

2.G. Response Functions

As the name implies, a **response function** χ_c represents the response (i.e., change in some extensive quantity Q) of the system due to the change in an intensive state variable \mathcal{Y} (here in its role of a generalized force), while the variables in the list c are kept constant. In mathematical terms,

$$\chi_c = \left(\frac{\partial Q}{\partial \mathcal{Y}} \right)_c \quad (2.134a)$$

The most commonly used response functions are the heat capacity, susceptibility and expansivity.

2.G.1. Heat Capacities

The **heat capacity** C_c measures the heat change in response to a temperature change while c is kept constant.

$$C_c = \left(\frac{\bar{d}Q}{dT} \right)_c \quad (2.134b)$$

For a system with state variables

$$(\mathbf{x}, \mathcal{Y}) = (S, X, \{N_j\}; T, Y, \{\mu_j'\}) \quad (2.134c)$$

the 1st & 2nd laws for reversible processes give

$$\begin{aligned} \bar{d}Q &= T dS \\ &= dU - Y dX - \sum_j \mu_j' dN_j \end{aligned} \quad (2.134d)$$

$$\rightarrow C_c = \left(\frac{\partial U}{\partial T} \right)_c - Y \left(\frac{\partial X}{\partial T} \right)_c - \sum_j \mu_j' \left(\frac{\partial N_j}{\partial T} \right)_c \quad (2.134e)$$

which implies the independent variables of the system are (T, c) .

For example, let $c = (X, \{N_j\})$. Then

$$dU = \left(\frac{\partial U}{\partial T} \right)_{X, \{N_j\}} dT + \left(\frac{\partial U}{\partial X} \right)_{T, \{N_j\}} dX + \sum_j \left(\frac{\partial U}{\partial N_j} \right)_{T, X, \{N_{k \neq j}\}} dN_j \quad (2.134f)$$

and (2.134d) becomes

$$\begin{aligned} \bar{d}Q &= \left(\frac{\partial U}{\partial T} \right)_{X, \{N_j\}} dT + \left[\left(\frac{\partial U}{\partial X} \right)_{T, \{N_j\}} - Y \right] dX \\ &\quad + \sum_j \left[\left(\frac{\partial U}{\partial N_j} \right)_{T, X, \{N_{k \neq j}\}} - \mu_j' \right] dN_j \end{aligned} \quad (2.134)$$

so that

$$C_{X, \{N_j\}} = \left(\frac{\partial U}{\partial T} \right)_{X, \{N_j\}} \quad (2.135)$$

Actually, (2.135) can also be read off directly from (2.134d).

For $c = (Y, \{N_j\})$, we have

$$dX = \left(\frac{\partial X}{\partial T} \right)_{Y, \{N_j\}} dT + \left(\frac{\partial X}{\partial Y} \right)_{T, \{N_j\}} dY + \sum_j \left(\frac{\partial X}{\partial N_j} \right)_{T, Y, \{N_{k \neq j}\}} dN_j \quad (2.136)$$

Now, we wish to obtain a relation between $C_{X,\{N_j\}}$ & $C_{Y,\{N_j\}}$. Therefore, instead of using (2.134e), we put (2.136) into (2.134) to get

$$\begin{aligned} \bar{d}Q = & \left\{ C_{X,\{N_j\}} + \left[\left(\frac{\partial U}{\partial X} \right)_{T,\{N_j\}} - Y \right] \left(\frac{\partial X}{\partial T} \right)_{Y,\{N_j\}} \right\} dT \\ & + \left(\frac{\partial U}{\partial X} \right)_{T,\{N_j\}} - Y \left[\left(\frac{\partial X}{\partial Y} \right)_{T,\{N_j\}} dY \right. \\ & \left. + \sum_j \left\{ \left(\frac{\partial U}{\partial N_j} \right)_{T,X,\{N_{k \neq j}\}} - \mu_j + \left[\left(\frac{\partial U}{\partial X} \right)_{T,\{N_j\}} - Y \right] \left(\frac{\partial X}{\partial N_j} \right)_{T,Y,\{N_{k \neq j}\}} \right\} dN_j \right] \end{aligned} \quad (2.137)$$

so that

$$C_{Y,\{N_j\}} = C_{X,\{N_j\}} + \left[\left(\frac{\partial U}{\partial X} \right)_{T,\{N_j\}} - Y \right] \left(\frac{\partial X}{\partial T} \right)_{Y,\{N_j\}} \quad (2.138)$$

