Basic Thermodynamics

Handout 4

Thermodynamics potentials

Define the **enthalpy** $\boxed{H = U + PV}$

Define the **Helmholtz function** $\boxed{F = U - TS}$ (sometimes called Helmholtz free energy)

Define the **Gibbs function** $\boxed{G = H - TS}$ (sometimes called the Gibbs free energy).

These are all functions of state, so that one can write down the following **exact differentials**:

$$\boxed{\begin{aligned} \mathrm{d}U &= T\mathrm{d}S - p\mathrm{d}V \\ \mathrm{d}H &= T\mathrm{d}S + V\mathrm{d}p \\ \mathrm{d}F &= -S\mathrm{d}T - p\mathrm{d}V \\ \mathrm{d}G &= -S\mathrm{d}T + V\mathrm{d}p \end{aligned}}$$

Note that each thermodynamic potential has a pair of independent variables:

$U = U(S, V)$; $H = H(S, p)$; $F = F(T, V)$; $G = G(T, p)$

These can be used to immediately write down various expressions such as

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \qquad p = -\left(\frac{\partial F}{\partial V}\right)_T$$

This can be used to derive expressions such as:

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\left(\frac{\partial}{\partial T}\right)_V \frac{F}{T}$$

Maxwell's relations

The **Maxwell relations** follow straightforwardly from the exact differentials:

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

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

Thermodynamic equilibrium

Consider a p–V system in contact with a large reservoir which is in equilibrium at temperature T_0 and pressure p_0. The **availability** is defined by

$$A = U - T_0 S + p_0 V \tag{1}$$

The equilibrium state of the system is achieved by minimizing A.

For the following particular cases, minimizing A corresponds to

- system is thermally isolated and has fixed V — maximize S
- system has fixed T and V — minimize F
- system has fixed T and p — minimize G

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

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

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

$$\mathrm{d}z = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y. \tag{3}$$

Substituting (3) into (2) 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 $\mathrm{d}x$ give 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 $\mathrm{d}z$ give the **reciprocity theorem**:

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

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