

Unit 2-19: Chemical Equilibrium and an Example: A Gas in Equilibrium with Adsorption Sites

Suppose we have the following chemical reaction among species A_1 , A_2 , and A_3 ,



What determines the equilibrium concentrations of A_1 , A_2 , and A_3 ?

Consider the total entropy as a function of N_1 , N_2 and N_3 , the number of particles of each species. Equilibrium will be achieved when the N_1 , N_2 , N_3 adjust so as to maximize $S(N_1, N_2, N_3)$.

$$dS = 0 = \sum_i \left(\frac{\partial S}{\partial N_i} \right) dN_i = \sum_i \left(\frac{-\mu_i}{T} \right) dN_i \quad \text{note, all species are in equilibrium at a common } T \quad (2.19.2)$$

Now, from the chemical equation, if N_3 decreases by $-dN$, then N_1 and N_2 increase by $\left(\frac{n_1}{n_3}\right)dN$ and $\left(\frac{n_2}{n_3}\right)dN$ respectively.

Or if $dN_3 = -n_3 dN$, then $dN_1 = n_1 dN$ and $dN_2 = n_2 dN$.

So the Eq. (2.19.2) for chemical equilibrium becomes,

$$\left(\frac{\mu_1}{T}\right) dN_1 + \left(\frac{\mu_2}{T}\right) dN_2 + \left(\frac{\mu_3}{T}\right) dN_3 = 0 \quad \Rightarrow \quad \mu_1 n_1 + \mu_2 n_2 - \mu_3 n_3 = 0 \quad (2.19.3)$$

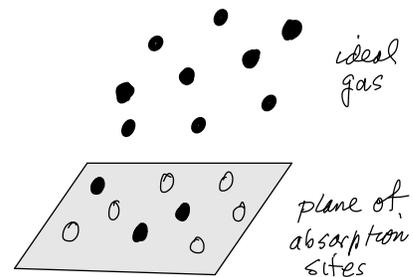
$$\Rightarrow \quad \boxed{\mu_1 n_1 + \mu_2 n_2 = \mu_3 n_3} \quad (2.19.4)$$

In equilibrium, the system will adjust the N_i such that the $\mu_i(T, V, N_i)$ satisfy this equation.

Example: An ideal gas in equilibrium with a plane of adsorption sites

An ideal gas of point particles exists in equilibrium at a temperature T and pressure p above a surface containing N_0 adsorption sites. Each adsorption site can hold at most one particle of the gas. The binding energy of a particle to an adsorption site is $-\epsilon$. What is the fraction of occupied adsorption sites as a function of T and p ?

We will regard the ideal gas of particles above the plane, and the gas of adsorbed particles on the plane, as two separate systems in equilibrium with each other. Since they can exchange energy and particles they are in equilibrium at the same temperature and chemical potential. Alternatively, we can view this as a problem of chemical equilibrium. If A denotes the particles in the gas above the plane, and B denotes the particles adsorbed on the plane, then the process of adsorption of gas particles is like a chemical reaction $A \leftrightarrow B$. Equilibrium will then occur when $\mu_A = \mu_B$.



We will solve this problem by taking the following steps:

- 1) Find the number N of occupied adsorption sites assuming the gas of adsorbed particles on the plane is at temperature T and chemical potential μ .
- 2) Find the chemical potential $\mu(T, p)$ of the ideal gas above the plane at temperature T and pressure p .
- 3) Insert μ from (2) into the result from (1) since the chemical potentials of the two systems must be equal in equilibrium. From this we will get N/N_0 as a function of T and p .

Step (1)

We can do this either in the canonical ensemble or in the grand canonical ensemble. We will do it *both* ways!

canonical ensemble: We start by computing the partition function Q_N .

Let $\{\alpha\}$ be the set of states of adsorbed particles that have exactly N sites occupied and the rest empty. Then,

$$Q_N = \sum_{\alpha} e^{-\beta E_{\alpha}} \quad (2.19.5)$$

In a more general case E_{α} might depend on the particular state α (for example if there were interactions between the particles on different adsorption sites). But in our example the energy is just $-\epsilon$ for each adsorbed particle. Thus $E_{\alpha} = -\epsilon N$ is the same for all the states $\{\alpha\}$ – it does not matter which of the sites are occupied and which are empty since they all have the same binding energy $-\epsilon$.