Consider now a system of n moles of a monatomic substance. Using lower case letters to denote molar quantities, we can write (2.135) as

$$c_{X,n} \equiv \frac{1}{n} C_{X,n} = \frac{1}{n} \left(\frac{\partial U}{\partial T} \right)_{X,n} = \left(\frac{\partial u}{\partial T} \right)_{X,n} \quad (2.138a)$$

Similarly, (2.138) becomes

$$c_{Y,n} \equiv \frac{1}{n} C_{Y,n} = c_{X,n} + \left[\left(\frac{\partial u}{\partial X} \right)_{T,n} - Y \right] \left(\frac{\partial X}{\partial T} \right)_{Y,n} \quad (2.138b)$$

Alternatively, we can also calculate C_c directly from the entropy. Thus, for reversible processes,

$$C_c = \left(\frac{\bar{d}Q}{dT} \right)_c = T \left(\frac{\partial S}{\partial T} \right)_c \quad (2.139a)$$

which implies

$$S = S(T, c) \quad (2.139b)$$

For example, setting $c = (X, \{N_j\})$ gives

$$dS = \left(\frac{\partial S}{\partial T} \right)_{X,\{N_j\}} dT + \left(\frac{\partial S}{\partial X} \right)_{T,\{N_j\}} dX + \sum_j \left(\frac{\partial S}{\partial N_j} \right)_{T,X,\{N_{k \neq j}\}} dN_j \quad (2.139c)$$

$$\rightarrow (\bar{d}Q)_{X,\{N_j\}} = T \left(\frac{\partial S}{\partial T} \right)_{X,\{N_j\}} dT \quad (2.140)$$

(2.139a) then becomes

$$\begin{aligned} C_{X,\{N_j\}} &= T \left(\frac{\partial S}{\partial T} \right)_{X,\{N_j\}} \\ &= -T \left(\frac{\partial^2 A}{\partial T^2} \right)_{X,\{N_j\}} \quad [(2.97) \text{ of } \S 2.F.3 \text{ used. }] \end{aligned} \quad (2.141)$$

Next, we set $c = (Y, \{N_j\})$ so that

$$dS = \left(\frac{\partial S}{\partial T} \right)_{Y,\{N_j\}} dT + \left(\frac{\partial S}{\partial Y} \right)_{T,\{N_j\}} dY + \sum_j \left(\frac{\partial S}{\partial N_j} \right)_{T,Y,\{N_{k \neq j}\}} dN_j \quad (2.142a)$$

$$\rightarrow C_{Y,\{N_j\}} = T \left(\frac{\partial S}{\partial T} \right)_{Y,\{N_j\}} \quad (2.142b)$$

$$= -T \left(\frac{\partial^2 G}{\partial T^2} \right)_{Y, \{N_j\}} \quad [(2.109) \text{ of } \S 2.F.4 \text{ used. }] \quad (2.144a)$$

In order to obtain a relation between $C_{X, \{N_j\}}$ & $C_{Y, \{N_j\}}$, we use

$$dX = \left(\frac{\partial X}{\partial T} \right)_{Y, \{N_j\}} dT + \left(\frac{\partial X}{\partial Y} \right)_{T, \{N_j\}} dY + \sum_j \left(\frac{\partial X}{\partial N_j} \right)_{T, Y, \{N_{k \neq j}\}} dN_j$$

to write (2.139c) as

$$\begin{aligned} dS = & \left[\left(\frac{\partial S}{\partial T} \right)_{X, \{N_j\}} + \left(\frac{\partial S}{\partial X} \right)_{T, \{N_j\}} \left(\frac{\partial X}{\partial T} \right)_{Y, \{N_j\}} \right] dT \\ & + \left(\frac{\partial S}{\partial X} \right)_{T, \{N_j\}} \left(\frac{\partial X}{\partial Y} \right)_{T, \{N_j\}} dY \\ & + \sum_j \left[\left(\frac{\partial S}{\partial N_j} \right)_{T, X, \{N_{k \neq j}\}} + \left(\frac{\partial S}{\partial X} \right)_{T, \{N_j\}} \left(\frac{\partial X}{\partial N_j} \right)_{T, Y, \{N_{k \neq j}\}} \right] dN_j \end{aligned} \quad (2.143a)$$

