

# Introduction to Physical Chemistry – Lecture 10

## I. LECTURE OVERVIEW

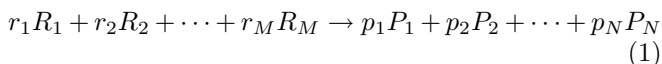
In this lecture, we will consider the problem of thermodynamic equilibrium in chemically reacting systems. We will focus on ideal gases, because they are the simplest to analyze. However, we will use the techniques developed to study other kinds of related equilibrium phenomena, such as osmotic pressure, freezing point depression, and a gas dissolved in a liquid.

In terms of the material you will need to know for the final, this is the last lecture of the course. There will be one remaining lecture after this one, however, it will be more for the purposes of general knowledge, and will therefore not be tested on the final exam.

## II. CHEMICAL REACTIONS

A *chemical reaction* refers to a process whereby one set of compounds interact with one another to form another set of compounds. The initial set of compounds are termed the *reactants*, and the final set of compounds are termed the *products*. This is illustrated in Figure 1.

The general representation of a chemical reaction is as follows:



where the reactants are  $R_1, \dots, R_M$ , and the products are  $P_1, \dots, P_N$ . The quantities  $r_1, \dots, r_M, p_1, \dots, p_N$  are referred to as the *stoichiometric coefficients* of the reaction.

The stoichiometric coefficients must be such that the reaction is *balanced*. This means that for every atom type that appears in the reaction, the total number of

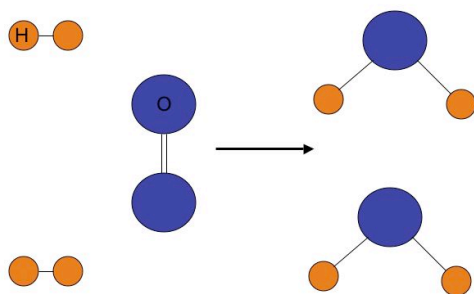
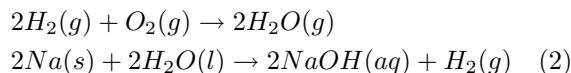


FIG. 1: Illustration of a chemical reaction: Two hydrogen molecules and one oxygen molecule react to form two water molecules.

atoms on the reactant side must equal the total number of atoms (of the same type) on the product side. With this criterion, it is possible to show that there is a smallest set of stoichiometric coefficients, and any other valid set of stoichiometric coefficients must be an integer multiple of this smallest set.

Here are two examples of chemical reactions:



In the first reaction, two hydrogen molecules in the gas state react with one oxygen molecule in the gas state to form two water molecules in the gas state. In the second reaction, two atoms of sodium in the solid state react with two water molecules in the liquid state to form aqueous sodium hydroxide (aqueous meaning dissolved in water) and one molecule of hydrogen in the gas state.

We now turn our attention to a very important quantity, the *extent of reaction*. The extent of reaction determines how far along a reaction has proceeded. Instead of directly defining the extent of reaction, we will define it operationally (i.e. given the extent of reaction, how do we use it to calculate things).

Note that in the reaction where hydrogen and oxygen react to form water, two hydrogen molecules are consumed for every oxygen molecule consumed, and two water molecules are produced for every oxygen molecule consumed. So, in a general reaction, where the reactant stoichiometric coefficients are  $r_1, \dots, r_M$ , and the product stoichiometric coefficients are  $p_1, \dots, p_N$ , note that  $r_1$  molecules of  $R_1$  are consumed for every  $p_1$  molecules of  $P_1$  produced. More generally,  $r_i$  molecules of  $R_i$  are consumed for every  $p_j$  molecules of  $P_j$  produced,  $r_i$  molecules of  $R_i$  are consumed for every  $r_j$  molecules of  $R_j$  consumed, and  $p_i$  molecules of  $P_i$  are produced for every  $p_j$  molecules of  $P_j$  produced.

So, if  $\zeta$  denotes the extent of reaction, then this means that  $r_1\zeta$  moles of  $R_1$  have reacted,  $r_2\zeta$  moles of  $R_2$  have reacted,  $\dots$ ,  $r_M\zeta$  moles of  $R_M$  have reacted, and  $p_1\zeta$  moles of  $P_1$  have been produced,  $p_2\zeta$  moles of  $P_2$  have been produced,  $\dots$ ,  $p_N\zeta$  moles of  $P_N$  have been produced.

