

Physics 112

Equilibrium in Chemical Reactions

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I. FORMALISM

This is a considerably shortened version of Ch. 9 of Kittel and Kroemer.

We saw in an earlier handout [1], that for a system at constant V and T the (generalized) (Helmholtz) free energy, F , is minimized in equilibrium with respect, for example, to the energy exchanged with a reservoir. From the thermodynamic identity, discussed in another handout[2],

$$dF = -SdT - PdV \quad (1)$$

we see that dF is indeed zero at constant V and T , showing F is extremal (i.e. at a maximum or minimum). The more detailed discussion in handout [1] is needed to see that it is indeed a minimum.

In this handout we discuss chemical reactions, which take place not at constant volume, but at constant pressure P (so V adjusts itself to maintain the pressure at the specified value). We saw in handout [2] that we should use the (generalized) Gibbs free energy $G = F + PV$ for systems at fixed P and T since the thermodynamic identity for G is

$$dG = -SdT + VdP. \quad (2)$$

(In previous handouts I put a “tilde” on the symbol for the generalized free energy to emphasize that it can apply to non-equilibrium situations. Here, however, I will adhere to standard usage and write the generalized Gibbs free energy simply as G .) It follows that

$$\boxed{dG = 0} \quad (3)$$

if P and T are fixed, so G is a maximum or minimum. A more detailed discussion, analogous to that Ref. [1] for F , shows that G is actually a minimum. Here we consider a mixture of chemicals which can react, and use the result that $dG = 0$ when there is a small change in the concentration of the different chemical species, to gain information about the equilibrium concentrations. The main result will be Eq. (17) below.

As shown in class and handout [2], the chemical potential is the Gibbs free energy per particle:

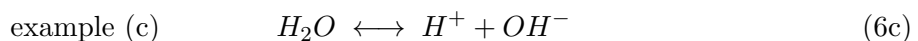
$$G = N\mu. \quad (4)$$

When we have several chemical species, each has its own chemical potential so the total Gibbs free energy is

$$G = \sum_j N_j \mu_j \quad (5)$$

where j denotes a particular chemical species.

We next give some examples of chemical reactions which we will use to illustrate the theory in what follows:



Example (a) is a standard chemical reaction in which an acid is formed. Example (b) describes the equilibrium between atomic and molecular hydrogen (of importance in astronomy since there is hydrogen in the intergalactic medium), and example (c) describes the dissociation of water into H^+ and OH^- ions (which is of importance in chemistry).

If we label a chemical species by A_j and indicate by ν_j the (integer) amount of species j in the reaction, then the reaction can be written symbolically as

$$\sum_j \nu_j A_j = 0. \quad (7)$$

For our three examples in Eqs. (6), we have

$$\begin{aligned} A_1 &= H_2, & A_2 &= Cl_2, & A_3 &= HCl, \\ \nu_1 &= 1, & \nu_2 &= 1, & \nu_3 &= -2, \end{aligned} \quad (8a)$$

$$\begin{aligned} A_1 &= H_2, & A_2 &= H, \\ \nu_1 &= 1, & \nu_2 &= -2, \end{aligned} \quad (8b)$$

and

$$\begin{aligned} A_1 &= H_2O, & A_2 &= H^+, & A_3 &= OH^-, \\ \nu_1 &= 1, & \nu_2 &= -1, & \nu_3 &= -1. \end{aligned} \quad (8c)$$

The problem is to determine the equilibrium concentration of the different species. Suppose the number of molecules of species j changes by dN_j , then the change in Gibbs free energy is

$dG = \sum_j \mu_j dN_j$. However, in equilibrium this must vanish, since G is a minimum, so

$$\sum_j \mu_j dN_j = 0. \quad (9)$$

The changes in molecular number, dN_j are not independent, however, because the reaction must proceed as specified in Eq. (7). In fact we must have $dN_j \propto \nu_j$ since each time the reaction in Eq. (7) takes place the number of molecules of species j changes by ν_j . Hence we can write the condition for equilibrium, Eq. (9), as

$$\boxed{\sum_j \mu_j \nu_j = 0.} \quad (10)$$

To proceed further we assume that the chemical species form an ideal gas. We showed in handout [3] that, if the molecule has no internal degrees of freedom (and we set the energy of the molecule at rest to be zero)

