7.5: Partial Derivatives with Respect to T T , p p , and V V

7.5.1 Tables of partial derivatives

The tables in this section collect useful expressions for partial derivatives of the eight state functions T, p, V, U, H, A, G, and S in a closed, single-phase system. Each derivative is taken with respect to one of the three easily-controlled variables T, p, or V while another of these variables is held constant. We have already seen some of these expressions, and the derivations of the others are indicated below.

We can use these partial derivatives (1) for writing an expression for the total differential of any of the eight quantities, and (2) for expressing the finite change in one of these quantities as an integral under conditions of constant T, p, or V. For instance, given the expressions

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \qquad \text{and} \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\alpha V \tag{7.5.1}$$

we may write the total differential of S, taking T and p as the independent variables, as

$$\mathrm{d}S = \frac{C_p}{T}\,\mathrm{d}T - \alpha V\,\mathrm{d}p \tag{7.5.2}$$

Furthermore, the first expression is equivalent to the differential form

$$\mathrm{d}S = \frac{C_p}{T}\,\mathrm{d}T \tag{7.5.3}$$

provided p is constant; we can integrate this equation to obtain the finite change ΔS under isobaric conditions as shown in Eq. 7.4.12.

Both general expressions and expressions valid for an ideal gas are given in Tables 7.1, 7.2, and 7.3.

> We may derive the general expressions as follows. We are considering differentiation with respect only to T, p, and V. Expressions for $(\partial V/\partial T)_p$, $(\partial V/\partial p)_T$, and $(\partial p/\partial T)_V$ come from Eqs. 7.1.1, 7.1.2, and 7.1.7 and are shown as functions of α and κ_T. The reciprocal of each of these three expressions provides the expression for another partial derivative from the general relation
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> $$(\partial y/\partial x)_z = \frac{1}{(\partial x/\partial y)_z} \tag{7.5.4}$$
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> This procedure gives us expressions for the six partial derivatives of T, p, and V.
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> The remaining expressions are for partial derivatives of U, H, A, G, and S. We obtain the expression for $(\partial U/\partial T)_V$ from Eq. 7.3.1, for $(\partial U/\partial V)_T$ from Eq. 7.2.4, for $(\partial H/\partial T)_p$ from Eq. 7.3.2, for $(\partial A/\partial T)_V$ from Eq. 5.4.9, for $(\partial A/\partial V)_T$ from Eq. 5.4.10, for $(\partial G/\partial p)_T$ from Eq. 5.4.12, for $(\partial G/\partial T)_p$ from Eq. 5.4.11, for $(\partial S/\partial T)_V$ from Eq. 7.4.6, for $(\partial S/\partial T)_p$ from Eq. 7.4.11, and for $(\partial S/\partial p)_T$ from Eq. 5.4.18.
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> We can transform each of these partial derivatives, and others derived in later steps, to two other partial derivatives with the same variable held constant and the variable of differentiation changed. The transformation involves multiplying by an appropriate partial derivative of T, p, or V. For instance, from the partial derivative $(\partial U/\partial V)_T = (\alpha T/\kappa_T) - p$, we obtain
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> $$\left(\frac{\partial U}{\partial p}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T = \left(\frac{\alpha T}{\kappa_T} - p\right)(-\kappa_T V) = (-\alpha T + \kappa_T p)\,V \tag{7.5.5}$$
>
> The remaining partial derivatives can be found by differentiating $U = H - pV$, $H = U + pV$, $A = U - TS$, and $G = H - TS$ and making appropriate substitutions. Whenever a partial derivative appears in a derived expression, it is replaced with an expression derived in an earlier step. The expressions derived by these steps constitute the full set shown in Tables 7.1, 7.2, and 7.3.
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> Bridgman devised a simple method to obtain expressions for these and many other partial derivatives from a relatively small set of formulas (*Phys. Rev.*, **3**, 273–281, 1914; *The Thermodynamics of Electrical Phenomena in*

Metals and a Condensed Collection of Thermodynamic Formulas, Dover, New York, 1961, p. 199–241).

7.5.2 The Joule–Thomson coefficient

The Joule–Thomson coefficient of a gas was defined in Eq. 6.3.3 by $\mu_{\mathrm{JT}} = (\partial T/\partial p)_H$. It can be evaluated with measurements of T and p during adiabatic throttling processes as described in Sec. 6.3.1.

To relate μ_{JT} to other properties of the gas, we write the total differential of the enthalpy of a closed, single-phase system in the form

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p \tag{7.5.6}$$

and divide both sides by $\mathrm{d}p$:

$$\frac{\mathrm{d}H}{\mathrm{d}p} = \left(\frac{\partial H}{\partial T}\right)_p \frac{\mathrm{d}T}{\mathrm{d}p} + \left(\frac{\partial H}{\partial p}\right)_T \tag{7.5.7}$$

Next we impose a condition of constant H; the ratio $\mathrm{d}T/\,\mathrm{d}p$ becomes a partial derivative:

$$0 = \left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H + \left(\frac{\partial H}{\partial p}\right)_T \tag{7.5.8}$$

Rearrangement gives

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{(\partial H/\partial p)_T}{(\partial H/\partial T)_p} \tag{7.5.9}$$

The left side of this equation is the Joule–Thomson coefficient. An expression for the partial derivative $(\partial H/\partial p)_T$ is given in Table 7.1, and the partial derivative $(\partial H/\partial T)_p$ is the heat capacity at constant pressure (Eq. 5.6.3). These substitutions give us the desired relation

$$\mu_{\mathrm{JT}} = \frac{(\alpha T - 1)V}{C_p} = \frac{(\alpha T - 1)V_{\mathrm{m}}}{C_{p,\mathrm{m}}} \tag{7.5.10}$$