## III. THE GIBBS POTENTIAL IN AN IDEAL GAS

In preparation for what we will need shortly, we need to compute how the Gibbs potential (the Gibbs free energy) varies as a function of temperature and pressure in an ideal gas.

So, suppose we have one mole of an ideal gas at some temperature  $T$ , and pressure  $P_1$ . If we change the pressure from  $P_1$  to  $P_2$ , while keeping the temperature fixed, how does the Gibbs free energy  $G$  change?

We have,

$$d\bar{G} = -\bar{S}dT + \bar{V}dP = \bar{V}dP \text{ (constant temperature)} \quad (3)$$

Therefore,

$$\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V} = \frac{RT}{P} \quad (4)$$

since we are dealing with an ideal gas. Integrating, we get,

$$\bar{G}(T, P_2) = \bar{G}(T, P_1) + RT \ln \frac{P_2}{P_1} \quad (5)$$

To minimize the number of variables we need to keep track of, we typically pick a reference value of  $P_1$ , called the *standard pressure*. The most common values for the standard pressure are either 1 atm or 1 bar = 100,000 Pa. If we denote the standard pressure by  $P_{ref}$  (the “ref” denotes “reference”), then we get,

$$\bar{G}(T, P) = \bar{G}(T, P_{ref}) + RT \ln \frac{P}{P_{ref}} \quad (6)$$

We may also define a reference temperature, called the *standard pressure*, with respect to which the Gibbs potential may be computed. Since, at constant pressure, we have  $d\bar{G} = -\bar{S}dT$ , we obtain,

$$\bar{G}(T, P_{ref}) = \bar{G}(T_{ref}, P_{ref}) - \int_{T_{ref}}^T \bar{S}(T', P_{ref})dT' \quad (7)$$

There a number of standard temperatures in use:  $0^\circ \text{C} = 273 \text{K}$ ,  $25^\circ \text{C} = 298 \text{K}$ , and  $300 \text{K}$ .

Together, the standard temperature and pressure are abbreviated as “STP”.

## IV. CHEMICAL EQUILIBRIUM

### A. Criterion for chemical equilibrium: The equilibrium constant

Consider a reaction that is occurring at constant temperature and pressure in some container. Constant temperature can be achieved by immersing the container in a thermal bath, and constant pressure can be maintained by allowing the container to have at least one movable wall, that can adjust in response to changing internal conditions.

Eventually, the mixture reaches a state where it is in equilibrium. At this point, the rate of the forward reaction and the rate of the reverse reaction are equal. This also means that the conversion from reactants to products or vice versa are both reversible processes at equilibrium.

Now, for a reversible process occurring at constant temperature and pressure, we have  $dG = 0$ . We can use this to develop our criterion for chemical equilibrium.

Suppose that, at equilibrium at the temperature  $T$  and pressure  $P$ , there are  $n_{R_i}$  moles of reactant  $R_i$ , for  $i = 1, \dots, M$ , and  $n_{P_i}$  moles of product  $P_i$ , for  $i = 1, \dots, N$ . If the extent of reaction changes from  $\zeta_{equil}$  to  $\zeta_{equil} + d\zeta$ , then the number of moles of reactant  $R_i$  becomes  $n_{R_i} - r_i d\zeta$ , while the number of moles of product  $P_i$  becomes  $n_{P_i} + p_i d\zeta$ .

When the extent of reaction is  $\zeta_{equil}$ , the total number of moles in the system is  $n = n_{R_1} + \dots + n_{R_M} + n_{P_1} + \dots + n_{P_N}$ . This means that the mole fraction of  $R_i$ , denoted  $x_{R_i}$ , and the mole fraction of  $P_i$ , denoted  $x_{P_i}$ , is given by,

$$\begin{aligned} x_{R_i} &= \frac{n_{R_i}}{n_{R_1} + \dots + n_{R_M} + n_{P_1} + \dots + n_{P_N}} \\ x_{P_i} &= \frac{n_{P_i}}{n_{R_1} + \dots + n_{R_M} + n_{P_1} + \dots + n_{P_N}} \end{aligned} \quad (8)$$