$$\mu_j(T) = k_B T \log \left(\frac{n_j}{n_{Qj}} \right) \quad (11)$$

where

$$\boxed{n_{Qj} \equiv 1/V_{Qj} = \left(\frac{m_j k_B T}{2\pi \hbar^2} \right)^{3/2}}, \quad (12)$$

is the *quantum concentration*. When there are internal degrees of freedom we showed in class, and in Qu. 4, HW 5, that n_{Qj} is replaced by $n_{Qj} Z_j(\text{int})$, where $Z_j(\text{int})$ is the partition function for the internal degrees of freedom. In general we will only include the state of lowest energy (of the internal degrees of freedom), so

$$Z_j(\text{int}) = \exp(-\beta E_{0,j}), \quad (13)$$

Note, however, that we will not, in general, be able to set the ground state energies $E_{0,j}$ to be zero for *all* chemical species j because of the *binding energy* of the molecules. Allowing for this, the expression for the chemical potential of species j in Eq. (11) is modified to

$$\boxed{\mu_j(T) = k_B T \log \left(\frac{n_j}{n_{Qj} Z(\text{int})} \right)}. \quad (14)$$

Note that if we just include the lowest of the internal energy states, so $Z_j(\text{int})$ is given by Eq. (13), the expression for the chemical potential in Eq. (14) can be written as

$$\mu_j(T) = E_{0,j} + k_B T \log \left(\frac{n_j}{n_{Qj}} \right), \quad (15)$$

which is just the simpler expression in Eq. (11) above, but shifted by the energy of the chemical species, $E_{0,j}$.

The equilibrium condition, Eq. (10) can therefore be written

$$\sum_j \nu_j \log \left(\frac{n_j}{n_{Qj} Z_j(\text{int})} \right) = 0, \quad (16)$$

or, equivalently, exponentiating this we have

$$\prod_j \left(\frac{n_j}{n_{Qj} Z_j(\text{int})} \right)^{\nu_j} = 1. \quad (17)$$

Now n_{Qj} and $Z(\text{int})$ depend only on T and not on pressure or the concentrations. Hence we can write $\prod_j [n_{Qj} Z_j(\text{int})]^{\nu_j} = K(T)$, where $K(T)$ is only a function of T , and so Eq. (17) can be written as

$$\prod_j n_j^{\nu_j} = K(T), \quad (18)$$

which is often called the *law of mass action*. It says that the combination of concentrations on the LHS only depends on temperature. This means that if one concentration changes the others must also change to compensate.

Equation (17) is the main result of this handout. Sometimes its simpler form, Eq. (18), will suffice. Note that Eq. (17) is just *one* condition that must be satisfied and so it is not enough to determine *all* the equilibrium concentrations n_j . For that, additional information must be given, as discussed in the examples below.

II. EXAMPLES

We now apply Eq. (17) to the examples (b) and (c).

Example (b), $H_2 \longleftrightarrow 2H$

As stated in Eq. (8b) we have $\nu_{H_2} = 1, \nu_H = -2$. We take the zero of energy to be the energy of two isolated hydrogen atoms at rest, and neglect the internal degrees of the freedom of the atom or molecule so $Z_H(\text{int}) = 1$. The molecule has a binding energy ΔE of 4.5 eV $\simeq 50,000\text{K}$, so $Z_{H_2}(\text{int}) = \exp(\beta\Delta E)$. Equation (17) then becomes

$$\frac{n_{H_2}}{n_{QH_2} e^{\beta\Delta E}} = \left(\frac{n_H}{n_{QH}} \right)^2, \quad (19)$$

or equivalently,

$$\frac{n_H^2}{n_{H_2}} = e^{-\beta\Delta E} \frac{(n_{QH})^2}{n_{QH_2}}, \quad (20)$$

which is sometimes called the **Saha equation**.

From Eq. (12) we have $n_{QH_2} = 2^{3/2}n_{QH}$, and, to maintain simplicity of the expressions, we will replace the factor of $2^{3/2}$ by unity. The other factors are much more important. We are particularly interested in the ratio of atomic to molecular hydrogen. Taking the square root of Eq. (19) gives

$$\frac{n_H}{\sqrt{n_{H_2}}} = e^{-\beta\Delta E/2} \sqrt{n_{QH_2}}, \quad (21)$$

so

$$\boxed{\frac{n_H}{n_{H_2}} \simeq \frac{e^{-\beta\Delta E/2}}{\sqrt{n_{H_2}/n_{QH_2}}}.} \quad (22)$$

Note that Eq. (22) by itself does not tell us the two concentrations n_H and n_{H_2} but only a condition which must be satisfied by them. (Clearly one equation cannot determine two quantities.) However, if we provide *additional* information, for example that we start with a concentration n_0 of hydrogen molecules and the only source of atomic hydrogen is the dissociation of these molecules, then have a second condition, $n_{H_2} + n_H/2 = n_0$, which can be combined with Eq. (22) to determine *both* n_H and n_{H_2} .

