

Unit 1-8: Response Functions

Several second derivatives of thermodynamic potentials have well known physical meanings. These are generally known as *response functions*. They tell how one system variable will vary if another system variable is changed. Response functions include:

$$\begin{aligned}
 \text{The specific heat at constant volume:} \quad C_V &= \left(\frac{dQ}{dT} \right)_{V,N} = T \left(\frac{\partial S}{\partial T} \right)_{V,N} \\
 \text{The specific heat at constant pressure:} \quad C_p &= \left(\frac{dQ}{dT} \right)_{p,N} = T \left(\frac{\partial S}{\partial T} \right)_{p,N} \\
 \text{The isothermal compressibility:} \quad \kappa_T &= -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} \\
 \text{The adiabatic compressibility:} \quad \kappa_S &= -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{S,N} \\
 \text{The coefficient of thermal expansion:} \quad \alpha &= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p,N}
 \end{aligned} \tag{1.8.1}$$

C_V tells how much the temperature will change if one adds heat to the system while keeping the system volume constant, $\Delta T = \Delta Q/C_V$. C_p is similar, but when one keeps the pressure constant.

κ_T tells how much the volume will proportionally decrease if one increases the pressure while keeping the system temperature constant, $\Delta V/V = -\kappa_T \Delta p$. κ_S is similar, but keeping the system entropy constant, as in an adiabatic process (adiabatic = constant entropy).

α tells how much the volume will proportionally expand when the temperature is increased, keeping pressure constant, $\Delta V/V = \alpha \Delta T$.

All the above may be viewed as a second derivative of an appropriate thermodynamic potential.

$$\begin{aligned}
 C_V &= T \left(\frac{\partial S}{\partial T} \right)_{V,N} = -T \left(\frac{\partial^2 A}{\partial T^2} \right)_{V,N} && \text{since} \quad \left(\frac{\partial A}{\partial T} \right)_{V,N} = -S(T, V, N) \\
 C_p &= T \left(\frac{\partial S}{\partial T} \right)_{p,N} = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_{p,N} && \text{since} \quad \left(\frac{\partial G}{\partial T} \right)_{p,N} = -S(T, p, N) \\
 \kappa_T &= -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} = -\frac{1}{V} \left(\frac{\partial^2 G}{\partial p^2} \right)_{T,N} && \text{since} \quad \left(\frac{\partial G}{\partial p} \right)_{T,N} = V(T, p, N) \\
 \kappa_S &= -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{S,N} = -\frac{1}{V} \left(\frac{\partial^2 H}{\partial p^2} \right)_{S,N} && \text{since} \quad \left(\frac{\partial H}{\partial p} \right)_{S,N} = V(S, p, N) \\
 \alpha &= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p,N} = \frac{1}{V} \left(\frac{\partial^2 G}{\partial T \partial p} \right)_N && \text{since} \quad \left(\frac{\partial G}{\partial p} \right)_{T,N} = V(T, p, N)
 \end{aligned} \tag{1.8.2}$$

Since all the various thermodynamic potentials can be derived from one another via Legendre transforms, it follows that the second derivatives must be related. If we consider only cases where N is held constant (as in all the above response functions) then there can only be three *independent* second derivatives. These are, for example,

$$\left(\frac{\partial^2 G}{\partial T^2} \right)_{p,N} = -\frac{C_p}{T}, \quad \left(\frac{\partial^2 G}{\partial p^2} \right)_{T,N} = -V\kappa_T, \quad \left(\frac{\partial^2 G}{\partial T \partial p} \right)_N = V\alpha \tag{1.8.3}$$

Therefore all the other second derivatives of all the other potentials must be some combination of these.

We will first consider how to express C_V in terms of these three. Then we will do similarly with κ_S . Along the way we will derive and use several mathematical relations involving partial derivatives.