The partial pressures (see the very beginning of Lecture 3) of  $R_i$  and  $P_i$  are then given by,

$$\begin{aligned} p_{R_i} &= x_{R_i} P = \frac{n_{R_i}}{n_{R_1} + \dots + n_{R_M} + n_{P_1} + \dots + n_{P_N}} P \\ p_{P_i} &= x_{P_i} P = \frac{n_{P_i}}{n_{R_1} + \dots + n_{R_M} + n_{P_1} + \dots + n_{P_N}} P \end{aligned} \quad (9)$$

Therefore, the molar Gibbs free energies are given by,

$$\begin{aligned} \bar{G}_{R_i} &= \bar{G}_{R_i}(T, P_{ref}) + RT \ln \frac{p_{R_i}}{P_{ref}} \\ &= \bar{G}_{R_i}(T, P_{ref}) + RT \ln \frac{P}{P_{ref}} + RT \ln x_{R_i} \\ &= \bar{G}_{R_i}(T, P_{ref}) + RT \ln \frac{P}{P_{ref}} + RT \ln n_{R_i} \\ &\quad - RT \ln(n_{R_1} + \dots + n_{R_M} + n_{P_1} + \dots + n_{P_N}) \\ \bar{G}_{P_i} &= \bar{G}_{P_i}(T, P_{ref}) + RT \ln \frac{P}{P_{ref}} + RT \ln n_{P_i} \\ &\quad - RT \ln(n_{R_1} + \dots + n_{R_M} + n_{P_1} + \dots + n_{P_N}) \end{aligned} \quad (10)$$

Therefore, the total value of the Gibbs free energy at equilibrium is given by,

$$\begin{aligned} G &= n_{R_1} \bar{G}_{R_1} + \dots + n_{R_M} \bar{G}_{R_M} + n_{P_1} \bar{G}_{P_1} + \dots + n_{P_N} \bar{G}_{P_N} \\ &= n_{R_1} \bar{G}_{R_1}(T, P_{ref}) + \dots + n_{R_M} \bar{G}_{R_M}(T, P_{ref}) \\ &\quad + n_{P_1} \bar{G}_{P_1}(T, P_{ref}) + \dots + n_{P_N} \bar{G}_{P_N}(T, P_{ref}) \\ &\quad + nRT \ln \frac{P}{P_{ref}} \\ &\quad + RT(n_{R_1} \ln n_{R_1} + \dots + n_{R_M} \ln n_{R_M} \\ &\quad + n_{P_1} \ln n_{P_1} + \dots + n_{P_N} \ln n_{P_N}) - RTn \ln n \end{aligned} \quad (11)$$

Therefore,

$$\begin{aligned}
dG &= dn_{R_1} \bar{G}_{R_1}(T, P_{ref}) + \dots + dn_{R_M} \bar{G}_{R_M}(T, P_{ref}) \\
&\quad + dn_{P_1} \bar{G}_{P_1}(T, P_{ref}) + \dots + dn_{P_N} \bar{G}_{P_N}(T, P_{ref}) \\
&\quad + (dn)RT \ln \frac{P}{P_{ref}} \\
&\quad + RT(dn_{R_1} \ln n_{R_1} + \dots + dn_{R_M} \ln n_{R_M} \\
&\quad + dn_{P_1} \ln n_{P_1} + \dots + dn_{P_N} \ln n_{P_N} \\
&\quad + dn_{R_1} + \dots + dn_{R_M} \\
&\quad + dn_{P_1} + \dots + dn_{P_N}) \\
&\quad - RT dn \ln n - RT dn
\end{aligned} \tag{12}$$

Using the fact that  $dn = dn_{R_1} + \dots + dn_{R_M} + dn_{P_1} + \dots + dn_{P_N}$  gives,

