

12.8: Liquid-Gas Equilibria

This section describes multicomponent systems in which a liquid phase is equilibrated with a gas phase.

12.8.1 Effect of liquid pressure on gas fugacity

If we vary the pressure of a liquid mixture at constant temperature and composition, there is a small effect on the fugacity of each volatile component in an equilibrated gas phase. One way to vary the pressure at essentially constant liquid composition is to change the partial pressure of a component of the gas phase that has negligible solubility in the liquid.

At transfer equilibrium, component i has the same chemical potential in both phases: $\mu_i(l) = \mu_i(g)$. Combining the relations $[\partial\mu_i(l)/\partial p]_{T,\{n_i\}} = V_i(l)$ and $\mu_i(g) = \mu_i^\circ(g) + RT \ln(f_i/p^\circ)$ (Eqs. 9.2.49 and 9.3.12), we obtain

$$\frac{d \ln(f_i/p^\circ)}{dp} = \frac{V_i(l)}{RT} \quad (12.8.1)$$

(equilibrated liquid and gas mixtures, constant T and liquid composition)

Equation 12.8.1 shows that an increase in pressure, at constant temperature and liquid composition, causes an increase in the fugacity of each component in the gas phase.

Integration of Eq. 12.8.1 between pressures p_1 and p_2 yields

$$f_i(p_2) = f_i(p_1) \exp \left[\int_{p_1}^{p_2} \frac{V_i(l)}{RT} dp \right] \quad (12.8.2)$$

(equilibrated liquid and gas mixtures, constant T and liquid composition)

The exponential on the right side is called the **Poynting factor**.

The integral in the Poynting factor is simplified if we make the approximation that $V_i(l)$ is independent of pressure. Then we obtain the approximate relation

$$f_i(p_2) \approx f_i(p_1) \exp \left[\frac{V_i(l)(p_2 - p_1)}{RT} \right] \quad (12.8.3)$$

(equilibrated liquid and gas mixtures, constant T and liquid composition)

The effect of pressure on fugacity is usually small, and can often be neglected. For typical values of the partial molar volume $V_i(l)$, the exponential factor is close to unity unless $|p_2 - p_1|$ is very large. For instance, for $V_i(l) = 100 \text{ cm}^3 \text{ mol}^{-1}$ and $T = 300 \text{ K}$, we obtain a value for the ratio $f_i(p_2)/f_i(p_1)$ of 1.004 if $p_2 - p_1$ is 1 bar, 1.04 if $p_2 - p_1$ is 10 bar, and 1.5 if $p_2 - p_1$ is 100 bar. Thus, unless the pressure change is large, we can to a good approximation neglect the effect of total pressure on fugacity. This statement applies only to the fugacity of a substance in a gas phase that is equilibrated with a liquid phase of constant composition containing the same substance. If the liquid phase is absent, the fugacity of i in a gas phase of constant composition is of course approximately proportional to the total gas pressure.

We can apply Eqs. 12.8.2 and 12.8.3 to *pure* liquid A, in which case $V_i(l)$ is the molar volume $V_A^*(l)$. Suppose we have pure liquid A in equilibrium with pure gaseous A at a certain temperature. This is a one-component, two-phase equilibrium system with one degree of freedom (Sec. 8.1.7), so that at the given temperature the value of the pressure is fixed. This pressure is the saturation vapor pressure of pure liquid A at this temperature. We can make the pressure p greater than the saturation vapor pressure by adding a second substance to the gas phase that is essentially insoluble in the liquid, without changing the temperature or volume. The fugacity f_A is greater at this higher pressure than it was at the saturation vapor pressure. The vapor pressure p_A , which is approximately equal to f_A , has now become greater than the saturation vapor pressure. It is, however, safe to say that the difference is negligible unless the difference between p and p_A is much greater than 1 bar.

As an application of these relations, consider the effect of the size of a liquid droplet on the equilibrium vapor pressure. The calculation of Prob. 12.8(b) shows that the fugacity of H_2O in a gas phase equilibrated with liquid water in a small droplet is

slightly greater than when the liquid is in a bulk phase. The smaller the radius of the droplet, the greater is the fugacity and the vapor pressure.