Referring to Eq. (22), one might have naively expected that the ratio n_H/n_{H_2} would be just the Boltzmann factor, $e^{-\beta\Delta E}$. However, the actual result differs from this in two rather surprising and interesting ways:

1. The exponent has $\Delta E/2$ rather than ΔE . This arises because each dissociation gives two hydrogen atoms, and so the binding energy *per hydrogen atom* is $\Delta E/2$. Since the atoms must be created in pairs there is a constraint that the number of them is even. However, if N_H is large, this constraint is unimportant, and so we get the Boltzmann factor with $\Delta E/2$.
2. The factor $\sqrt{n_{H_2}/n_{QH_2}}$ in the denominator. In the dilute (classical) limit this is very small compared with unity (remember $1/n_{QH_2} \equiv V_{QH_2}$ and the condition for the classical limit is [3] $nV_Q \ll 1$), and so the fraction of atomic hydrogen is *much greater* than one would expect simply from the Boltzmann factor. The reason is that the two separated atoms have much more entropy than the single molecule. This is called the *entropy of dissociation*.

My understanding is that the temperature in intergalactic space is much less than $\Delta E/2k_B \simeq 25,000$ K, so just from the Boltzmann factor one would expect the hydrogen there to be in the

molecular form, but actually it is mainly atomic because the concentration of hydrogen is incredibly low, so the entropy of dissociation is extremely high and this turns out to dominate over the Boltzmann factor.

Example (c), $H_2O \longleftrightarrow H^+ + OH^-$

As stated in Eq. (8c), we have $\nu_{H_2O} = 1, \nu_{H^+} = -1, \nu_{OH^-} = -1$. Hence, according to Eq. (18)

$$\frac{n_{H^+} n_{OH^-}}{n_{H_2O}} = K(T), \quad (23)$$

where $K(T)$ only depends on temperature.

As in the previous example, one needs additional information to determine the concentrations. For example, in pure water, the number of positive and negative ions must be equal, and one finds experimentally at room temperature

$$\boxed{n_{H^+} = n_{OH^-} = 10^{-7} \text{ mol l}^{-1}}, \quad (24)$$

where the units are moles per liter. In other words, there is a small amount of dissociation of the water molecule into its constituent ions.

Now suppose we add an acid (which provides additional H^+ ions), or a base (which provides additional OH^- ions), to the water. According to the law of mass action, Eq. (23), as long as the ionization fraction remains small compared with unity (so the concentration of water, n_{H_2O} , remains more or less unchanged), the product $n_{H^+} n_{OH^-}$ is a constant given, according to Eq. (24), by

$$\boxed{n_{H^+} n_{OH^-} = 10^{-14} \text{ mol}^2 \text{ l}^{-2}}. \quad (25)$$

I emphasize that, according to Eq. (18), this is valid even if an acid or base has been added to the water which results in $n_{H^+} \neq n_{OH^-}$. Note that if n_{H^+} increases, the density of OH^- ions must *decrease* in order that the product remains given by Eq. (25), and vice versa.

The acidity of a solution in water is specified by its pH value which is *defined* to be

$$\boxed{\text{pH} \equiv -\log_{10} n_{H^+}}. \quad (26)$$

Hence pure water has a pH of 7. An acidic solution has a pH less than 7, with a very strong acid having a value of around zero. A basic solution has a pH larger than 7.

[1] Physics 112 handout: *The (generalized) free energy is a minimum in equilibrium*,
<http://physics.ucsc.edu/~peter/112/fmin.pdf>.

- [2] Physics 112 handout: *Various "Free Energies"*, <http://physics.ucsc.edu/~peter/112/thermofun.pdf>.
- [3] Physics 112 handout: *The classical ideal gas*, <http://physics.ucsc.edu/~peter/112/ideal.pdf>.