$$\begin{aligned}
dG &= dn_{R_1} \bar{G}_{R_1}(T, P_{ref}) + \dots + dn_{R_M} \bar{G}_{R_M}(T, P_{ref}) \\
&\quad + dn_{P_1} \bar{G}_{P_1}(T, P_{ref}) + \dots + dn_{P_N} \bar{G}_{P_N}(T, P_{ref}) \\
&\quad + RT(dn_{R_1} + \dots + dn_{R_M} \\
&\quad + dn_{P_1} + \dots + dn_{P_N}) \ln \frac{P}{P_{ref}} \\
&\quad + RT(dn_{R_1} \ln x_{R_1} + \dots + dn_{R_M} \ln x_{R_M} \\
&\quad + dn_{P_1} \ln x_{P_1} + \dots + dn_{P_N} \ln x_{P_N}) \\
&= dn_{R_1} \bar{G}_{R_1}(T, P_{ref}) + \dots + dn_{R_M} \bar{G}_{R_M}(T, P_{ref}) \\
&\quad + dn_{P_1} \bar{G}_{P_1}(T, P_{ref}) + \dots + dn_{P_N} \bar{G}_{P_N}(T, P_{ref}) \\
&\quad + RT(dn_{R_1} \ln \frac{p_{R_1}}{P_{ref}} + \dots + dn_{R_M} \ln \frac{p_{R_M}}{P_{ref}} \\
&\quad + dn_{P_1} \ln \frac{p_{P_1}}{P_{ref}} + \dots + dn_{P_N} \ln \frac{p_{P_N}}{P_{ref}})
\end{aligned} \tag{13}$$

We are almost there :-). We now apply the equality  $dn_{R_1} = -r_1 d\zeta, \dots, dn_{R_M} = -r_M d\zeta, dn_{P_1} = p_1 d\zeta, \dots, dn_{P_N} = p_N d\zeta$  to get,

$$\begin{aligned}
dG &= d\zeta \times \\
&\quad [(p_1 \bar{G}_{P_1}(T, P_{ref}) + \dots + p_N \bar{G}_{P_N}(T, P_{ref}) \\
&\quad - r_1 \bar{G}_{R_1}(T, P_{ref}) - \dots - r_M \bar{G}_{R_M}(T, P_{ref})) \\
&\quad + RT \ln \frac{(p_{P_1}/P_{ref})^{p_1} \times \dots \times (p_{P_N}/P_{ref})^{p_N}}{(p_{R_1}/P_{ref})^{r_1} \times \dots \times (p_{R_M}/P_{ref})^{r_M}}]
\end{aligned} \tag{14}$$

This looks cumbersome, but we can clean up this expression. First of all, note that if  $r_1$  moles of  $R_1, \dots, r_M$  moles of  $R_M$ , react at  $T$  and  $P_{ref}$  to form  $p_1$  moles of  $P_1, \dots, p_N$  moles of  $P_N$ , then the change in free energy is given by,

$$\begin{aligned}
\Delta \bar{G}_{rxn}(T, P_{ref}) &= p_1 \bar{G}_{P_1}(T, P_{ref}) + \dots + p_N \bar{G}_{P_N}(T, P_{ref}) \\
&\quad - r_1 \bar{G}_{R_1}(T, P_{ref}) - \dots - r_M \bar{G}_{R_M}(T, P_{ref})
\end{aligned}$$

where  $\Delta \bar{G}_{rxn}(T, P_{ref})$  is the *molar free energy change of the reaction*.

Using the fact that  $dG = 0$  at equilibrium, allows us to re-arrange the expression before the previous one to get,

$$\frac{(p_{P_1}/P_{ref})^{p_1} \times \dots \times (p_{P_N}/P_{ref})^{p_N}}{(p_{R_1}/P_{ref})^{r_1} \times \dots \times (p_{R_M}/P_{ref})^{r_M}} = e^{-\frac{\Delta \bar{G}_{rxn}(T, P_{ref})}{RT}} \tag{16}$$

This expression is very powerful. The criterion for equilibrium,  $dG = 0$ , in the context of chemical equilibrium, leads us to a relationship between the partial pressures of the various chemicals and the free energy change associated with the reaction. The quantity,  $\exp[-\Delta \bar{G}_{rxn}(T, P_{ref})/RT]$ , is referred to as the *equilibrium constant*, and is denoted by  $K_{eq}(T, P_{ref})$ .

If we re-express the equilibrium equation in terms of mole fractions, then using the relationships previously derived, and manipulating the equations some, gives,

$$\frac{x_{P_1}^{p_1} \times \dots \times x_{P_N}^{p_N}}{x_{R_1}^{r_1} \times \dots \times x_{R_M}^{r_M}} = \left(\frac{P}{P_{ref}}\right)^{-(p_1 + \dots + p_N - r_1 - \dots - r_M)} K_{eq}(T, P_{ref}) \tag{17}$$

In the next subsection, we will see how this criterion can be used to completely characterize the equilibrium state of a system.

## B. Working with the equilibrium constant

The equilibrium condition can be combined with the concept of extent of reaction to uniquely compute the equilibrium mole fractions.