12.8.2 Effect of liquid composition on gas fugacities

Consider system 1 in Fig. 9.5. A binary liquid mixture of two volatile components, A and B, is equilibrated with a gas mixture containing A, B, and a third gaseous component C of negligible solubility used to control the total pressure. In order for A and B to be in transfer equilibrium, their chemical potentials must be the same in both phases:

$$\mu_A(l) = \mu_A^\circ(g) + RT \ln \frac{f_A}{p^\circ} \quad \mu_B(l) = \mu_B^\circ(g) + RT \ln \frac{f_B}{p^\circ} \quad (12.8.4)$$

Suppose we make an infinitesimal change in the liquid composition at constant T and p . This causes infinitesimal changes in the chemical potentials and fugacities:

$$d\mu_A(l) = RT \frac{df_A}{f_A} \quad d\mu_B(l) = RT \frac{df_B}{f_B} \quad (12.8.5)$$

By inserting these expressions in the Gibbs–Duhem equation $x_A d\mu_A = -x_B d\mu_B$ (Eq. 9.2.43), we obtain

$$\frac{x_A}{f_A} df_A = -\frac{x_B}{f_B} df_B \quad (12.8.6)$$

(binary liquid mixture equilibrated with gas, constant T and p)

This equation is a relation between changes in gas-phase fugacities caused by a change in the liquid-phase composition. It shows that a composition change at constant T and p that increases the fugacity of A in the equilibrated gas phase must decrease the fugacity of B.

Now let us treat the liquid mixture as a binary solution with component B as the solute. In the ideal-dilute region, at constant T and p , the solute obeys Henry's law for fugacity:

$$f_B = k_{H,B} x_B \quad (12.8.7)$$

For composition changes in the ideal-dilute region, we can write

$$\frac{df_B}{dx_B} = k_{H,B} = \frac{f_B}{x_B} \quad (12.8.8)$$

With the substitution $dx_B = -dx_A$ and rearrangement, Eq. 12.8.8 becomes

$$-\frac{x_B}{f_B} df_B = dx_A \quad (12.8.9)$$

Combined with Eq. 12.8.6, this is $(x_A/f_A) df_A = dx_A$, which we can rearrange and integrate as follows within the ideal-dilute region:

$$\int_{f_A^*}^{f_A} \frac{df_A}{f_A} = \int_1^{x_A'} \frac{dx_A}{x_A} \quad \ln \frac{f_A}{f_A^*} = \ln x_A' \quad (12.8.10)$$

The result is

$$f_A = x_A f_A^* \quad (12.8.11)$$

(ideal-dilute binary solution)

Here f_A^* is the fugacity of A in a gas phase equilibrated with pure liquid A at the same T and p as the mixture. Equation 12.8.11 is Raoult's law for fugacity applied to component A.

If component B obeys Henry's law at all compositions, then the Henry's law constant $k_{H,B}$ is equal to f_B^* and B obeys Raoult's law, $f_B = x_B f_B^*$, over the entire range of x_B .

We can draw two conclusions:

1. Figure 12.11 illustrates the case of a binary mixture in which component B has only positive deviations from Raoult's law, whereas component A has both positive and negative deviations (f_A is slightly less than $x_A f_A^*$ for x_B less than 0.3). This

unusual behavior is possible because both fugacity curves have two inflection points instead of the usual one. Other types of unusual nonideal behavior are possible (M. L. McGlashan, *J. Chem. Educ.*, **40**, 516–518, 1963).

12.8.3 The Duhem–Margules equation

To a good approximation, by assuming an ideal gas mixture and neglecting the effect of total pressure on fugacity, we can apply Eq. 12.8.20 to a liquid–gas system in which the total pressure is *not* constant, but instead is the sum of p_A and p_B . Under these conditions, we obtain the following expression for the rate at which the total pressure changes with the liquid composition at constant T :

$$\begin{aligned} \frac{dp}{dx_A} &= \frac{d(p_A + p_B)}{dx_A} = \frac{dp_A}{dx_A} - \frac{x_A p_B}{x_B p_A} \frac{dp_A}{dx_A} = \frac{dp_A}{dx_A} \left(1 - \frac{x_A/x_B}{p_A/p_B} \right) \\ &= \frac{dp_A}{dx_A} \left(1 - \frac{x_A/y_B}{y_A/y_B} \right) \end{aligned} \quad (12.8.21)$$

Here y_A and y_B are the mole fractions of A and B in the gas phase given by $y_A = p_A/p$ and $y_B = p_B/p$.

