. A rubber band held stretched and then warmed with a hair dryer pulls harder — which derivative does that measure?

3. **Adiabatic demagnetisation.** A paramagnetic salt obeys Curie's law $m = \mathcal{C}B_0/T$ and has a field-independent lattice heat capacity C_{lat}. Show that $C_{B_0} = C_{\mathrm{lat}} + \mathcal{C}B_0^2/T^2$ and that $(\partial T/\partial B_0)_S = \mathcal{C}B_0 T/(\mathcal{C}B_0^2 + C_{\mathrm{lat}}T^2)$. Deduce the sign of the temperature change when the field is reduced adiabatically, and explain in terms of entropy why cooling needs the magnetic contribution to be a substantial fraction of the total. What does that suggest about the useful temperature range?

4. **The throttling derivative.** A fluid is forced steadily through a porous plug from P_1 to $P_2 < P_1$, insulated, with negligible kinetic energy change, so the enthalpy per particle is the same on both sides. Using Jacobians and a Maxwell relation, show that

$$\mu_{\mathrm{JT}} \equiv \left(\frac{\partial T}{\partial P}\right)_{H,N} = \frac{V}{C_P}\left(T\alpha - 1\right).$$

   Verify that it vanishes for an ideal gas and check its dimensions. For the van der Waals fluid, show that $T\alpha > 1$ at low temperature and $T\alpha < 1$ at high temperature, and say which sign corresponds to cooling on expansion.

Solution Sketches

1. From $dE = T\,dS - P\,dV$ at fixed T, $(\partial E/\partial V)_T = T(\partial S/\partial V)_T - P$, and (1) converts the first term; differentiating $C_V = T(\partial S/\partial T)_V$ with respect to V and exchanging the order of differentiation gives the second. For van der Waals, $(\partial E/\partial V)_T = aN^2/V^2$ and $(\partial C_V/\partial V)_T = 0$. For the proposal, the stated P gives $T(\partial P/\partial T)_V - P = 0$, so consistency demands $(\partial E/\partial V)_T = 0$, whereas the stated E gives $cN^2/V^2 \neq 0$. An attractive term in the energy is not optional decoration: it forces a matching $-cN^2/V^2$ in the pressure, which is precisely the van der Waals a.

2. $(\partial S/\partial L)_T = -(\partial f/\partial T)_L = -a(L/L_0 - L_0^2/L^2) < 0$ for $L > L_0$: stretching orders the chains. The cyclic rule gives $(\partial L/\partial T)_f = -(\partial f/\partial T)_L/(\partial f/\partial L)_T$, and $(\partial f/\partial L)_T = aT(1/L_0 + 2L_0^2/L^3) > 0$, so $\alpha_L < 0$ and the band contracts on heating at fixed tension. From the $T\,dS$ equation in (T, L), $(\partial T/\partial L)_S = T(\partial f/\partial T)_L/C_L > 0$, so adiabatic stretching warms it. The hair dryer measures $(\partial f/\partial T)_L$ at fixed length, the derivative in the Maxwell relation — a direct reading of the entropy change under stretching.

3. From (11), $(\partial S/\partial B_0)_T = -\mathcal{C}B_0/T^2$, so $S(T, B_0) = S(T, 0) - \mathcal{C}B_0^2/(2T^2)$, and $T(\partial S/\partial T)_{B_0}$ then gives C_{B_0}. The magnetocaloric derivative is positive, so reducing B_0 adiabatically lowers T. In entropy terms: at fixed T the field orders the moments and lowers S; removing it at fixed S forces the lattice to surrender entropy to the spins, which it can only do by cooling. The method works while $\mathcal{C}B_0^2/T^2$ is not small beside C_{lat}, and since C_{lat} falls as T^3 on cooling while the magnetic term grows as T^{-2}, it is a low-temperature technique. Unit T9 returns to this.

4. $(\partial T/\partial P)_H = -(\partial H/\partial P)_T/C_P$, and $dH = T\,dS + V\,dP$ gives $(\partial H/\partial P)_T = T(\partial S/\partial P)_T + V = -TV\alpha + V$ by (2). Dimensions: $\mathrm{m^3/(J\,K^{-1})} = \mathrm{K\,Pa^{-1}}$. For an ideal gas $\alpha = 1/T$ exactly, so $\mu_{\text{JT}} = 0$: throttling changes nothing, since its enthalpy depends only on T. For van der Waals the attraction dominates at low T, giving $T\alpha > 1$ and $\mu_{\text{JT}} > 0$, so temperature falls with pressure — work is done against the attraction. At high T the finite molecular volume dominates, $T\alpha < 1$, and throttling warms the gas. The locus $T\alpha = 1$ is the inversion curve, developed in T4.

References

1. G. K. White and S. J. Collocott, “Heat Capacity of Reference Materials: Cu and W,” *J. Phys. Chem. Ref. Data* **13**, 1251–1257 (1984). Table 2 gives the recommended C_P and C_V for copper; the text states the relation used to obtain the second column and the molar volume 7.09 cm^3 at 300 K.

2. J. Pátek, J. Hrubý, J. Klomfar, M. Součková and A. H. Harvey, “Reference Correlations for Thermophysical Properties of Liquid Water at 0.1 MPa,” *J. Phys. Chem. Ref. Data* **38**, 21–29 (2009). Tables 3 and 8; stated uncertainties relative to IAPWS-95 are 0.0001% in density, 0.005% in speed of sound and 0.1% in isobaric heat capacity.

3. R. Span and W. Wagner, “A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa,” *J. Phys. Chem. Ref. Data* **25**, 1509–1596 (1996). Source of the critical constants in Section 6.2.

4. B. S. Finn, “Laplace and the Speed of Sound,” *Isis* **55**, 7–19 (1964). Source for the historical account in Section 8.1, including Newton’s value in the second edition of the *Principia* and Laplace’s 1816 and 1823 results.

5. H. E. Bass, L. C. Sutherland, A. J. Zuckerwar, D. T. Blackstock and D. M. Hester, “Atmospheric absorption of sound: Further developments,” *J. Acoust. Soc. Am.* **97**, 680–683 (1995); erratum *ibid.* **99**, 1259 (1996). Absorption formulas built on the vibrational relaxation of nitrogen and oxygen.

6. H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, 2nd ed. (Wiley, 1985), chapter 7, for an alternative systematic treatment of the reduction of derivatives.