Suppose that the container where the reaction occurs is initially populated with  $n_{R_1,0}$  moles of  $R_1, \dots, n_{R_M,0}$  moles of  $R_M, n_{P_1,0}$  moles of  $P_1, \dots, n_{P_N,0}$  moles of  $P_N$ . If the extent of reaction at equilibrium is  $\zeta_{equil}$ , then at equilibrium there are  $n_{R_1,0} - r_1 \zeta_{equil}$  moles of  $R_1, \dots, n_{R_M,0} - r_M \zeta_{equil}$  moles of  $R_M, n_{P_1,0} + p_1 \zeta_{equil}$  moles of  $P_1, \dots, n_{P_N,0} + p_N \zeta_{equil}$  moles of  $P_N$ . The equilibrium population fractions are then,

$$\begin{aligned}
x_{R_1} &= \frac{n_{R_1,0} - r_1 \zeta_{equil}}{n_0 + (p_1 + \dots + p_N - r_1 - \dots - r_M) \zeta_{equil}} \\
&\vdots \\
x_{R_M} &= \frac{n_{R_M,0} - r_M \zeta_{equil}}{n_0 + (p_1 + \dots + p_N - r_1 - \dots - r_M) \zeta_{equil}} \\
x_{P_1} &= \frac{n_{P_1,0} + p_1 \zeta_{equil}}{n_0 + (p_1 + \dots + p_N - r_1 - \dots - r_M) \zeta_{equil}} \\
&\vdots \\
x_{P_N} &= \frac{n_{P_N,0} + p_N \zeta_{equil}}{n_0 + (p_1 + \dots + p_N - r_1 - \dots - r_M) \zeta_{equil}}
\end{aligned} \tag{18}$$

where  $n_0 = n_{R_1,0} + \dots + n_{R_M,0} + n_{P_1,0} + \dots + n_{P_N,0}$ .

Substituting these values into the equilibrium equation allows us to solve for  $\zeta_{equil}$ , and thereby obtain the equilibrium composition of the system. In practice, actually doing this can be very difficult, and the equilibrium equation must be solved by numerical methods (i.e. on the computer). However, for simple reactions,  $\zeta_{equil}$  may be determined by hand.

### C. Determining the direction of a chemical reaction

To determine the direction of a chemical reaction when it is not in equilibrium, we have to look at the derivative  $(\partial G/\partial \zeta)_{T,P}$ . If this quantity is positive, then the reaction will proceed in the forward direction (that is,  $\zeta$  will increase). If this quantity is negative, then the reaction will proceed in the reverse direction (that is,  $\zeta$  will decrease). In short, a chemical reaction will proceed in such a way as to decrease  $G$ .

This is one example of a more general principle: *A system that comes to equilibrium at a given temperature and pressure minimizes the value of the Gibbs free energy for that temperature and pressure.*

This principle is identical to the principle that entropy always increases for an isolated system. We have already proven this statement in the context of phase transitions at the end of the last lecture.

Because of this principle of minimal free energy, a reaction for which  $\Delta \bar{G}_{rxn}(T, P_{ref}) < 0$  is said to be *spontaneous*, while a reaction for which  $\Delta \bar{G}_{rxn}(T, P_{ref}) > 0$  is said to be not spontaneous.

One has to be careful with these terms, however. Simply because a reaction has a negative  $\Delta \bar{G}$  does not mean that it will occur in the direction implied by saying it is spontaneous. If we are beyond the equilibrium point (for example, we add an excess of products), then the reaction will go backwards.

Saying that  $\Delta \bar{G} < 0$  implies that a reaction is spontaneous means that, if we start off with a component population that contains only reactants, then the reaction will proceed significantly forward, to a much greater extent than if  $\Delta \bar{G} > 0$ . If  $\Delta \bar{G} > 0$ , then  $\Delta \bar{G} < 0$  for the reverse reaction, and so we say that the reverse reaction is spontaneous.

It is understandable if this is confusing. The confusion is due to the somewhat misleading terminology.

