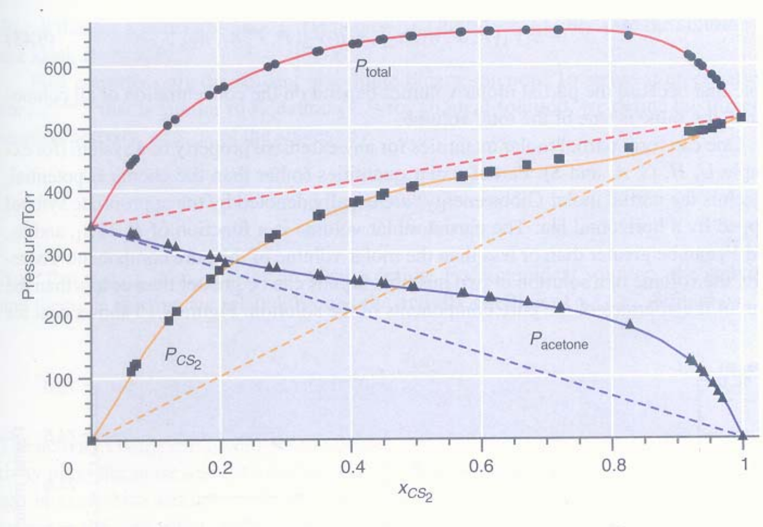


FIGURE 9.13 The data in Table 9.3 are plotted versus x_{CS_2}. The dashed lines show the expected behavior if Raoult's law were obeyed.

Figure 9.13

Thermodynamically, real and miscible solutions show:

$$\triangle G_{mixing} = nRT\sum_i x_i \ln x_i < 0$$

$$\triangle S_{mixing} = -\left(\frac{\partial \triangle G_{mixing}}{\partial T}\right)_{P,n_1,n_2} = -nR\sum_i x_i \ln x_i > 0$$

$$\triangle V_{mixing} \neq 0 \qquad \text{and}$$

$$\triangle H_{mixing} \neq 0 \tag{9.42}$$

For ideal solution:

$$V_m^{ideal} = x_A V_{m,A}^* + (1 - x_A) V_{m,B}^* \tag{9.43}$$

This is not applicable for real solution (Figure 14)

Note that $\triangle V_m = V_m^{real} - V_m^{ideal} \lessgtr 0$ depending on composition.

The deviations are small but evident depending on the composition!

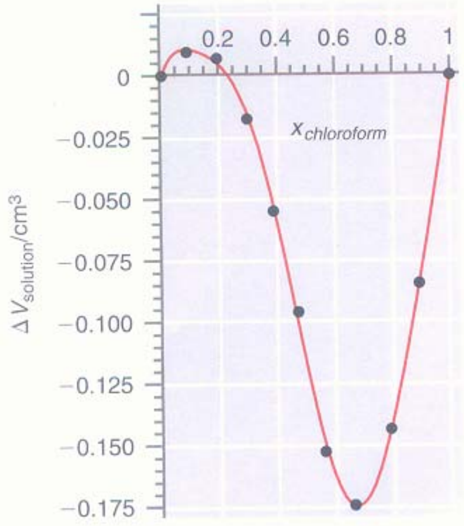


FIGURE 9.14

Deviations in the volume from the behavior expected for 1 mol of an ideal solution [Equation (9.43)] are shown for the acetone–chloroform system as a function of the mole fraction of chloroform.

Partial molar quantity:

1 mole of pure water (25℃) = 18.1 cm^3 ..... (a)

1 mole of water added to ethanol-water solution with x_{H_2O} = 0.75

⇒ Increased by 16 cm^3 ..... (b)

a ≠ b (Partial molar volume)

⇒ Local structure around water in the solution is more compact.

Partial molar volume is defined (with bar on) as:

$$\overline{V_1}(P,T,n_1,n_2) = \left(\frac{\partial V}{\partial n_1}\right)_{P,T,n_2} \tag{9.44}$$

▶1 mole of component 1 is added to such a large volume so that the solution composition is assumed constant.

So, for binary solution,

$$V = n_1\overline{V_1}(P,T,n_1,n_2) + n_2\overline{V_2}(P,T,n_1,n_2) \tag{9.45}$$

Partial molar quantities for any extensive properties (U, H, G, A, S) can be formed.(Chemical potential is the partial molar Gibbs energy)

Figure 9.15 : Partial molar volume of acetone and chloroform.
$\overline{V_1}$ increases as $\overline{V_2}$ decreases, like Gibbs-Duhem eg.

FIGURE 9.15

The partial molar volumes of chloroform (yellow curve) and acetone (red curve) in a chloroform–acetone binary solution are shown as a function of $x_{chloroform}$.