The coefficients of the differentials in (2.143a) & (2.142a) must be equal. Hence,

$$\left(\frac{\partial S}{\partial T} \right)_{Y, \{N_j\}} = \left(\frac{\partial S}{\partial T} \right)_{X, \{N_j\}} + \left(\frac{\partial S}{\partial X} \right)_{T, \{N_j\}} \left(\frac{\partial X}{\partial T} \right)_{Y, \{N_j\}} \quad (2.143b)$$

$$\left(\frac{\partial S}{\partial Y} \right)_{T, \{N_j\}} = \left(\frac{\partial S}{\partial X} \right)_{T, \{N_j\}} \left(\frac{\partial X}{\partial Y} \right)_{T, \{N_j\}} \quad (2.143c)$$

$$\left(\frac{\partial S}{\partial N_j} \right)_{T, X, \{N_{k \neq j}\}} = \left(\frac{\partial S}{\partial N_j} \right)_{T, X, \{N_{k \neq j}\}} + \left(\frac{\partial S}{\partial X} \right)_{T, \{N_j\}} \left(\frac{\partial X}{\partial N_j} \right)_{T, Y, \{N_{k \neq j}\}} \quad (2.143d)$$

Now, (2.143c) & (2.143d) are simply identities given in (2.7-8) of §2.B. (2.143b) gives the desired relation

$$C_{Y, \{N_j\}} = C_{X, \{N_j\}} + T \left(\frac{\partial S}{\partial X} \right)_{T, \{N_j\}} \left(\frac{\partial X}{\partial T} \right)_{Y, \{N_j\}} \quad (2.144)$$

Comparing (2.144) with (2.138) gives

$$\left(\frac{\partial S}{\partial X} \right)_{T, \{N_j\}} = \frac{1}{T} \left[\left(\frac{\partial U}{\partial X} \right)_{T, \{N_j\}} - Y \right] \quad (2.145)$$

$$= - \left(\frac{\partial Y}{\partial T} \right)_{X, \{N_j\}} \quad [(2.100) \text{ used. }] \quad (2.145a)$$

$\frac{\partial}{\partial T}$ (2.145 a) then gives

$$\begin{aligned} \left(\frac{\partial^2 Y}{\partial T^2} \right)_{X, \{N_j\}} &= - \left[\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial X} \right)_{T, \{N_j\}} \right]_{X, \{N_j\}} \\ &= - \left[\frac{\partial}{\partial X} \left(\frac{\partial S}{\partial T} \right)_{X, \{N_j\}} \right]_{T, \{N_j\}} \quad [(2.4) \text{ of } \S 2.B \text{ used. }] \\ &= - \left[\frac{\partial}{\partial X} \left(\frac{C_{X, \{N_j\}}}{T} \right) \right]_{T, \{N_j\}} \quad [(2.141) \text{ used. }] \\ &= - \frac{1}{T} \left(\frac{\partial C_{X, \{N_j\}}}{\partial X} \right)_{T, \{N_j\}} \end{aligned} \quad (2.146)$$

Consider now a system of n moles of a monatomic substance. Writing (2.141) in terms of molar quantities gives

$$c_x = T \left(\frac{\partial s}{\partial T} \right)_x = -T \left(\frac{\partial^2 a}{\partial T^2} \right)_x \quad (2.146a)$$

Similarly, (2.144) gives

$$c_Y = T \left(\frac{\partial s}{\partial T} \right)_Y = -T \left(\frac{\partial^2 g}{\partial T^2} \right)_Y \quad (2.146b)$$

Also, (2.145 & a) become

$$\left(\frac{\partial s}{\partial x} \right)_T = \frac{1}{T} \left[\left(\frac{\partial u}{\partial x} \right)_T - Y \right] = - \left(\frac{\partial Y}{\partial T} \right)_x$$

and (2.146) gives

$$\left(\frac{\partial^2 Y}{\partial T^2} \right)_x = - \frac{1}{T} \left(\frac{\partial c_x}{\partial x} \right)_T \quad (2.146c)$$

2.G.2. Susceptibilities & Expansivities

Susceptibility χ_c measures the change in an extensive mechanical variable X due to a change in its conjugate Y , while c is kept constant. It is defined as

$$\chi_c = \left(\frac{\partial X}{\partial Y} \right)_c \quad (2.147a)$$

Expansivity α_c measures the change in an extensive mechanical variable X due to a change in the temperature T , while c is kept constant. It is defined as

$$\alpha_c = \left(\frac{\partial X}{\partial T} \right)_c \quad (2.147b)$$

In particular,

$$\begin{aligned} \chi_{T, \{N_j\}} &= \left(\frac{\partial X}{\partial Y} \right)_{T, \{N_j\}} = \text{isothermal susceptibility.} & (2.147) \\ &= - \left(\frac{\partial^2 G}{\partial Y^2} \right)_{T, \{N_j\}} \quad [(2.110) \text{ used. }] \end{aligned}$$

$$\begin{aligned} \chi_{S, \{N_j\}} &= \left(\frac{\partial X}{\partial Y} \right)_{S, \{N_j\}} = \text{adiabatic susceptibility.} & (2.148) \\ &= - \left(\frac{\partial^2 H}{\partial Y^2} \right)_{S, \{N_j\}} \quad [(2.86) \text{ used. }] \end{aligned}$$