### D. Entropy of mixing and dependence of the free energy on mole fractions

Suppose we have  $M$  components in separate compartments, and suppose that there are  $n_i$  moles of component  $i$ . Suppose also that each of these components are at pressure  $P$  and temperature  $T$ . The total free energy is given by,

$$G_{unmixed}(T, P; n_1, \dots, n_M) = n_1(\bar{G}_1(T, P_{ref}) + RT \ln \frac{P}{P_{ref}}) + \dots + n_M(\bar{G}_M(T, P_{ref}) + RT \ln \frac{P}{P_{ref}}) + RT(n_1 \ln x_1 + \dots + n_M \ln x_M) = n_1(\bar{G}_1(T, P_{ref}) + RT \ln \frac{P}{P_{ref}}) + \dots + n_M(\bar{G}_M(T, P_{ref}) + RT \ln \frac{P}{P_{ref}}) + RT(n_1 + \dots + n_M) \times (x_1 \ln x_1 + \dots + x_M \ln x_M) \quad (20)$$

After mixing the components together, the free energy becomes,

$$G_{mixed}(T, P; n_1, \dots, n_M) = n_1(\bar{G}_1(T, P_{ref}) + RT \ln \frac{P}{P_{ref}}) + \dots + n_M(\bar{G}_M(T, P_{ref}) + RT \ln \frac{P}{P_{ref}}) + RT(n_1 \ln x_1 + \dots + n_M \ln x_M) = n_1(\bar{G}_1(T, P_{ref}) + RT \ln \frac{P}{P_{ref}}) + \dots + n_M(\bar{G}_M(T, P_{ref}) + RT \ln \frac{P}{P_{ref}}) + RT(n_1 + \dots + n_M) \times (x_1 \ln x_1 + \dots + x_M \ln x_M) \quad (20)$$

and so, the free energy of mixing,  $\Delta G_{mix} = G_{mixed} - G_{unmixed}$ , is given by,

$$\Delta G_{mix} = (n_1 + \dots + n_M)RT(x_1 \ln x_1 + \dots + x_M \ln x_M) \quad (21)$$

We would like to compute the entropy of mixing, however. That is, we would like to determine  $\Delta S_{mix} = S_{mixed} - S_{unmixed}$ . To do this, note that,

$$G_{unmixed} = H_{unmixed} - TS_{unmixed} \\ G_{mixed} = H_{mixed} - TS_{mixed} \quad (22)$$

and so,

$$\Delta G_{mix} = (H_{mixed} - H_{unmixed}) - T\Delta S_{mix} \quad (23)$$

Now, note that, because enthalpy only depends on temperature for an ideal gas, the enthalpies of the individual components are unaffected by mixing process, hence  $H_{mixed} = H_{unmixed}$ . So, we obtain,

$$\Delta S_{mix} = -(n_1 + \dots + n_M)R(x_1 \ln x_1 + \dots + x_M \ln x_M) \quad (24)$$

If we assume a total of one mole, that is, we assume  $n_1 + \dots + n_M = 1$ , then we get the *molar entropy of mixing*, given by,

$$\Delta \bar{S}_{mix} = -R(x_1 \ln x_1 + \dots + x_M \ln x_M) \quad (25)$$

Note that  $\Delta \bar{S}_{mix}$  is always positive. This makes sense, because, when we mix compounds together, the system becomes more disordered. In a more precise sense, the number of ways of having the components all mixed together is far larger than the number of ways of keeping the components unmixed. In fact, if we choose to compute the entropy of mixing using the Boltzmann formula (see Lecture 6), we show that,

$$\Delta \bar{S}_{mix} = k \ln \frac{\Omega_{mixed}}{\Omega_{unmixed}} = -R(x_1 \ln x_1 + \dots + x_M \ln x_M) \quad (26)$$

The derivation does not require more complex combinatorics than what was used for the example of the ideal gas spreading throughout a box. However, it is more involved than earlier derivations, so we will omit it here.

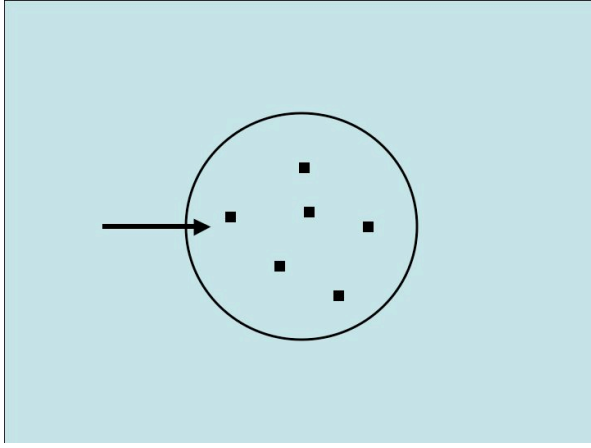


FIG. 2: A solute dissolved in a container with semipermeable walls will induce liquid flow into the compartment, thereby increasing the pressure.