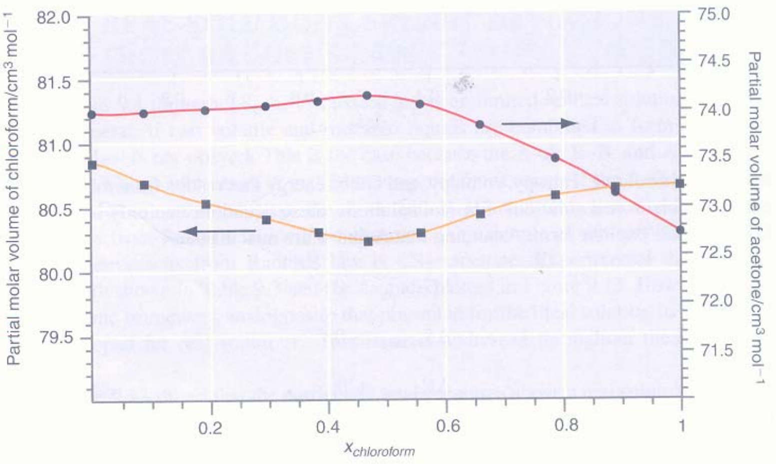


Figure 9.15

In terms of partial molar volume, Gibbs-Duhem eq takes the form:
(Partial molar volume and chemical potential are related in the same way to the G-D eq)

$$x_1 d\overline{V_1} + x_2 d\overline{V_2} = 0 \quad \text{or} \quad d\overline{V_1} = -\frac{x_2}{x_1} d\overline{V_2} \qquad (9.46)$$

(Note : "-" on partial molar quantities)

9.10 Ideal Dilute Solution

For dilute solution, ideal solution model is applied.
Chemical potential of a component in real solution is separated in two terms (like ideal solution): a standard state one and a partial pressure dependent one.

$$\mu_i^{solution} = \mu_i^* + RT\ln\frac{P_i}{P_i^*} \qquad (9.47)$$

Recall that for a pure substance,

$$\mu_i^*(vapor) = \mu_i^*(liquid) = \mu_i^*$$

$$(\, P_i \neq x_i P_i^* \text{ for } \; real \;\; solution)$$

First consider only the solvent. We define activity as:

$$a_{solvent} = \frac{P_{solvent}}{P_{solvent}^*} \qquad (9.48)$$

Note for ideal solution:

$$a_{solvent} = x_{solvent}$$

For nonideal solution, activity coefficient (γ_{solvent}) is introduced as:

$$\gamma_{solvent} = \frac{a_{solvent}}{x_{solvent}} \qquad (9.49)$$

Ideal behavior is obtained as $x_{solute} \to 0$.

Chemical potential vs activity

Combining egs (9.47) and (9.48)

$$\mu_i^{solution} = \mu_i^* + RT\ln a_i \qquad (9.50)$$

→ Central eq describing real solution to follow.

Ideal dilute solution is defined as:

$$x_{solute} \rightarrow 0, \quad x_{solvent} \rightarrow 1$$

See Figure 9.16 where the Raoult's law(dotted line) is observed in the limit $x_{acetone} \rightarrow 1$ and $x_{CS_2} \rightarrow 0$

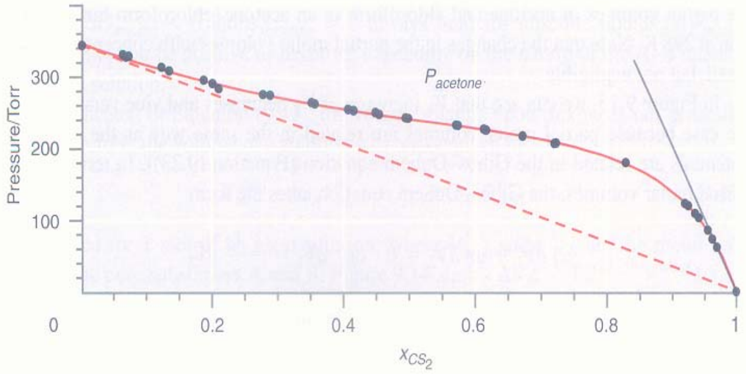


FIGURE 9.16

The partial pressure of acetone from Table 9.3 is plotted as a function of x_{CS_2}. Note that the $P_{acetone}$ follows Raoult's law as $x_{CS_2} \rightarrow 0$, and Henry's law as $x_{CS_2} \rightarrow 1$.

