DS 2:
More Partial Derivatives

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1 Proper and improper derivatives

(a) Consider a small quantity given by

$$C_V \mathrm{d}T + \frac{RT}{V}\mathrm{d}V, \tag{1}$$

where C_V and R are constants and T and V are functions of state.

(i) Show that this quantity is an *improper* differential.

(ii) Let us call the above quantity $đQ$. Show that $đQ/T$ is a perfect differential.

2 Homogeneous functions

A function $f(x_1, x_2, \ldots, x_n)$ is said to be homogeneous of order k if

$$f(\lambda x_1, \lambda x_2, \ldots, \lambda x_n) = \lambda^k \times f(x_1, x_2, \ldots, x_n). \tag{2}$$

(a) Argue that entropy has to be a first-order homogeneous function of U, V, and N.

(b) Consider a simplified case of a function $g \equiv g(x, y, z)$ such that

$$g(\lambda x, y, z) = \lambda g(x, y, z). \tag{3}$$

Since the above equation holds for *all* values of λ, choose a "special" value of λ to show that

$$f(x, y, z) = x f(1, y, z). \tag{4}$$

Use this result to show that

$$\left(\frac{\partial f}{\partial x}\right)_{y,z} = \frac{f}{x}. \tag{5}$$

(c) Using the earlier result, show that if g_1 and g_2 are two such functions of x that are homogeneous,

$$\left(\frac{\partial g_1}{\partial g_2}\right)_{y,z} = \frac{g_1}{g_2}. \tag{6}$$

(d) Use the above result to show that

$$\left(\frac{\partial N}{\partial V}\right)_{P,T} = \frac{N}{V}. \tag{7}$$

3 Fundamental relations and equations of state

In class, we saw that entropy had to satisfy three postulates that I condense here in a mathematical form (using the same numbering as Callen, to avoid confusion):

- **Postulate 2:** Entropy is a function of extensive parameters, defined for all physical equilibrium states, and maximised at equilibrium.
- **Postulate 3:** Entropy is a continuous, differentiable, homogeneous function of first order, and increasing such that
$$\left(\frac{\partial S}{\partial U}\right)_{V,N} > 0. \tag{8}$$
- **Postulate 4:** Entropy vanishes at zero temperature (i.e.)
$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = 0 \qquad \Longrightarrow \qquad S = 0. \tag{9}$$

(a) Consider the following ten fundamental relations. Find which of them are inconsistent with the postulates given above:

(i) $S = A_1 (NVU)^{1/3}$

(ii) $S = A_2 \left(\frac{NU}{V}\right)^{2/3}$

(iii) $S = A_3 \left(NU + B_1 V^2\right)$

(iv) $S = A_4 \left(\frac{V^3}{NU}\right)$

(v) $S = A_5 \left(N^2 V U^2\right)^{1/5}$

(vi) $S = A_6 N \ln\left(\frac{B_2 UV}{N^2}\right)$

(vii) $S = A_7 \, (NU)^{1/2} \exp\left(-B_3 \frac{V^2}{N^2}\right)$

(viii) $S = A_8 \, (NU)^{1/2} \exp\left(-B_4 \frac{UV}{N}\right)$

(ix) $U = A_9 \left(\frac{S^2}{V} \exp\left(B_5 \frac{S}{N}\right)\right)$

(x) $U = A_{10} NV \left(1 + B_6 \frac{S}{N}\right) \exp\left(-B_7 \frac{S}{N}\right)$

(b) Suppose you are given the following three equations of state
$$\begin{aligned} T &= \frac{3As^2}{v}, \\ P &= \frac{As^3}{v}, \\ \mu &= -\frac{As^3}{v}, \end{aligned} \tag{10}$$
where $s = S/N$, and $v = V/N$. Find $U(S,V,N)$ and also $S(U,V,N)$.

(c) Show that $S(U,V,N)$ determined above satisfies all the postulates.