We can use Eq. 12.8.21 to make several predictions for a binary liquid–gas system at constant T .

- In some binary liquid–gas systems, the total pressure at constant temperature exhibits a maximum or minimum at a particular liquid composition. At this composition, dp/dx_A is zero but dp_A/dx_A is positive. From Eq. 12.8.21, we see that at this composition x_A/x_B must equal y_A/y_B , meaning that the liquid and gas phases have identical mole fraction compositions. The liquid with this composition is called an *azeotrope*. The behavior of systems with azeotropes will be discussed in Sec. 13.2.5.

12.8.4 Gas solubility

The activity of B in the gas phase is given by $a_B(g) = f_B/p^\circ$. If the solute is a nonelectrolyte and we choose a standard state based on mole fraction, the activity in the solution is $a_B(\text{sln}) = \Gamma_{x,B} \gamma_{x,B} x_B$. The equilibrium constant is then given by

$$K = \frac{\Gamma_{x,B} \gamma_{x,B} x_B}{f_B/p^\circ} \quad (12.8.22)$$

and the solubility, expressed as the equilibrium mole fraction of solute in the solution, is given by

$$x_B = \frac{K f_B/p^\circ}{\Gamma_{x,B} \gamma_{x,B}} \quad (12.8.23)$$

(nonelectrolyte solute in equilibrium with gas)

At a fixed T and p , the values of K and $\Gamma_{x,B}$ are constant. Therefore any change in the solution composition that increases the value of the activity coefficient $\gamma_{x,B}$ will decrease the solubility for the same gas fugacity. This solubility decrease is often what happens when a salt is dissolved in an aqueous solution, and is known as the *salting-out effect* (Prob. 12.11).

Unless the pressure is much greater than p° , we can with negligible error set the pressure factor $\Gamma_{x,B}$ equal to 1. When the gas solubility is low and the solution contains no other solutes, the activity coefficient $\gamma_{x,B}$ is close to 1. If furthermore we assume ideal gas behavior, then Eq. 12.8.23 becomes

$$x_B = K \frac{p_B}{p^\circ} \quad (12.8.24)$$

(nonelectrolyte solute in equilibrium with ideal gas, $\Gamma_{x,B}=1$, $\gamma_{x,B}=1$)

The solubility is predicted to be proportional to the partial pressure. The solubility of a gas that dissociates into ions in solution has a quite different dependence on partial pressure. An example is the solubility of gaseous HCl in water to form an electrolyte solution, shown in Fig. 10.1.

If the actual conditions are close to those assumed for Eq. 12.8.24, we can use Eq. 12.1.13 to derive an expression for the temperature dependence of the solubility for a fixed partial pressure of the gas:

$$\left(\frac{\partial \ln x_B}{\partial T} \right)_{p_B} = \frac{d \ln K}{dT} = \frac{\Delta_{\text{sol},B} H^\circ}{RT^2} \quad (12.8.25)$$

At the standard pressure, $\Delta_{\text{sol,B}}H^\circ$ is the same as the molar enthalpy of solution at infinite dilution.

Since the dissolution of a gas in a liquid is invariably an exothermic process, $\Delta_{\text{sol,B}}H^\circ$ is negative, and Eq. 12.8.25 predicts the solubility decreases with increasing temperature.

Note the similarity of Eq. 12.8.25 and the expressions derived previously for the temperature dependence of the solubilities of solids (Eq. 12.5.8) and liquids (Eq. 12.6.3). When we substitute the mathematical identity $dT = -T^2 d(1/T)$, Eq. 12.8.25 becomes

$$\left[\frac{\partial \ln x_B}{\partial (1/T)} \right]_{p_B} = -\frac{\Delta_{\text{sol,B}}H^\circ}{R} \quad (12.8.26)$$

We can use this form to evaluate $\Delta_{\text{sol,B}}H^\circ$ from a plot of $\ln x_B$ versus $1/T$.

