Pressure

$$\boxed{dS = (1/T)\,dU + (P/T)\,dV - (\mu_1/T)\,dN + \ldots}$$

If matter cannot flow between the system and its environment but the volume of the system is unconstrained, then variation of the total entropy of the system of interest and its environment can be written as:

$$dS = (1/T_1)\,dU_1 + (P_1/T_1)\,dV_1 + (1/T_e)\,dU_e + (P_e/T_e)\,dV_e$$

Pressure

$$dS = 1/T_1 * dU_1 + P_1/T_1 * dV_1 + 1/T_e * dU_e + P_e/T_e * dV_e$$

Since both the total internal energy $U = U_1 + U_e$ and the total volume $V = V_1 + V_e$ of the system plus its environment are conserved:

$$dU_e = - dU_1 \qquad dV_e = - dV_1$$

$$dS = (1/T_1 - 1/T_e) * dU_1 + (P_1/T_1 - P_e/T_e)* dV_1$$

In equilibrium, $dS = 0$ for ***arbitrary*** dU_1 and dV_1 , so $T_1 = T_e$ as well as $\mathbf{P_1 = P_e}$

Electrochemical Potential

$$\boxed{dS = 1/T * dU + P/T * dV - \mu_1/T * dN + \ldots}$$

If volume of a system is fixed but particles of one kind can flow between the system and its environment, then variation of the total entropy of the system of interest and its environment can be written as:

$$dS = (1/T_1)\ dU_1 - (\mu_1/T_1)\ dN_1 + (1/T_e)\ dU_e - (\mu_e/T_e)\ \ dN_e$$

Electrochemical Potential

$$dS = 1/T_1 * dU_1 - \mu_1/T_1 * dN_1 + 1/T_e * dU_e - \mu_e/T_e * dN_e$$

Since both the total internal energy $U = U_1 + U_e$ and the total number of particles $N = N_1 + N_e$ of the system plus its environment are conserved:

$$dU_e = - dU_1 \qquad dN_e = - dN_1$$

$$dS = (1/T_1 - 1/T_e) * dU_1 - (\mu_1/T_1 - \mu_e/T_e) * dN_1$$

In equilibrium, $dS = 0$ for ***arbitrary*** dU_1 and dN_1 , so $T_1 = T_e$ as well as $\boldsymbol{\mu_1 = \mu_e}$

Exercise: show that matter flows from high chemical potential to low chemical potential.

Chemical Equilibrium

A chemical reaction: $2 * H_2 + O_2 \Leftrightarrow 2 * H_2O$ **or**

$2 * H_2 + 1 * O_2 - 2 * H_2O \Leftrightarrow 0$

Any generic 3-component reaction : $v_1 * A_1 + v_2 * A_2 + v_3 * A_3 \Leftrightarrow 0$

Any reaction : $\Sigma v_j * A_j \Leftrightarrow 0$

Here A_j stands for any chemical substance and v_j are stoichiometric coefficients determined from the condition of conservation of atoms of a given type in a reaction.

Chemical Equilibrium

The final products of a chemical reaction must be in equilibrium.

If we consider a closed isolated system of fixed volume and internal energy, then there is no interaction with the environment.

Since the environment is absent, the entropy of the system alone has to be maximum in equilibrium with respect to its internal unconstrained coordinates (N_1, N_2 …). The system is its own environment in this case:

$$\boxed{dS = 1/T * dU + P/T * dV - \mu_1/T * dN_1 + \ldots} \Rightarrow dS = - \mu_1/T * dN_1 - \mu_2/T * dN_2 \ldots$$

$dV = 0 \quad dU = 0$

Chemical Equilibrium

In equilibrium, $dS = 0$, therefore: $$dS = - \Sigma\, \mu_j/T * dN_j = 0$$

Conservation of the total number of each atomic species in chemical reactions demands:

$$dN_j = v_j * dN$$

where dN is some number that is the same for all chemical components of the reaction (characterizes the extent of the reaction)

$$dS = - \Sigma\, v_j * \mu_j/T * dN = 0 \longrightarrow \boxed{\Sigma\, v_j * \mu_j = 0}$$

Therefore, not all chemical potentials are independent from each other in a chemical reaction.

