Chemical potential

Definition

The **chemical potential** controls the flow of particles between different parts of a system, just like temperature controls the flow of heat. It is defined by

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}. \tag{1}$$

In lectures, we considered a pV system made up of two parts in contact such that the two parts can exchange internal energy, volume and particles. We applied the entropy maximum statement of the Second Law to show that, in equilibrium,

$$\left(\frac{\partial S_1}{\partial U_1}\right)_{V,N} = \left(\frac{\partial S_2}{\partial U_2}\right)_{V,N}$$

$$\left(\frac{\partial S_1}{\partial V_1}\right)_{U,N} = \left(\frac{\partial S_2}{\partial V_2}\right)_{U,N}$$

$$\left(\frac{\partial S_1}{\partial N_1}\right)_{U,V} = \left(\frac{\partial S_2}{\partial N_2}\right)_{U,V}. \tag{2}$$

From the definitions of T, p and μ [the latter in eqn. (1)], these conditions may be expressed

$$T_1 = T_2, \qquad p_1 = p_2, \qquad \mu_1 = \mu_2.$$

Thermodynamic potentials

With a variable number of particles of a single type, the fundamental eq. takes the form

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N. \tag{3}$$

The Helmholtz and Gibbs functions follow:

$$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}N \tag{4}$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}N. \tag{5}$$

Hence,

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{p,T}. \tag{6}$$

G is extensive and may be written $G = Ng(p,T)$. Therefore, from (6),

$$G = \mu N. \tag{7}$$

If more than one type of particle is present, eqs. (3)–(7) generalise to

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i \;\; \text{etc, and} \;\; G = \sum_i \mu_i N_i \tag{8}$$

Gibbs–Duhem equation

Differentiating (7) and equating to (5), we obtain

$$\mathrm{d}\mu = -s\mathrm{d}T + v\mathrm{d}p, \tag{9}$$

where $s = S/N$ and $v = V/N$ are the entropy and volume per particle, respectively. Eqn. (9) relates the intensive variables of a system and is known as the **Gibbs–Duhem equation**. The generalisation to many components is

$$\sum_i x_i \mathrm{d}\mu_i = -s\mathrm{d}T + v\mathrm{d}p, \tag{10}$$

where $x_i = N_i/N$.

Phase equilibrium

It can be shown that for a two-component system, equilibrium is reached when $\mu_1 = \mu_2$. This is true for any constraints imposed on the system. Consider the phase boundary in the $p - T$ plane for a discontinuous phase transition, e.g. liquid–vapour or solid–liquid. All along the phase boundary $\mu_1 = \mu_2$, so if two nearby points on the phase boundary are separated by intervals $\mathrm{d}p$ and $\mathrm{d}T$, then $\mathrm{d}\mu_1 = \mathrm{d}\mu_2$. Therefore, from (9),

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{L}{T\Delta V}. \tag{11}$$

This is the **Clausius–Clapeyron equation**. Here, $L = T\Delta S$ is the latent heat. Note that L and ΔV must both be normalised consistently, e.g. both per mole, or both per unit mass.

The Clausius–Clapeyron equation can be integrated to obtain the equation of the phase boundary in the $p - T$ plane. For the liquid–vapour phase boundary the result is

$$p \approx p_0 e^{-\frac{L}{RT}} \tag{12}$$

assuming L is a constant and $pV_{\mathrm{vap}} = RT$. On the liquid–solid phase boundary the result is

$$p \approx p_0 + \frac{L}{\Delta V}\ln(\frac{T}{T_0}) \tag{13}$$
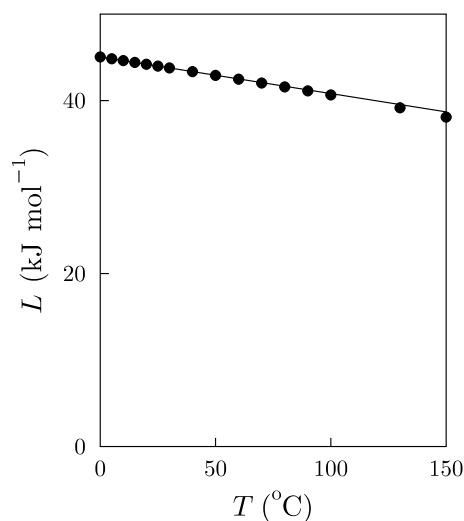
assuming L and ΔV are constant.

In general, L is only approximately constant. For the liquid–vapour phase boundary, the temperature dependence of L is approximately

$$L(T) = \Delta C_p T + L_0, \tag{14}$$

where $\Delta C_p = C_{p_{\mathrm{vap}}} - C_{p_{\mathrm{liq}}}$. Equation (14) follows from eqn. (11) assuming (i) that the vapour is an ideal gas, (ii) that $V_{\mathrm{vap}} >> V_{\mathrm{liq}}$, and (iii) that the heat capacities of the two phases are independent of temperature. ΔC_p would usually be negative since $L \to 0$ as $T \to T_c$.

The figure shows the temperature dependence of L for water. The observed linear variation with negative gradient is consistent with (14).

[Figure courtesy of S.J. Blundell & K.M. Blundell, *Concepts in Thermal Physics*, (OUP, 2006)]