Chapter 8

Reduction and evaluation of partial derivatives

8.1   Introduction

The previous chapters made clear what part (partial) derivatives play in thermodynamics. They are essential for deriving relations between the different thermodynamic quantities. These relations are important for determining the (changes in) energies in processes (note that this is what thermodynamics is really about). In order to attribute actual values to the energy changes, it is nevertheless necessary for the values of the partial derivatives that occur in the expressions to be known.

Sometimes, it is easy to find the value of a partial derivative, such as $(\partial v/\partial T)_P$ for an ideal gas, for which $Pv = RT$. Usually, such a neat state equation is not known, however. Chapter 4 discussed a number of partial derivatives for which is known that they equal T, $-P$, v or $-s$. Chapter 7 also defines a number of partial derivatives: the thermal expansion coefficient, β, the isothermal compression coefficient, κ, and the specific heat at constant pressure and volume, c_p and c_v respectively. These are not a problem, but most others are; for example, what do $(\partial h/\partial T)_P$ or $(\partial g/\partial s)_v$ equal? How is it still possible to determine a value for such partial derivatives?

In the previous chapters, a number of relations with partial derivatives have been discussed that allow for the reduction and rewriting of partial derivatives. Chapter 5 introduced the reciprocal rule, the cyclic rule and the chain rule. The Maxwell relations have been derived in chapter 6. All these tools can be used to reduce and rewrite partial derivatives to quantities or parameters that can be measured or looked up.

8.2   Systematic evaluation of partial derivatives

The introduction explains that it is preferred to write partial derivatives in quantities that can be measured or looked up. These quantities are the pressure, P, the temperature, T, the volume, v, the entropy, s and the defined quantities based on partial derivatives defined in chapter 7 β, κ, c_v and c_P. The final four reflect the sensitivity of a thermodynamic variable as a result of a change in T, P or v while another variable is constant.

Based on the total differential for the enthalpy $h(s, P)$, $dh = Tds + vdP$, it is quite easy to see that $(\partial h/\partial s)_P = T$ and $(\partial h/\partial P)_s = v$. From the total differential for the internal energy $u(s, v)$, $du = Tds - Pdv$ it follows that $(\partial u/\partial s)_v = T$ and $(\partial u/\partial v)_s = -P$. These four partial derivatives can be easily rewritten to measurable quantities. Then there are four partial derivatives that follow from the Gibbs energy, g and the Helmholtz energy, a. These eight partial derivatives are provided in table 4.1. So what about a derivative like $(\partial h/\partial P)_T$ or even $(\partial P/\partial u)_g$? For the last two derivatives, it is more difficult to find an expression that contains only measurable quantities.

The rest of this chapter will discuss a *systematic method* that allows for rewriting *any* thermodynamic partial derivative into an expression that contains only *quantities that can be measured or*

Step-by-step plan for the reduction and evaluation of partial derivatives

- Tools for the reduction and evaluation of a partial derivative:

  - Differential expressions for the thermodynamic energies (table 4.1).
  - Calculation rules for partial derivatives (table 5.1).
  - Maxwell relations (table 6.1).
  - Definitions of κ, β, c_v en c_p (equations 7.3, 7.4, 7.8 and 7.9).
  - Nernst-Lindemann relation (equation 7.10).

- Steps for the reduction and evaluation of a partial derivative:

  - If the partial derivative contains a thermodynamic energy, then it must be brought to the numerator using the calculation rules.
  - The thermodynamic energy must be eliminated with the help of the differential expression for that energy.
  - The remaining partial derivatives must be further rewritten to the definitions of κ, β, c_p and c_v with the help of the calculation rules and/or the Maxwell relations.
  - c_v is eliminated via the Nernst-Lindeman relation.

Table 8.1: *Step-by-step plan for the reduction and evaluation of partial derivatives.*

looked up. Rewriting uses the calculation rules for partial derivatives as derived in chapter 5. The Maxwell relations discussed in chapter 6 are also used.

The partial derivative can only be eliminated by rewriting it to partial derivatives that are known. These are the partial derivatives that equal κ, β, c_v and c_P from chapter 7 and the partial derivatives that equal T, P, v and s (see table 4.1). The first step is to eliminate the energies (h, u, g of a). These are rewritten in such a way that there is a form that can be eliminated with the help of the expressions from the total differentials of the energies. For instance, $(\partial h/\partial P)_T$, where h is a function of P and T. This partial derivative is not immediately known. However, h is known as a function of s and P: $dh = Tds + dvP$. The partial derivatives $(\partial h/\partial s)_P = T$ and $(\partial h/\partial P)_s = v$ in which h is a function of s and P are thus also known. It is a matter of rewriting the required partial differential $(\partial h/\partial P)_T$ into an expression that contains the known partial differentials. $(\partial h/\partial P)_T$ can be rewritten as [1]

$$\left(\frac{\partial h}{\partial P}\right)_T = \left(\frac{\partial h}{\partial s}\right)_P \left(\frac{\partial s}{\partial P}\right)_T + \left(\frac{\partial h}{\partial P}\right)_s \left(\frac{\partial P}{\partial P}\right)_T. \tag{8.1}$$

h is first differentiated to s with a fixed P, a derivative that is known, and then s is differentiated to P with a fixed T as would have been the case for h. Furthermore, h is differentiated to P at a fixed s, another known derivative, this P must then be differentiated to P, which was the ultimate goal.