Figure 9.16

In this limit, acetone molecules at the surface are surrounded by the acetone molecules.

$$\rightarrow P_{acetone} = x_{acetone} P^{*}_{acetone}$$

In the opposite limit where

$$x_{acetone} \rightarrow 0 \qquad \text{(Now consider solute)}$$

→Acetone molecules at the surfaces are surrounded by CS_2.

$$P_{acetone} \neq x_{acetone} P^{*}_{acetone}$$

But it is apparent that from Figure 9.16 that

$$P_{acetone} \propto x_{acetone} \quad (linear) \Rightarrow$$

$$P_{acetone} = x_{acetone} k_H^{acetone} \qquad as \;\; x_{acetone} \rightarrow 0 \qquad (9.51)$$

Eg. (9.51) is called Henry's law(k_H = Henry's constant).

As the solution approaches ideal,

$$k_H^i \rightarrow P_i^*$$

For Figure 9.13,

$$k_H^{CS_2} = 2010\ Torr\ (P_{CS_2}^* = 512.3)$$
$$k_H^{acetone} = 1950 \quad (P_{acetone}^* = 343.8)$$

⇒ Henry's constants > vapor pressure

⇒ The system shows positive deviation from the Raoult's law.
(See Table 9.4 for aqueous solutions of a number of solutes.)

The ideal dilute solution can be concluded as a solution in which solvent follow Raoult's law and the solute of Henry's law.

9.11 Activities are defined w.r.t standard state.

For the solvent in dilute solution ($x_{solvent}$ → 1):

$$a_i = \frac{P_i}{P_i^*} \text{ and } \gamma_i = \frac{a_i}{x_i} \qquad (9.52)$$

By doing so,
activity (See fig 13)→ concentration and $\gamma \rightarrow 1$*and solution→ideal as* $x_i \rightarrow 1$

Figure 9.13 shows that the activity approaches unity as $x_{solvent}$ → 1.

Activity calculated by (9.52) is called **Raoult's law standard state based activity**. But Eq (9.52) and its standard state is not appropriate for solute which obeys Henry's law. So, in this case,

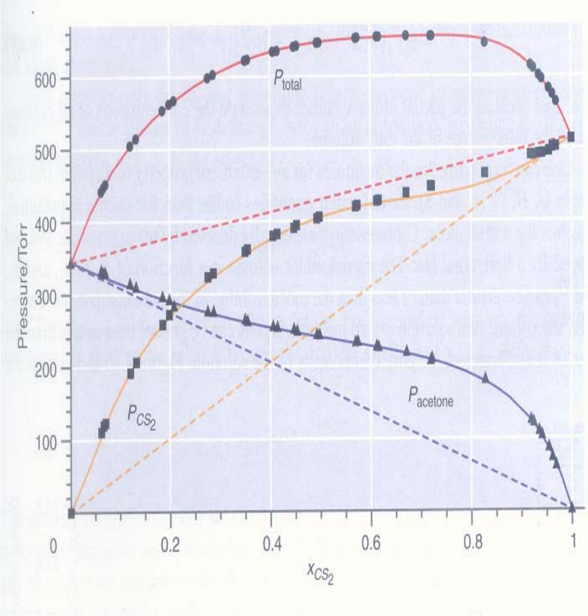


FIGURE 9.13

The data in Table 9.3 are plotted versus x_{CS_2}. The dashed lines show the expected behavior if Raoult's law were obeyed.

$$\mu_{solute}^{solution} = \mu_{solute}^{*} + RT\ln\frac{k_H^{solute}x_{solute}}{P_{solute}^{*}} \quad as \quad x_{solute}\rightarrow 0 \qquad (9.53)$$

$$= [\mu_{solute}^{*} + RT\ln\frac{k_H^{solute}}{P_{solute}^{*}}] + RT\ln x_{solute}$$

$$= \mu_{solute}^{*H} + RT\ln x_{solute}$$

where the Henry's law standard state chemical potential is given by

$$\mu_{solute}^{*H} = \mu_{solute}^{*} + RT\ln\frac{k_H^{solute}}{P_{solute}^{*}} \qquad (9.54)$$

Activity and activity coefficients based on Henry's are defined:

$$a_i = \frac{P_i}{k_i^H} \quad \text{and} \quad \gamma_i = \frac{a_i}{x_i} \qquad (9.55)$$

By doing so,
activity (See fig 13)→ concentration, $\gamma\rightarrow 1$ and solution→ideal as $x_i\rightarrow 0$

Example Problem 9.8

Calculate the activity coefficient for CS_2 at $x_{CS_2} = 0.3502$ using data from Table 9.3. (x_{CS2} vs P_{CS2} and $P_{Acetone}$) Assume a Raoult's law ss.