## V. OTHER KINDS OF EQUILIBRIA

In this section we will briefly discuss other kinds of equilibrium phenomena. These are sufficiently ubiquitous to mention here.

### A. Osmotic pressure

A phenomenon of major biological importance is *osmotic pressure*: Imagine a body of water separated into two regions by a semipermeable membrane (see Figure 2). We add a small quantity of solute to the water on one side of the membrane, so that the mole fraction of the water has been reduced from 1 to  $x_{water} = 1 - x_{solute}$ . The membrane is such that the solute particles are too big to pass through, but the water molecules may pass freely from one side to another.

In this situation, something fascinating happens: Water will actually flow into the solute region and increase the pressure on the solute side, until thermodynamic equilibrium is reached. The resulting pressure at equilibrium is known as *osmotic pressure*.

Osmotic pressure is important because cell membranes are semipermeable. Therefore, cells need to have mechanisms to carefully regulate the internal concentrations of various components, so that they don't swell up and burst. In fact, the reason why cells swell up and burst when the external salt/sugar concentration is very low is exactly because water then flows into the cells until the osmotic pressure increase beyond what the membrane can handle. Conversely, when the external salt/sugar concentration is very high, then water flows out of the cells and they shrivel up.

To compute the osmotic pressure, we regard the water molecules as constituting an independent system that comes to equilibrium at some temperature  $T$  and pressure  $P$ . Now, although the pressure starts to rise on one

side of the system, so that there is not a uniform pressure at equilibrium, we can still use the equality of chemical potential (the molar Gibbs free energy) to determine the equilibrium point.

The short answer as to why this is true is that, since the pressure can change in response to material flows, the relevant condition to study the equilibrium process is one of constant *volume*. For constant volume processes, we work with the Helmholtz free energy,  $A$ . As can be seen from the end of the last lecture, the molar free energies  $\mu$  are unaffected.

So, at equilibrium we want,

$$\mu_{water}(T, P, 1) = \mu_{water}(T, P + \Delta P, 1 - x_{solute}) \quad (27)$$

where  $\mu_{water}(T, P; x)$  denotes the molar free energy of the water at temperature  $T$ ,  $P$ , and molar fraction  $x$ .

Now, if the solute does not interact with the solvent, then we can compute the molar free energy in much the same way as we did for an ideal gas. From the statistical-mechanical approach, we get,

$$\begin{aligned} \mu_{water}(T, P + \Delta P, 1 - x_{solute}) &= \mu_{water}(T, P + \Delta P, 1) \\ &\quad + RT \ln(1 - x_{solute}) \end{aligned} \quad (28)$$

From the relationship  $dG = VdP$  at constant temperature, and using the fact that for a liquid,  $\bar{V}$  is largely independent of pressure, gives,

$$\mu_{water}(T, P, 1) = \mu_{water}(T, P, 1) + \bar{V}\Delta P + RT \ln(1 - x_{solute}) \quad (29)$$

If  $x_{solute}$  is small, then  $\ln(1 - x_{solute}) = -x_{solute}$ , and so, we get,

$$\Delta P = \frac{RTx_{solute}}{\bar{V}} \quad (30)$$

The quantity  $\Delta P$  is the osmotic pressure. Note that for a liquid,  $\bar{V}$  is generally very small, so that the osmotic pressure rises very quickly with  $x_{solute}$ .

### B. Freezing point depression

The condition for solid-liquid equilibrium is,

$$\mu_{solid}(T, P) = \mu_{liquid}(T, P) \quad (31)$$

If the mole fraction of the liquid is now reduced from 1 to  $1 - x_{solute}$  due to the addition of a solute, then at the pressure  $P$ , the temperature at which solid-liquid equilibrium is achieved will in general shift. When  $x_{solute}$  is small, we have, at equilibrium,

$$\mu_{solid}(T + dT, P) = \mu_{liquid}(T + dT, P) + RT \ln(1 - x_{solute}) \quad (32)$$

so that,

$$\begin{aligned} \mu_{solid}(T, P) - \bar{S}_{solid}(T, P)dT &= \mu_{liquid}(T, P) \\ &\quad - \bar{S}_{liquid}(T, P)dT \\ &\quad - RTx_{solute} \end{aligned} \quad (33)$$

