Basic Thermodynamics

Handout 5

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:

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

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:

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

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

ATB
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