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[1] This can be proved by rewriting $(\partial h/\partial P)_T$ with the help of the rules for the manipulation of a Jacobian:

$$\left(\frac{\partial h}{\partial P}\right)_T = \frac{\partial(h,T)}{\partial(P,T)} = \frac{\partial(h,T)}{\partial(s,P)}\frac{\partial(s,P)}{\partial(P,T)} = \left| \begin{matrix} \left(\frac{\partial h}{\partial s}\right)_P & \left(\frac{\partial h}{\partial P}\right)_s \\ \left(\frac{\partial T}{\partial s}\right)_P & \left(\frac{\partial T}{\partial P}\right)_s \end{matrix} \right| \left| \begin{matrix} \left(\frac{\partial s}{\partial P}\right)_T & \left(\frac{\partial s}{\partial T}\right)_P \\ \left(\frac{\partial P}{\partial P}\right)_T & \left(\frac{\partial P}{\partial T}\right)_P \end{matrix} \right| =$$

$$\left[-\left(\frac{\partial h}{\partial P}\right)_s \left(\frac{\partial T}{\partial s}\right)_P \right] + \left[\left(\frac{\partial s}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_P - \left(\frac{\partial s}{\partial T}\right)_P \left(\frac{\partial P}{\partial P}\right)_T \right] =$$

$$-\left(\frac{\partial h}{\partial s}\right)_P \left(\frac{\partial T}{\partial P}\right)_s \left(\frac{\partial s}{\partial T}\right)_P \left(\frac{\partial P}{\partial P}\right)_T + \left(\frac{\partial h}{\partial P}\right)_s \left(\frac{\partial T}{\partial s}\right)_P \left(\frac{\partial s}{\partial T}\right)_P \left(\frac{\partial P}{\partial P}\right)_T = \left(\frac{\partial h}{\partial s}\right)_P \left(\frac{\partial s}{\partial P}\right)_T + \left(\frac{\partial h}{\partial P}\right)_s \left(\frac{\partial P}{\partial P}\right)_T.$$

Expression 8.1 can now be simplified to

$$\left(\frac{\partial h}{\partial P}\right)_T = T\left(\frac{\partial s}{\partial P}\right)_T + v\left(\frac{\partial P}{\partial P}\right)_T = T\left(\frac{\partial s}{\partial P}\right)_T + v \tag{8.2}$$

after all $(\partial P/\partial P)_T = 1$. The energy h has been eliminated completely and only one partial derivative remains. This does not contain an energy quantity. The first rewriting part is complete. This remaining partial derivative must now be rewritten to the quantities β, κ, c_P and/or C_v. This is done by using the calculation rules and/or the Maxwell relations. In this case, a Maxwell relation is used and shows that $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$ (see table 6.1) and relation 7.4 shows that $-\left(\frac{\partial v}{\partial T}\right)_P = -\beta v$. Combining the found results gives

$$\left(\frac{\partial h}{\partial T}\right)_P = -T\beta v + v = v(1 - \beta T). \tag{8.3}$$

The result is an expression containing only quantities that can be measured. Note that if the partial derivative for c_v appears, that it can then be placed and eliminated later via the Nernst-Lindemand relation that gives relation between c_v and c_P.

With the method described above, all partial derivatives can be rewritten and usable relations can be found between the energy of a system and changing quantities as pressure, temperature and volume. The method is summarised in table 8.1 and an example is provided in figure 8.1.

Rewrite the partial derivative $\left(\frac{\partial P}{\partial g}\right)_v$ to an expression with only measurable quantities (β, κ, C_p, P, T, v and s).

- There is a thermodynamic energy in the expression and it must be brought to the numerator; this is done with the help of the reciprocal rule:

$$\left(\frac{\partial P}{\partial g}\right)_v = \left(\frac{\partial g}{\partial P}\right)_v^{-1}.$$

- The thermodynamic energy must be eliminated with the help of the differential expression for the Gibbs energy, $g \to dg = -sdT + vdP$:

$$\left(\frac{\partial g}{\partial P}\right)_v^{-1} = \left[\left(\frac{\partial g}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_v + \left(\frac{\partial g}{\partial P}\right)_T \left(\frac{\partial P}{\partial P}\right)_v\right]^{-1} = \left[-s\left(\frac{\partial T}{\partial P}\right)_v + v \cdot 1\right]^{-1}.$$

- The expression $\left(\frac{\partial T}{\partial P}\right)_v$ must be further rewritten to κ, β, c_v and c_p by means of the calculation rules. Use of the minus 1 rule and substituting κ and β results in:

$$\left(\frac{\partial T}{\partial P}\right)_v = -\left(\frac{\partial T}{\partial v}\right)_P \left(\frac{\partial v}{\partial P}\right)_T = -\left(\frac{1}{v\beta}\right)(-\kappa v) = \frac{\kappa}{\beta}$$

- Combining it all results in:

$$\left(\frac{\partial P}{\partial g}\right)_v = \left[-s\left(\frac{\partial T}{\partial P}\right)_v + v \cdot 1\right]^{-1} = \left[-s\left(\frac{\kappa}{\beta}\right) + v\right]^{-1} = \frac{\beta}{\beta v - s\kappa}.$$

What is the meaning of the partial derivative $\left(\frac{\partial P}{\partial g}\right)_v$.

- The partial derivative represents the change of the pressure if the Gibbs energy changes and the volume remains constant. It turns out that the change depends on β, κ, s and v. Which of these parameters has the biggest influence depends on the values. These values can be looked up in tables or measured in an experiment.

Figure 8.1: *Example of the reduction and evaluation of a partial derivative.*