Thus,

$$Q_N = e^{\beta \epsilon N} \sum_{\alpha} (1) \quad (2.19.6)$$

The sum is over all states with exactly N of the N_0 sites occupied. The number of ways to choose which N of the N_0 sites are occupied is just,

$$\frac{N_0!}{N!(N_0 - N)!} \quad (2.19.7)$$

so the canonical partition function is,

$$Q_N = \frac{N_0!}{N!(N_0 - N)!} e^{\beta \epsilon N} \quad (2.19.8)$$

Next we find the Helmholtz free energy,

$$A(T, N) = -k_B T \ln Q_N = -\epsilon N - k_B T \left[\ln N_0! - \ln N! - \ln(N_0 - N)! \right] \quad (2.19.9)$$

Using Stirling's formula this becomes,

$$A(T, N) = -\epsilon N - k_B T \left[N_0 \ln N_0 - N_0 - N \ln N + N - (N_0 - N) \ln(N_0 - N) + (N_0 - N) \right] \quad (2.19.10)$$

$$= -\epsilon N - k_B T \left[N_0 \ln N_0 - N \ln N - (N_0 - N) \ln(N_0 - N) \right] \quad (2.19.11)$$

Then the chemical potential is given by,

$$\mu = \left(\frac{\partial A}{\partial N} \right)_T = -\epsilon + k_B T \left[\ln N + N \left(\frac{1}{N} \right) - \ln(N_0 - N) - \frac{N_0 - N}{(N_0 - N)} \right] = -\epsilon + k_B T \ln \left(\frac{N}{N_0 - N} \right) \quad (2.19.12)$$

We then have,

$$\frac{N}{N_0 - N} = e^{\beta(\epsilon + \mu)} \Rightarrow N = \frac{N_0 e^{\beta(\epsilon + \mu)}}{1 + e^{\beta(\epsilon + \mu)}} = \frac{N_0}{1 + e^{-\beta(\epsilon + \mu)}} \quad (2.19.13)$$

So finally the fraction of occupied adsorption sites is,

$$\boxed{\frac{N}{N_0} = \frac{1}{1 + e^{-\beta(\epsilon + \mu)}}} \quad (2.19.14)$$

grand canonical ensemble: Now we will do the same calculation but in the grand canonical ensemble!

Let $\{\alpha\}$ be the set of states of adsorbed particles, where the number of adsorbed particles is free to be anything from zero to N_0 . The grand partition function is then,

$$\mathcal{L} = \sum_{\alpha} e^{-\beta(E_{\alpha} - \mu N_{\alpha})} \quad (2.19.15)$$

where N_{α} is the number of occupied sites in state α , and $E_{\alpha} = -\epsilon N_{\alpha}$ is the state's energy.

For each adsorption site i we will define a variable s_i such that,

$$s_i = \begin{cases} 1 & \text{if site } i \text{ is occupied} \\ 0 & \text{if site } i \text{ is empty} \end{cases} \quad (2.19.16)$$

A state α is then represented by the set of $\{s_i\}$ for that configuration, and we can write,

$$N_{\alpha} = \sum_i s_i \quad \text{and} \quad E_{\alpha} = -\epsilon \sum_i s_i \quad (2.19.17)$$

The partition function can then be written as,

$$\mathcal{L} = \sum_{\{s_i\}} e^{-\beta[-\epsilon \sum_i s_i - \mu \sum_i s_i]} = \sum_{\{s_i\}} e^{\beta(\epsilon + \mu) \sum_i s_i} \quad (2.19.18)$$

We can then factor the exponential since the degrees of freedom s_i are non-interacting with each other,

$$\mathcal{L} = \sum_{s_1} \sum_{s_2} \dots \sum_{s_{N_0}} e^{\beta(\epsilon + \mu)(s_1 + s_2 + \dots + s_{N_0})} = \sum_{s_1} \sum_{s_2} \dots \sum_{s_{N_0}} e^{\beta(\epsilon + \mu)s_1} e^{\beta(\epsilon + \mu)s_2} \dots e^{\beta(\epsilon + \mu)s_{N_0}} \quad (2.19.19)$$

$$= \left(\sum_{s_1} e^{\beta(\epsilon + \mu)s_1} \right) \left(\sum_{s_2} e^{\beta(\epsilon + \mu)s_2} \right) \dots \left(\sum_{s_{N_0}} e^{\beta(\epsilon + \mu)s_{N_0}} \right) = \left(\sum_s e^{\beta(\epsilon + \mu)s} \right)^{N_0} \quad (2.19.20)$$

since each term is exactly the same after doing the sum on s_i . We thus get,

$$\mathcal{L} = \left(\sum_{s=0}^1 e^{\beta(\epsilon + \mu)s} \right)^{N_0} = \left[1 + e^{\beta(\epsilon + \mu)} \right]^{N_0} \quad (2.19.21)$$

The grand potential is then,

$$\Phi(T, \mu) = -k_B T \ln \mathcal{L} = -k_B T N_0 \ln \left[1 + e^{\beta(\epsilon + \mu)} \right] \quad (2.19.22)$$

The average number of adsorbed sites is then,

$$N = - \left(\frac{\partial \Phi}{\partial \mu} \right)_T = \frac{k_B T N_0 \beta e^{\beta(\epsilon + \mu)}}{1 + e^{\beta(\epsilon + \mu)}} = \frac{N_0}{1 + e^{-\beta(\epsilon + \mu)}} \quad (2.19.23)$$

This is exactly the same result as we found in Eq. (2.19.13) using the *canonical* ensemble!

