Consider a material with equation of state

$$P = \frac{\alpha T}{V^2}$$

where α is a constant. The heat capacity of this material at constant volume is linear in temperature: $C_V = A(V)T$.

(a) By using Maxwell relations or otherwise find the derivative of entropy $(\partial S/\partial V)_T$.

(b) Show that the coefficient $A(V)$ is independent of V.

(c) Find $S(T,V)$ assuming that the value $S(T_0, V_0)$ is known.

(d) Find the heat capacity at constant pressure $C_P = T\,(\partial S/\partial T)_P$.

(a) Conservation of energy tells us that changes in energy depend on heat flow (TdS) and work (PdV) via

$$dU = TdS - PdV$$

The Helmholtz free energy is defined as $F = U - TS$, so

$$dF = TdS - PdV - (TdS + SdT) = -SdT - PdV$$

Now, the chain rule in differential form tells us that, for a generic function $z = z(x,y)$,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x$$

and so one can identify

$$-S = \left(\frac{\partial F}{\partial T}\right)_V$$
$$-P = \left(\frac{\partial F}{\partial V}\right)_T$$

Equality of mixed partial derivatives then tells us that

$$-\frac{\partial^2 F}{\partial T \partial V} = \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

This is one of the *Maxwell relations* that follow from taking mixed partial derivatives of various thermodynamic quantities.

The computation is now straightforward:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{V^2}$$

(b) The heat capacity is defined as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

and since $dU = TdS - PdV$, we can write

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

and identify $A(V) = \left(\frac{\partial S}{\partial T}\right)_V$. Differentiating with respect to volume gives

$$\begin{aligned}\frac{\partial A(V)}{\partial V} &= \frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V \\ &= \frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T \\ &= \frac{\partial}{\partial T}\left(\frac{\alpha}{V^2}\right) \\ &= 0\end{aligned}$$

where we have again used equality of mixed partial derivatives to interchange the order of the differentiation with respect to T and V.

(c) Integrating from the known value of $S(T_0, V_0)$ gives

$$\begin{aligned}S(T,V) &= S(T_0,V_0) + \int_{V_0}^{V} dV\,\left(\frac{\partial S}{\partial V}\right)_{T=T_0} + \int_{T_0}^{T} dT\,\left(\frac{\partial S}{\partial T}\right)_{V=V} \\ &= S_0 + \int_{V_0}^{V} dV\,\frac{\alpha}{V^2} + \int_{T_0}^{T} dT\,A \\ &= S_0 + \alpha\left(\frac{1}{V_0} - \frac{1}{V}\right) + A(T - T_0)\end{aligned}$$

(d) One can differentiate the expression for entropy in the last part to obtain

$$\begin{aligned}C_P &= T\left(\frac{\partial S}{\partial T}\right)_P \\ &= T\frac{\partial}{\partial T}\left[S_0 + \alpha\left(\frac{1}{V_0} - \frac{1}{V}\right) + A(T - T_0)\right]_P \\ &= T\left[\frac{\alpha}{V^2}\left(\frac{\partial V}{\partial T}\right)_P + A\left(\frac{\partial T}{\partial T}\right)_P\right] \\ &= \frac{\alpha T}{V^2}\left(\frac{1}{2}\sqrt{\frac{\alpha}{PT}}\right) + AT \\ &= \frac{\alpha}{2V} + AT\end{aligned}$$

where we have used the equation of state to write

$$V = \left(\frac{\alpha T}{P}\right)^{1/2}$$

and compute $\left(\frac{\partial V}{\partial T}\right)_P$.