For a PVT system, i.e., $X = V$, it is more common to make use of the intensive (or density) version of these responses defined by

$$\begin{aligned} \kappa_{T, \{N_j\}} &= - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T, \{N_j\}} = \text{isothermal compressibility.} & (2.153) \\ &= - \frac{1}{V} \left(\frac{\partial^2 G}{\partial P^2} \right)_{T, \{N_j\}} \end{aligned}$$

$$\begin{aligned} \kappa_{S, \{N_j\}} &= - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{S, \{N_j\}} = \text{adiabatic compressibility.} & (2.154) \\ &= - \frac{1}{V} \left(\frac{\partial^2 H}{\partial P^2} \right)_{S, \{N_j\}} \end{aligned}$$

and

$$\alpha_{P, \{N_j\}} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P, \{N_j\}} = \text{thermal expansivity.} \quad (2.155)$$

If the system is monatomic, (2.153-5) simplify to

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T \quad (2.155a)$$

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_S \quad (2.155b)$$

$$\alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P \quad (2.155c)$$

The proof for the following identities is left as a homework problem.

$$\chi_{T, \{N_j\}} (C_{Y, \{N_j\}} - C_{X, \{N_j\}}) = T (\alpha_{Y, \{N_j\}})^2 \quad (2.150)$$

$$C_{Y, \{N_j\}} (\chi_{T, \{N_j\}} - \chi_{S, \{N_j\}}) = T (\alpha_{Y, \{N_j\}})^2 \quad (2.151)$$

$$\frac{C_{Y, \{N_j\}}}{C_{X, \{N_j\}}} = \frac{\chi_{T, \{N_j\}}}{\chi_{S, \{N_j\}}} \quad (2.152)$$

Ex. 2.8.

Compute c_v , c_p , κ_T , κ_S and α_P for a monatomic ideal gas using

$$s = \frac{5}{2} R + R \ln \left[\frac{v}{v_0} \left(\frac{T}{T_0} \right)^{3/2} \right] \quad (1a)$$

$$Pv = RT \quad (1b)$$

Answer

(a) The molar heat capacity c_v :

$$T \left(\frac{\partial (1a)}{\partial T} \right)_v \text{ gives}$$

$$c_v = T \left(\frac{\partial s}{\partial T} \right)_v = T \left(\frac{3}{2} \frac{R}{T} \right) = \frac{3}{2} R$$

(b) The molar heat capacity c_p :

Using (1b) to eliminate v in (1a) gives

$$s = \frac{5}{2} R + R \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right]$$

$$\rightarrow c_p = T \left(\frac{\partial s}{\partial T} \right)_P = T \left(\frac{5}{2} \frac{R}{T} \right) = \frac{5}{2} R$$

(c) The isothermal compressibility κ_T :

Using (1b), we have

$$\kappa_T = -\frac{1}{v} \left[\frac{\partial}{\partial P} \left(\frac{RT}{P} \right) \right]_T = -\frac{RT}{v} \left(-\frac{1}{P^2} \right) = \frac{1}{P}$$

(d) The adiabatic compressibility κ_S :

Using (1b) to eliminate T in (1a) gives

$$s = \frac{5}{2}R + R \ln \left[\left(\frac{P}{P_0} \right)^{3/2} \left(\frac{V}{V_0} \right)^{5/2} \right]$$

which is inverted to give

$$V = V_0 \left(\frac{P_0}{P} \right)^{3/5} \exp \left(\frac{2s}{5R} - 1 \right)$$

$$\rightarrow \kappa_s = -\frac{1}{V} \left(-\frac{3}{5P} V \right) = \frac{3}{5P}$$

(e) The thermal expansivity α_P :

Using (1b), we have

$$\alpha_P = \frac{1}{V} \left[\frac{\partial}{\partial T} \left(\frac{RT}{P} \right) \right]_P = \frac{R}{VP} = \frac{1}{T}$$