Chemical Potential and Particle Exchange

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1 Equilibrium of Two Interacting Systems

Consider two systems, A and B, separated by a porous barrier which allows the two systems to exchange both energy and particles. Let the systems equilibrate.

The macroscopic state of the combined system is characterized by the total energy E_{tot}, total volume V_{tot}, and total number of particles N_{tot}, all of which are fixed:

$$V_{\text{tot}} = V_A + V_B = \text{constant} \tag{1}$$

$$E_{\text{tot}} = E_A + E_B = \text{constant} \tag{2}$$

$$N_{\text{tot}} = N_A + N_B = \text{constant} \tag{3}$$

Because the total quantities are conserved, a change in system A implies an equal and opposite change in system B (e.g., $dE_B = -dE_A$, $dN_B = -dN_A$).

The combined system will equilibrate by maximizing the total entropy, $S_{\text{tot}} = S_A + S_B$. At equilibrium, the derivatives of the total entropy with respect to the state variables of system A must be zero:

1. Energy Exchange (Thermal Equilibrium):

$$\left.\frac{\partial S_{\text{tot}}}{\partial E_A}\right|_{N_A,V_A} = 0 \implies \frac{\partial S_A}{\partial E_A} + \frac{\partial S_B}{\partial E_B}\frac{\partial E_B}{\partial E_A} = 0 \tag{4}$$

Since $\frac{\partial E_B}{\partial E_A} = -1$, this gives:

$$\frac{\partial S_A}{\partial E_A} = \frac{\partial S_B}{\partial E_B} \implies \frac{1}{T_A} = \frac{1}{T_B} \tag{5}$$

Thus, temperatures are equal at equilibrium.

2. Volume Exchange (Mechanical Equilibrium):

$$\left.\frac{\partial S_{\text{tot}}}{\partial V_A}\right|_{N_A,E_A} = 0 \implies \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_B}\frac{\partial V_B}{\partial V_A} = 0 \tag{6}$$

Since $\frac{\partial V_B}{\partial V_A} = -1$, this gives:

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B} \implies \frac{P_A}{T_A} = \frac{P_B}{T_B} \tag{7}$$

Since $T_A = T_B$, the pressures must be equal ($P_A = P_B$).

3. Particle Exchange (Chemical Equilibrium):

$$\left.\frac{\partial S_{\text{tot}}}{\partial N_A}\right|_{E_A,V_A} = 0 \implies \frac{\partial S_A}{\partial N_A} + \frac{\partial S_B}{\partial N_B}\frac{\partial N_B}{\partial N_A} = 0 \tag{8}$$

Since $\frac{\partial N_B}{\partial N_A} = -1$, this gives the condition:

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \tag{9}$$

What physical quantity does this derivative represent?

2 Defining the Chemical Potential

To interpret the derivative with respect to particle number, we define a new quantity called the **chemical potential**, denoted by μ:

$$\boxed{\mu \equiv -T \left(\frac{\partial S}{\partial N} \right)_{E,V}} \tag{10}$$

- The temperature T is included so that μ has the units of energy.
- The negative sign is a convention that ensures μ behaves like familiar potential energies.

Using this definition, the condition for particle equilibrium $\left(\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \right)$ can be rewritten. Since we already established that $T_A = T_B$ at equilibrium:

$$-\frac{\mu_A}{T_A} = -\frac{\mu_B}{T_B} \implies \mu_A = \mu_B \tag{11}$$

At equilibrium, the chemical potentials of the two systems must be equal.

3 Non-Equilibrium and Particle Flow

What happens when the systems are *not* in equilibrium?

The system with the larger value of $\left(\frac{\partial S}{\partial N}\right)$ will gain particles. This is because adding a particle to the system with a steep entropy gradient will generate more entropy than is lost by removing a particle from the other system, thereby increasing S_{tot} and satisfying the Second Law.

Because of the minus sign in our definition ($\mu = -T\frac{\partial S}{\partial N}$), a larger $\frac{\partial S}{\partial N}$ means a **smaller** chemical potential μ.

Therefore, to maximize entropy, **particles will spontaneously flow from the system with higher μ into the system with lower μ.**

This matches our intuition for potential energy in other fields: particles flow from regions of high potential to regions of low potential, just like mass moving in a gravitational field or positive charge moving in an electric field.

4 The Revised First Law of Thermodynamics

Now that we allow the number of particles N to vary, the entropy is a function of three macroscopic variables: $S(E, V, N)$. We can write its total differential as:

$$dS = \left(\frac{\partial S}{\partial E} \right)_{V,N} dE + \left(\frac{\partial S}{\partial V} \right)_{E,N} dV + \left(\frac{\partial S}{\partial N} \right)_{E,V} dN \tag{12}$$

Substituting our thermodynamic definitions for temperature, pressure, and chemical potential:

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN \tag{13}$$

Multiplying the entire equation by T and rearranging to solve for dE yields the fundamental thermodynamic identity (the revised First Law):

$$\boxed{dE = TdS - PdV + \mu dN} \tag{14}$$

This equation relates the change in internal energy to heat transfer (TdS), mechanical work ($-PdV$), and chemical work (μdN). From the above, we have that the chemical potential can be written as

$$\mu = \left.\frac{\partial E}{\partial N}\right|_{S,V}. \tag{15}$$

This makes clear that **the chemical potential is the energy cost of adding a particle to the system**, at fixed entropy and volume. In terms of the Helmholtz free energy $F = \langle E \rangle - TS$, we have

$$dF = -SdT - PdV + \mu dN, \tag{16}$$

from which we obtain a different expression for the chemical potential

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V}. \tag{17}$$