Since at the earlier equilibrium we have  $\mu_{solid}(T, P) = \mu_{liquid}(T, P)$ , we get,

$$dT = -\frac{RT}{\bar{S}_{liquid} - \bar{S}_{solid}} x_{solute} \quad (34)$$

As we showed in the last lecture,  $\bar{S}_{liquid} - \bar{S}_{solid} = \Delta\bar{S}_{fus} = \Delta\bar{H}_{fus}/T$ , so that,

$$dT = -\frac{RT^2}{\Delta\bar{H}_{fus}} x_{solute} \quad (35)$$

Therefore, the freezing point *decreases* as the result of impurities. This phenomenon, termed the *freezing point depression*, explains why salt added to ice causes the ice to melt.

### C. Gas dissolved in a liquid

Suppose a gas is over a liquid at some pressure  $P$ . The gas is different from the liquid (hydrogen gas over water, for example), so are not talking about a vapor-liquid equilibrium here. The issue here is that some of the gas will dissolve into the liquid, and the question we wish to answer is, how much?

Clearly, the higher the gas pressure, the more the gas will be “pushed” into the liquid. Conversely, the greater the mole fraction of the gas in the liquid, the greater the tendency for the gas to escape. At equilibrium, we have,

$$\mu_{gas}^{(l)}(T, P, x_{gas}) = \mu_{gas}^{(v)}(T, P) \quad (36)$$

where  $\mu_{gas}^{(l)}$  denotes the molar free energy of the gas when dissolved in the liquid state, at a mole fraction  $x_{gas}$ , while  $\mu_{gas}^{(v)}$  denotes the molar free energy of the gas in the vapor phase.

Now, for the vapor, we have  $\mu_{gas}^{(v)}(T, P) = \mu_{gas}^{(v)}(T, P_{ref}) + RT \ln \frac{P}{P_{ref}}$ . We would like to use a similar formula for the gas dissolved in the liquid. However, because the gas is in the liquid, it will have different properties than if it were dispersed through a vacuum medium. The gas particles can interact with the liquid, in such a way as to affect the tendency of the gas to remain dissolved. If the gas and liquid molecules are polar,

the interactions can be attractive. If the gas is nonpolar, such as air, and if the liquid molar are polar, such as water, then the liquid molecules will be more strongly attracted to each other than to the gas molecules, creating a tendency to force the gas molecules out of the liquid.

We therefore introduce a term, called the *fugacity*, denoted  $f$ , which is like an effective partial pressure of the gas when dissolved in the liquid. We have,

$$\mu_{gas}^{(l)}(T, P, x_{gas}) = \mu_{gas}^{(v)}(T, P_{ref}) + RT \ln \frac{f}{P_{ref}} \quad (37)$$

If we are dealing with an ideal gas mixture, then  $f = xP$ , that is, the fugacity is identical to the partial pressure. In the gas of an air-water mixture, the fugacity will be much larger, because the dissolved air will have a strong tendency to escape from the water, resulting in a larger effect partial pressure.

The equilibrium condition gives,

$$f = P \quad (38)$$

Now, when  $x_{gas} = 0$ , it makes sense that  $f = 0$ , for since there is no gas dissolved in the liquid, the effective pressure is zero. When  $x_{gas}$  is small, then  $f$  increases linearly with  $x_{gas}$  (this is simply from the concept of the derivative. The slope is  $(df/dx_{gas})_{x_{gas}=0}$ ). Defining  $C_H = (df/dx_{gas})_{x_{gas}=0}$  we get,

$$x_{gas} = \frac{P}{C_H} \quad (39)$$

This relationship is known as *Henry's Law*, and the quantity  $C_H$  is known as *Henry's Law Constant*. In general, it depends on the gas and liquid involved.

Note that the equilibrium fraction of gas dissolved in a liquid increases linearly with pressure. This explained why soda pop fizzes. The  $CO_2$  is forced into the liquid at high pressure. When you open the cap, the pressure drops, and so the equilibrium fraction of  $CO_2$  dropped significantly. The result is that, on the approach to equilibrium at the lower pressure,  $CO_2$  escapes from the liquid, resulting in the “fizz”.