Basic Thermodynamics

Handout 6

Maxwell's relations

The **Maxwell relations** follow straightforwardly from the exact differentials of the thermodynamic potentials:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$
$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$
$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

(Don't memorize them, remember how to derive them!)

Useful maths

Partial derivatives: Consider x as a function of two variables y and z. This can be written $x = x(y, z)$ and we have that

$$\mathrm{d}x = \left(\frac{\partial x}{\partial y}\right)_z \mathrm{d}y + \left(\frac{\partial x}{\partial z}\right)_y \mathrm{d}z. \qquad (1)$$

But rearranging $x = x(y, z)$ can lead to having z as a function of x and y so that $z = z(x, y)$ in which case

$$\mathrm{d}z = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y. \qquad (2)$$

Substituting (2) into (1) gives

$$\mathrm{d}x = \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left[\left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x\right] \mathrm{d}y.$$

The terms multiplying $\mathrm{d}x$ must equal unity, giving the **reciprocal theorem**:

$$\boxed{\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}}$$

and the terms multiplying $\mathrm{d}y$ must vanish, giving the **reciprocity theorem**:

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

Thermodynamic coefficients and moduli

Heat capacities:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V, \qquad C_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

Compressibilities:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T, \qquad \kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$$

Bulk moduli:

$$B_T = \frac{1}{\kappa_T} = -V\left(\frac{\partial p}{\partial V}\right)_T, \qquad B_S = \frac{1}{\kappa_S} = -V\left(\frac{\partial p}{\partial V}\right)_S$$

Thermal expansivities:

$$\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \qquad \beta_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S$$

Relations between coefficients and moduli

- $C_p - C_v = VT\beta_p^2/\kappa_T$
- $\kappa_T/\kappa_S = C_p/C_V = \gamma$

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