

5.2: Thermodynamic Equilibrium

The second law of thermodynamics implies that entropy does not decrease in any natural process. The final equilibrium state will thus be the state of maximum possible entropy. After attaining this maximum possible value, the entropy will remain constant. The criterion for equilibrium may thus be written as

$$\delta S = 0 \quad (5.2.1)$$

We can take S to be a function of U , V and N . The system, starting in an arbitrary state, adjusts U , V and N among its different parts and constitutes itself in such a way as to maximize entropy. Consider the system subdivided into various smaller subsystems, say, indexed by $i = 1, \dots, n$. The thermodynamic quantities for each such unit will be indicated by a subscript i . For an isolated system, the total internal energy, the total volume and the total number of particles will be fixed, so that the changes in the subsystems must be constrained as

$$\sum_i \delta U_i = 0, \quad \sum_i \delta V_i = 0, \quad \sum_i \delta N_i = 0 \quad (5.2.2)$$

Since S is extensive, $S = \sum_i S_i$ where $S_i = S_i(U_i, V_i, N_i)$. We can now maximize entropy subject to the constraints Equation 5.2.2 by considering the maximization of

$$S = \sum_i S_i - \lambda_1 \left(\sum_i U_i - U \right) - \lambda_2 \left(\sum_i V_i - V \right) - \lambda_3 \left(\sum_i N_i - N \right) \quad (5.2.3)$$

where the Lagrange multipliers $\lambda_1, \lambda_2, \lambda_3$ enforce the required constraints. The variables U_i, V_i and N_i can now be freely varied. Thus, for the condition of equilibrium, we get

$$dS = \sum_i \left[\left(\frac{\partial S}{\partial U_i} \right) - \lambda_1 \right] dU_i + \left[\left(\frac{\partial S}{\partial V_i} \right) - \lambda_2 \right] dV_i + \left[\left(\frac{\partial S}{\partial N_i} \right) - \lambda_3 \right] dN_i = 0 \quad (5.2.4)$$

Since the variations are now independent, this gives, for equilibrium,

$$\left(\frac{\partial S}{\partial U_i} \right) = \lambda_1, \quad \left(\frac{\partial S}{\partial V_i} \right) = \lambda_2, \quad \left(\frac{\partial S}{\partial N_i} \right) = \lambda_3 \quad (5.2.5)$$

This can be rewritten as

$$\frac{1}{T_i} = \lambda_1, \quad \frac{p_i}{T_i} = \lambda_2, \quad \frac{\mu_i}{T_i} = \lambda_3 \quad (5.2.6)$$

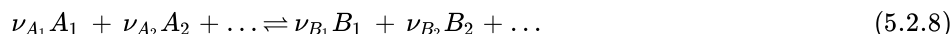
where we used

$$dS = \frac{dU}{T} + \frac{p}{T} dV - \frac{\mu}{T} dN \quad (5.2.7)$$

Equation 5.2.6 tells us that, for equilibrium, the temperature of all subsystems must be the same, the pressure in different subsystems must be the same and the chemical potential for different subsystems must be the same.

Reaction Equilibrium

Suppose we have a number of constituents $A_1, A_2, \dots, B_1, B_2, \dots$, at constant temperature and pressure which undergo a reaction of the form



The entropy of the system is of the form

$$S = \sum_k S_k(N_k) \quad (5.2.9)$$

where the summation covers all A 's and B 's. Since the temperature and pressure are constant, reaction equilibrium is obtained when the N_k change so as to maximize the entropy. This gives

$$dS = \frac{1}{T} \sum_k \mu_k dN_k = 0 \quad (5.2.10)$$

The quantities dN_k are not independent, but are restricted by the reaction. When the reaction happens, ν_{A_1} of A_1 -particles must be destroyed, ν_{A_2} of A_2 -particles must be destroyed, etc., while ν_{B_1} of B_1 particles are produced, etc. Thus we can write

$$dN_{A_1} = -\nu_{A_1} dN_0, \quad dN_{A_2} = -\nu_{A_2} dN_0, \dots, \quad dN_{B_1} = \nu_{B_1} dN_0, \quad dN_{B_2} = \nu_{B_2} dN_0, \dots, \text{ etc.} \quad (5.2.11)$$

where dN_0 is arbitrary. The condition of equilibrium thus reduces to

$$-\sum_A \nu_{A_i} \mu_{A_i} + \sum_B \nu_{B_i} \mu_{B_i} = 0 \quad (5.2.12)$$

With the understanding that the ν 's for the reactants will carry a minus sign while those for the products have a plus sign, we can rewrite this as

$$\sum_k \nu_k \mu_k = 0 \quad (5.2.13)$$

This condition of reaction equilibrium can be applied to chemical reactions, ionization and dissociation processes, nuclear reactions, etc.

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