Step (2)

Now we compute the chemical potential μ of the ideal gas at temperature T and pressure p . Again we could do this using either the canonical or the grand canonical ensemble. First we will use the canonical ensemble.

canonical ensemble: The canonical partition function is $Q_N = \frac{[Q_1]^N}{N!}$.

The single particle partition function is,

$$Q_1 = \frac{1}{h^3} \int d^3p \int d^3r e^{-\beta p^2/2m} = \frac{V}{h^3} \sqrt{\frac{2\pi m}{\beta}}^3 = V \sqrt{\frac{2\pi m k_B T}{h^2}}^3 = \frac{V}{\lambda^3} \quad (2.19.24)$$

The square root term comes from the Gaussian integral over each component of momentum, and it is raised to the power 3 since there are three components of momentum. The quantity,

$$\lambda(T) \equiv \sqrt{\frac{h^2}{2\pi m k_B T}} \quad \text{is called the } \textit{thermal wavelength} \text{ and it depends only on } T \quad (2.19.25)$$

We will see the physical meaning of this quantity later when we discuss the quantum ideal gas.

The Helmholtz free energy is now,

$$A = -k_B T \ln Q_N = -k_B T [N \ln Q_1 - N \ln N + N] \quad \text{where we used Stirling's formula} \quad (2.19.26)$$

The chemical potential is then,

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{T,V} = -k_B T \left[\ln Q_1 - \ln N - \frac{N}{N} + 1 \right] = -k_B T \ln \left(\frac{Q_1}{N} \right) = -k_B T \ln \left(\frac{V}{N \lambda^3} \right) \quad (2.19.27)$$

We thus have $\mu(T, V, N)$.

What we want is $\mu(T, p)$. To write μ in terms of T and p we need,

$$p = - \left(\frac{\partial A}{\partial V} \right)_{T,N} = k_B T \left(\frac{N}{Q_1} \right) \left(\frac{\partial Q_1}{\partial V} \right)_T = k_B T \left(\frac{N \lambda^3}{V} \right) \left(\frac{1}{\lambda^3} \right) = \frac{k_B T N}{V} \quad (2.19.28)$$

which, as expected, is just the ideal gas law. So we can then write,

$$\frac{V}{N \lambda^3} = \frac{k_B T}{p \lambda^3} \quad (2.19.29)$$

and so, inserting the above into Eq. (2.19.27) for μ , we then get,

$$\mu(T, p) = -k_B T \ln \left(\frac{k_B T}{p \lambda^3} \right) \quad (2.19.30)$$

or

$$\boxed{z = e^{\beta \mu} = \frac{p \lambda^3}{k_B T}} \quad (2.19.31)$$

grand canonical ensemble: We will now do the same calculation but in the grand canonical ensemble.

We have for the grand partition function,

$$\mathcal{L} = e^{z Q_1} \quad \text{where } z = e^{\beta \mu} \text{ and } Q_1 = \frac{V}{\lambda^3}. \quad (2.19.32)$$

Then we have for the grand potential,

$$-pV = \Phi = -k_B T \ln \mathcal{L} = -k_B T z Q_1 \quad \Rightarrow \quad p = \frac{k_B T}{V} z Q_1 = \frac{k_B T}{V} z \frac{V}{\lambda^3} = \frac{k_B T}{\lambda^3} z \quad (2.19.33)$$

and so,

$$z = e^{\beta \mu} = \frac{p \lambda^3}{k_B T} \quad (2.19.34)$$

This is exactly what we found in Eq. (2.19.31) from the canonical ensemble!

Step (3)

Now we substitute our result for $\mu(T, p)$ from step (2) into our result for N/N_0 from step (1).

$$\frac{N}{N_0} = \frac{1}{1 + e^{-\beta(\epsilon+\mu)}} = \frac{1}{1 + e^{-\beta\mu}e^{-\beta\epsilon}} = \frac{1}{1 + \left(\frac{k_B T}{p\lambda^3}\right) e^{-\beta\epsilon}} \quad (2.19.35)$$

So finally, substituting in for $\lambda(T)$, we get the fraction of adsorbed sites, N/N_0 , as a function of the temperature T and the pressure p of the gas above it,

$$\boxed{\frac{N}{N_0} = \left[1 + \frac{k_B T}{p} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} e^{-\epsilon/k_B T} \right]^{-1}} \quad (2.19.36)$$

Note: as $T \rightarrow 0$ we have $N/N_0 \rightarrow 1$, as expected – the system wants to go to its ground state; since filling an adsorption site lowers a particle’s energy, all the adsorption sites get filled.

And: as $T \rightarrow \infty$ we have $N/N_0 \rightarrow 0$, as expected – when there is lots of thermal energy, it is easy for an adsorbed particle to absorb ϵ of thermal energy and so desorb from the plane.

Note also one funny thing: Our result for N/N_0 *does* depend on the “arbitrary” quantity h . When we discuss the quantum ideal gas in the next unit, we will see that h is not really arbitrary, it is Planck’s constant!