Consider the Helmholtz free energy $A(T, V)$ – in the following we will always be holding N constant, so I will not write it to keep the notation simpler. We have,

$$-S(T, V) = \left(\frac{\partial A}{\partial T} \right)_V \quad (1.8.4)$$

Viewing S as a function of T and V we have,

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \Rightarrow T \left(\frac{\partial S}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial T}{\partial T} \right)_p + T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p \quad (1.8.5)$$

Since $(\partial T/\partial T)_p = 1$, using the definitions of C_p and C_V we get,

$$C_p = C_V + T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p \quad (1.8.6)$$

Now, making use of a Maxwell relation, we can write,

$$\left(\frac{\partial S}{\partial V} \right)_T = - \frac{\partial^2 A}{\partial V \partial T} = \left(\frac{\partial p}{\partial T} \right)_V \quad (1.8.7)$$

and using (see proof (1) below of this general partial derivate relationship),

$$\left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_p \left(\frac{\partial V}{\partial p} \right)_T = -1 \quad \left[\text{where } p, T, V \text{ are not mutually independent since } \left(\frac{\partial A}{\partial V} \right)_T = -p(V, T) \right] \quad (1.8.8)$$

we have

$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{-1}{\left(\frac{\partial T}{\partial V} \right)_p \left(\frac{\partial V}{\partial p} \right)_T} = - \frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} \quad (1.8.9)$$

In the last step above we used $1/(\partial T/\partial V)_p = (\partial V/\partial T)_p$ (see the proof (2) below of this general partial derivative relationship).

Thus, using the definitions of α and κ_T we get,

$$C_p = C_V - T \left(\frac{\partial V}{\partial T} \right)_p \frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = C_V - T \frac{(V\alpha)^2}{(-V\kappa_T)} \quad (1.8.10)$$

So

$$\boxed{C_V = C_p - \frac{TV\alpha^2}{\kappa_T}} \quad (1.8.11)$$

1) A general result for partial derivatives

Consider three variables satisfying a constraint, $f(x, y, z) = 0$. This means, for example, that we can solve for z as a function of x and y , or y as a function of x and z , or x as a function of z and y .

Because of this constraint there must exist a relation between the partial derivatives of these variables with respect to each other.

$$\text{constraint} \Rightarrow df = \left(\frac{\partial f}{\partial x} \right)_{y,z} dx + \left(\frac{\partial f}{\partial y} \right)_{x,z} dy + \left(\frac{\partial f}{\partial z} \right)_{x,y} dz = 0 \quad (1.8.12)$$

because x, y, z are constrained to vary such that $f = 0$ does not change.

If we then hold z constant, so that $dz = 0$, then dx and dy must vary such that,

$$\left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy = 0 \quad \Rightarrow \quad \left(\frac{\partial x}{\partial y}\right)_z = -\frac{(\partial f/\partial y)_{x,z}}{(\partial f/\partial x)_{y,z}} \quad (1.8.13)$$

Similarly, if we hold y constant, so that $dy = 0$, then dx and dz must vary such that,

$$\left(\frac{\partial z}{\partial x}\right)_y = -\frac{(\partial f/\partial x)_{y,z}}{(\partial f/\partial z)_{x,y}} \quad (1.8.14)$$

And if we hold x constant, so that $dx = 0$, then dy and dz must vary such that,

$$\left(\frac{\partial y}{\partial z}\right)_x = -\frac{(\partial f/\partial z)_{x,z}}{(\partial f/\partial y)_{x,z}} \quad (1.8.15)$$

Multiply these three results together and one finds,

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1} \quad (1.8.16)$$

2) Another general result for partial derivatives

Consider variables x, y , and z with some constraint among them. Solve for $x(y, z)$ as a function of y and z , and solve for $y(x, z)$ as a function of x and z .

Then we have,

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \quad \text{and} \quad dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \quad (1.8.17)$$

Suppose we vary dx keeping $dz = 0$. Then from the first of the above Eqs. (1.8.17) we have,

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy \quad \Rightarrow \quad \frac{dy}{dx} = \frac{1}{(\partial x/\partial y)_z} \quad (1.8.18)$$

From the second of Eqs. (1.8.17) we have,

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx \quad \Rightarrow \quad \frac{dy}{dx} = \left(\frac{\partial y}{\partial x}\right)_z \quad (1.8.19)$$

Comparing Eqs. (1.8.18) and (1.8.19) we conclude,

$$\boxed{\left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{(\partial x/\partial y)_z}} \quad (1.8.20)$$