Chemical Equilibrium: Example

Let us consider a chemical reaction of the form: $2A+B \Leftrightarrow C$, where $C = A_2B$

Let us assume that we know the fundamental relation for this system in the entropy representation (this is a highly idealized example but illustrates the method):

$$S = N*\ln(U) - \Sigma N_i*\ln(N_i/N)$$

Entropy of mixing

where: $N = N_A+N_B+N_C$, $N_i = (N_A,N_B,N_C)$

Initial conditions: $N_{A0}=2$, $N_{B0}=1$, $N_{C0}=0$, $T = T_0$

Here U is dimensionless for simplicity

Questions:

What are the mole numbers of A, B and C in equilibrium?
What is the temperature of the system in equilibrium?
What is the temperature change of the system after completion of the reaction?

Chemical Equilibrium: Example

Note that this idealized example reaction is done under conditions of constant volume and constant total energy. In usual chemical reactions pressure and temperature are held constant – we will study these types of reactions later.

$$S = N*\ln(U)-\Sigma N_i*\ln(N_i/N)$$

$$dS = 1/T * dU + P/T * dV - \mu_A/T * dN_A - \mu_B/T * dN_B - \ldots$$

$$\Downarrow$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N_A, N_B, N_C} = \frac{N}{U} \qquad \Rightarrow \qquad T = \frac{U}{N}$$

Chemical Equilibrium: Example

$$S = N*\ln(U)-\Sigma N_i*\ln(N_i/N)$$

$$dS = 1/T * dU + P/T * dV - \mu_A/T * dN_A - \mu_B/T * dN_B - \ldots$$

Definition of
chemical potential

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

Show this
(good math exercise)

$$\mu_i = -T\left(\ln(U) - \ln(N_i/N)\right)$$

$$\mu_i = -\frac{U}{N}\ln(U) + \frac{U}{N}\ln(N_i/N)$$

Chemical Equilibrium: Example

From the chemical equilibrium relation $\Sigma\, v_j{*}\mu_j = 0$ we derive:

$$\mu_i = -\frac{U}{N}\ln(U) + \frac{U}{N}\ln(N_i / N)$$

$$\sum_i \nu_i \mu_i = -\frac{2U}{N}\ln(U) + \frac{U}{N}\ln\left(\frac{N_A^2 N_B}{N_C N^2}\right) = 0$$

Conservation of atomic species gives:

$N_A + 2{*}N_C = 2 = const$ $\qquad$ $N_B + N_C = 1 = const$

These three equations along with the initial conditions for the mole numbers can be solved to give the equilibrium mole numbers N_A, N_B and N_C.

Chemical Equilibrium: Example

$$\sum_i \nu_i \mu_i = -\frac{2U}{N}\ln(U) + \frac{U}{N}\ln\left(\frac{N_A^2 N_B}{N_C N^2}\right) = 0$$

Eliminating N_A and N_B ⬇

$$\ln\left(\frac{4(1-N_C)^3}{N_C\left(3-2N_C\right)^2}\right) = 2\ln(U)$$

⬇

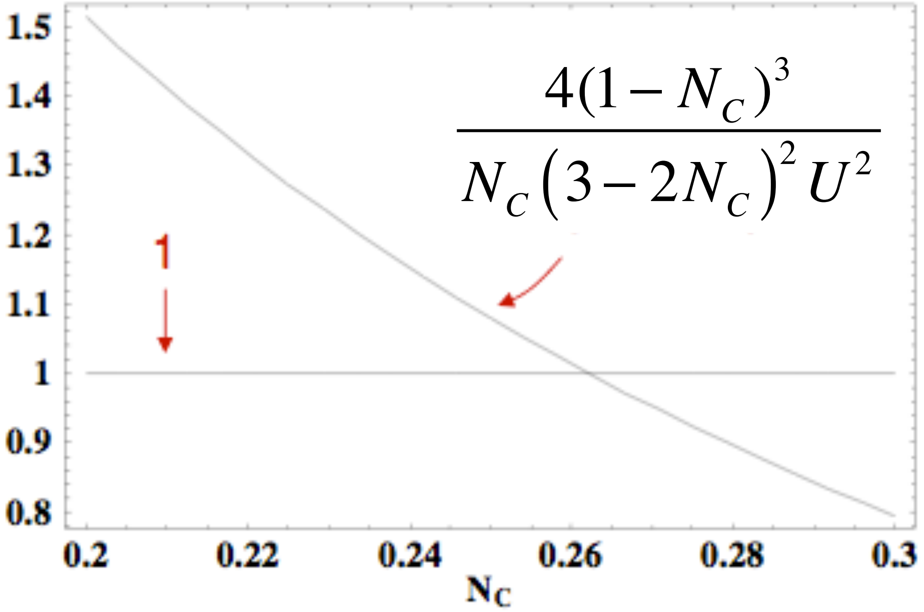
$$\frac{4(1-N_C)^3}{N_C\left(3-2N_C\right)^2 U^2} = 1$$