The **ideal solubility** of a gas is the solubility calculated on the assumption that the dissolved gas obeys Raoult's law for partial pressure: $p_B = x_B p_B^*$. The ideal solubility, expressed as a mole fraction, is then given as a function of partial pressure by

$$x_B = \frac{p_B}{p_B^*} \quad (12.8.27)$$

(ideal solubility of a gas)

Here p_B^* is the vapor pressure of pure liquid solute at the same temperature and total pressure as the solution. If the pressure is too low for pure B to exist as a liquid at this temperature, we can with little error replace p_B^* with the saturation vapor pressure of liquid B at the same temperature, because the effect of total pressure on the vapor pressure of a liquid is usually negligible (Sec. 12.8.1). If the temperature is above the critical temperature of pure B, we can estimate a hypothetical vapor pressure by extrapolating the liquid–vapor coexistence curve beyond the critical point.

We can use Eq. 12.8.27 to make several predictions regarding the ideal solubility of a gas at a fixed value of p_B .

1. Of course, these predictions apply only to solutions that behave approximately as ideal liquid mixtures, but even for many nonideal mixtures the predictions are found to have good agreement with experiment.

As an example of the general validity of prediction 1, Hildebrand and Scott (*The Solubility of Nonelectrolytes*, 3rd edition, Dover, New York, 1964, Chap. XV) list the following solubilities of gaseous Cl_2 in several dissimilar solvents at 0°C and a partial pressure of 1.01 bar: $x_B = 0.270$ in heptane, $x_B = 0.288$ in SiCl_4 , and $x_B = 0.298$ in CCl_4 . These values are similar to one another and close to the ideal value $p_B/p_B^* = 0.273$.

12.8.5 Effect of temperature and pressure on Henry's law constants

At the standard pressure $p^\circ = 1$ bar, the value of $\Gamma_{x,B}$ is unity, and Eqs. 12.1.13 and 12.1.14 then give the following expressions for the dependence of the dimensionless quantity $k_{\text{H,B}}/p^\circ$ on temperature:

$$\frac{d \ln(k_{\text{H,B}}/p^\circ)}{dT} = -\frac{d \ln K}{dT} = -\frac{\Delta_{\text{sol,B}}H^\circ}{RT^2} \quad (12.8.31)$$

($p=p^\circ$)

$$\frac{d \ln(k_{\text{H,B}}/p^\circ)}{d(1/T)} = -\frac{d \ln K}{d(1/T)} = \frac{\Delta_{\text{sol,B}}H^\circ}{R} \quad (12.8.32)$$

($p=p^\circ$)

These expressions can be used with little error at any pressure that is not much greater than p° , say up to at least 2 bar, because under these conditions $\Gamma_{x,B}$ does not differ appreciably from unity.

To find the dependence of $k_{\text{H,B}}$ on pressure, we substitute $\Gamma_{x,B}$ in Eq. 12.8.30 with the expression for $\Gamma_{x,B}$ at pressure p' found in Table 9.6:

$$k_{\text{H,B}}(p') = \frac{\Gamma_{x,B}(p')p^\circ}{K} = \frac{p^\circ}{K} \exp\left(\int_{p^\circ}^{p'} \frac{V_B^\infty}{RT} dp\right) \quad (12.8.33)$$

We can use Eq. 12.8.33 to compare the values of $k_{\text{H,B}}$ at the same temperature and two different pressures, p_1 and p_2 :

$$k_{\text{H,B}}(p_2) = k_{\text{H,B}}(p_1) \exp\left(\int_{p_1}^{p_2} \frac{V_{\text{B}}^{\infty}}{RT} dp\right) \quad (12.8.34)$$

An approximate version of this relation, found by treating V_{B}^{∞} as independent of pressure, is

$$k_{\text{H,B}}(p_2) \approx k_{\text{H,B}}(p_1) \exp\left[\frac{V_{\text{B}}^{\infty}(p_2 - p_1)}{RT}\right] \quad (12.8.35)$$

Unless $|p_2 - p_1|$ is much greater than 1 bar, the effect of pressure on $k_{\text{H,B}}$ is small; see Prob. 12.12 for an example.

This page titled [12.8: Liquid-Gas Equilibria](#) is shared under a [CC BY 4.0](#) license and was authored, remixed, and/or curated by [Howard DeVoe](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.