3) And yet one more general result for partial derivatives

If z and y are functions of u and v , i.e. $z(u, v)$ and $y(u, v)$, then,

$$dz = \left(\frac{\partial z}{\partial u}\right)_v du + \left(\frac{\partial z}{\partial v}\right)_u dv \quad \text{and} \quad dy = \left(\frac{\partial y}{\partial u}\right)_v du + \left(\frac{\partial y}{\partial v}\right)_u dv \quad (1.8.21)$$

Then keeping v fixed, i.e. $dv = 0$, and dividing the first of the two equations above by the second, we have,

$$\boxed{\left(\frac{\partial z}{\partial y}\right)_v = \frac{(\partial z/\partial u)_v}{(\partial y/\partial u)_v}} \quad (1.8.22)$$

Returning to thermodynamics, we now wish to show how to write κ_S in terms of C_p , κ_T , and α . *Warning:* the calculation will not be pretty!

Consider the enthalpy $H(S, p)$. We have,

$$\left(\frac{\partial H}{\partial p}\right)_S = V(S, p) \quad (1.8.23)$$

Regarding V as a function of S and p we have,

$$dV = \left(\frac{\partial V}{\partial p}\right)_S dp + \left(\frac{\partial V}{\partial S}\right)_p dS \quad \Rightarrow \quad -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_S \left(\frac{\partial p}{\partial p}\right)_T - \frac{1}{V} \left(\frac{\partial V}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T \quad (1.8.24)$$

Since $(\partial p/\partial p)_T = 1$, using the definitions of κ_T and κ_S , the above becomes,

$$\kappa_T = \kappa_S - \frac{1}{V} \left(\frac{\partial V}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T \quad (1.8.25)$$

Now we can use (see proof (3) above for this general partial derivate relationship),

$$\left(\frac{\partial V}{\partial S}\right)_p = \frac{(\partial V/\partial T)_p}{(\partial S/\partial T)_p} \quad (1.8.26)$$

and the Maxwell relation,

$$\left(\frac{\partial S}{\partial p}\right)_T = -\frac{\partial^2 G}{\partial p \partial T} = -\left(\frac{\partial V}{\partial T}\right)_p \quad (1.8.27)$$

then Eq. (1.8.25) becomes,

$$\kappa_T = \kappa_S + \frac{1}{V} \frac{(\partial V/\partial T)_p}{(\partial S/\partial T)_p} \left(\frac{\partial V}{\partial T}\right)_p = \kappa_S + \frac{1}{V} \frac{(V\alpha)^2}{(C_p/T)} \quad (1.8.28)$$

and so we get,

$$\boxed{\kappa_S = \kappa_T - \frac{TV\alpha^2}{C_p}} \quad (1.8.29)$$

See Callen for a systematic way to reduce all such derivatives to combinations of C_p , κ_T , and α .

The trick in the above calculations is to remember what variable is a function of what other variables. For example, in the last example we wanted to view V as being a function of S and p . So we took V as being the derivative of the enthalpy $H(S, p)$, to get $V(S, p)$. Suppose we were doing a calculation where we wanted to regard V as being a function of T and p . Then we would use the Gibbs free energy $G(T, p)$ to write, $V(T, p) = (\partial G/\partial p)_T$.

But the main point is not to remember how we did all the steps above, but rather to remember that it can be done! There are only a finite number of independent second derivatives of the thermodynamic potentials (if we keep N

fixed, then there are only the three C_p , κ_T , and α), and so all other second derivatives can be expressed in terms of this finite number.

Finally we will end with one more useful relation involving the specific heat at constant volume.

We had the definition, $C_V = T \left(\frac{\partial S}{\partial T} \right)_V$.

Since energy E is a function of S and V , i.e. $E(S, V)$, then we have $dE = TdS - pdV$ (for fixed N). Divide each term by dT and keep $dV = 0$ to get,

$$\left(\frac{\partial E}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V = C_V \quad (1.8.30)$$

So we have,

$$\boxed{C_V = \left(\frac{\partial E}{\partial T} \right)_V} \quad (1.8.31)$$

C_V is the derivative of the energy with respect to temperature, at constant volume.