Chemical Equilibrium: Example

Example: $U = \text{Exp}(9)$

Let us graphically solve the chemical equilibrium condition:

$$\frac{4(1-N_C)^3}{N_C(3-2N_C)^2U^2} = 1$$



N_C=0.263 N_A=1.474 N_B=0.737

Chemical Equilibrium: Example

Let us now find the temperature of the system before and after the chemical reaction

$$T = \frac{U}{N}$$

Initial temperature: $$T_0 = \frac{U}{2+1+0} = \frac{U}{3}$$

Final temperature: $$T_F = \frac{U}{1.474+0.737+0.263} = \frac{U}{2.474} = \frac{3}{2.474}T_0 = 1.21T_0$$

Temperature of the system increased in the reaction

The chemical equilibrium condition $\Sigma\, v_j{*}\mu_j = 0$ allowed us to find the final reaction products and the variation of temperature in a chemical reaction.

The Euler Equation

Using the additive property of the internal energy U, we can derive a useful thermodynamic relation – the Euler equation.

$$U\left(\lambda \cdot S, \lambda \cdot V, \lambda \cdot N_1, \ldots \lambda \cdot N_m\right) = \lambda \cdot U\left(S, V, N_1, \ldots N_m\right)$$

Let us differentiate this “extensivity condition” with respect to λ:

$$\frac{\partial U(\lambda \cdot S, \ldots)}{\partial(\lambda \cdot S)} \cdot \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U(\lambda \cdot S, \ldots)}{\partial(\lambda \cdot V)} \cdot \frac{\partial(\lambda V)}{\partial \lambda} + \frac{\partial U(\lambda \cdot N_1, \ldots)}{\partial(\lambda \cdot N_1)} \cdot \frac{\partial(\lambda N_1)}{\partial \lambda} + \ldots + \frac{\partial U(\lambda \cdot N_m, \ldots)}{\partial(\lambda \cdot N_m)} \cdot \frac{\partial(\lambda N_m)}{\partial \lambda}$$

$$= U(S, V, N_1, \ldots N_m)$$

The Euler Equation

$$\frac{\partial U(\lambda \cdot S,\ldots)}{\partial(\lambda \cdot S)} \cdot S + \frac{\partial U(\lambda \cdot S,\ldots)}{\partial(\lambda \cdot V)} \cdot V + \frac{\partial U(\lambda \cdot N_1,\ldots)}{\partial(\lambda \cdot N_1)} \cdot N_1 + \ldots + \frac{\partial U(\lambda \cdot N_m,\ldots)}{\partial(\lambda \cdot N_m)} \cdot N_m = U(S,V,N_1,\ldots N_m)$$

Setting $\lambda=1$ in the above equation, we obtain:

$$\frac{\partial U}{\partial S} \cdot S + \frac{\partial U}{\partial V} \cdot V + \frac{\partial U}{\partial N_1} \cdot N_1 + \ldots + \frac{\partial U}{\partial N_m} \cdot N_m = U$$

Using the definition of the intensive parameters, we arrive at the Euler equation:

$$\boxed{U = TS - PV + \mu_1 N_1 + \ldots + \mu_m N_m}$$

The Gibbs-Duhem Relation

Extensive thermodynamic coordinates (U, S, V, N …) are related to each other by the fundamental relation:

Euler equation form of the fundamental relation

$$U = U(S, V, N_1, \ldots, N_m) \quad \Rightarrow \quad \boxed{U = TS - PV + \mu_1 N_1 + \ldots + \mu_m N_m}$$

It turns out that intensive coordinates (whose number is one less than the number of extensive coordinates counting U) are also not all independent from each other. The first differential of the Euler equation (according to the rules of calculus):

we obtain: $dU = TdS + SdT - PdV - VdP + \mu_1 dN_1 + N_1 d\mu_1 + \ldots$

The Gibbs-Duhem Relation

$$dU = TdS + SdT - PdV - VdP + \mu_1 dN_1 + N_1 d\mu_1 + \ldots$$

Now, if we subtract the most general form of the first differential of the fundamental relation U(S,V,…) from the expression above:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N_1,\ldots} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N_1,\ldots} dV + \left(\frac{\partial U}{\partial N_1}\right)_{S,V,N_1,\ldots} dN_1 + \ldots$$

$$dU = TdS - PdV + \mu_1 dN_1 + \ldots$$

we derive the Gibbs-Duhem relation:

$$\boxed{SdT - VdP + N_1 d\mu_1 + \ldots = 0}$$