Solution

$$a_{CS_2}^{R} = \frac{P_{CS_2}}{P_{CS_2}^{*}} = \frac{358.3\ Torr}{512.3\ Torr} = 0.6994$$

$$\gamma_{CS_2}^{R} = \frac{a_{CS_2}^{R}}{x_{CS_2}} = \frac{0.6994}{0.3502} = 1.997$$

Calculated results are shown in Figure 9.17 as a function of x_{CS_2}. Note that $\gamma_{CS_2}^{R} \to 1$ as $x_{CS_2} \to 1$.

The activity and activity coefficients using Henry's law ss are calculated and seen in Figure 9.17 (Example Problem 9.8).

$$a_{CS_2}^{H} = \frac{P_{CS_2}}{k_{H,CS_2}} = \frac{358.3\ Torr}{2010\ Torr} = 0.1783$$

$$\gamma_{CS_2}^{H} = \frac{a_{CS_2}^{H}}{x_{CS_2}} = \frac{0.1783}{0.3502} = 0.5090$$

Note that $\gamma_{CS_2}^{H} \to 1$ as $x_{CS_2} \to 0$.

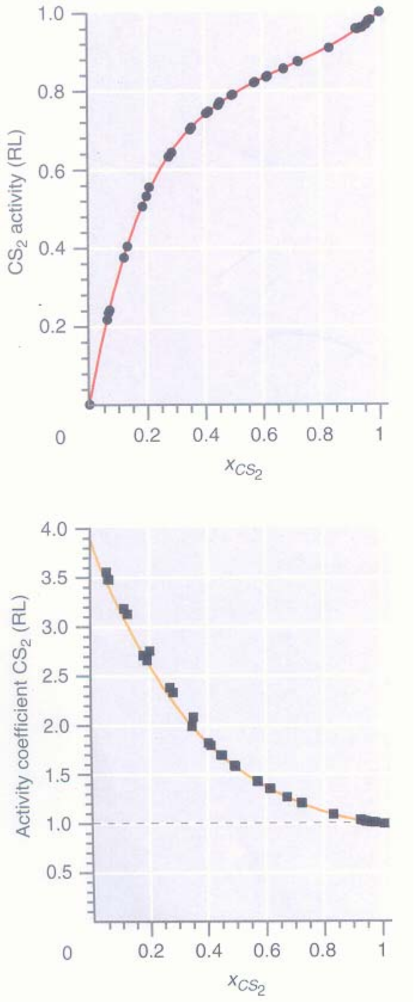


FIGURE 9.17

The activity and activity coefficient for CS_2 in a CS_2−acetone solution based on a Raoult's law standard state are shown as a function of x_{CS_2}.

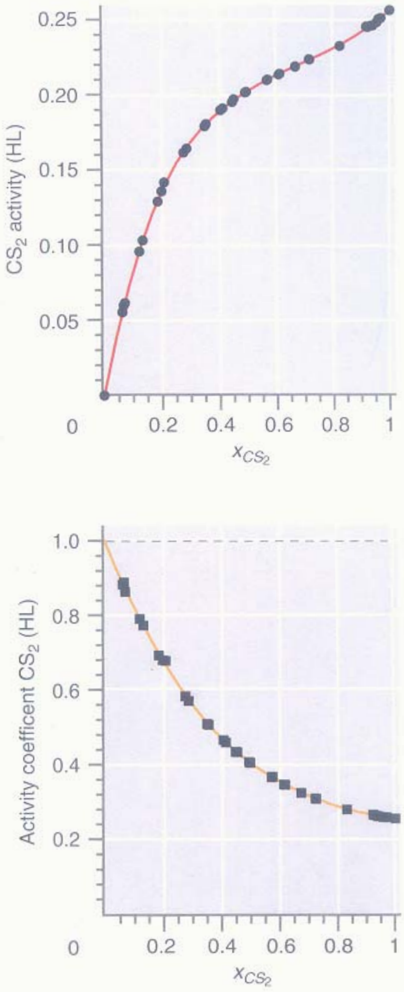


FIGURE 9.18

The activity and activity coefficient for CS_2 in a CS_2−acetone solution based on a Henry's law standard state are shown as a function of x_{CS_2}.

Mole fraction→molality

Divide Eq (9.56) by $n_{solvent}M_{solvent}$(= mass of solvent):

$$x_{solute} = \frac{n_{solute}}{n_{solvent} + n_{solute}} = \frac{m_{solute}}{\frac{1}{M_{solvent}} + m_{solute}} \qquad (9.56)$$

m_{solute} = molality of the solute,

$M_{solvent}$ = molecular mass of the solvent in $kg\,mol^{-1}$.

Note $m_{solute} = n_{solute}/n_{solvent}M_{solvent} \to x_{solute}/M_{solvent}$ as $x_{solute} \to 0$.

Using molality as concentration unit, activity and activity coefficient of the solute are defined by

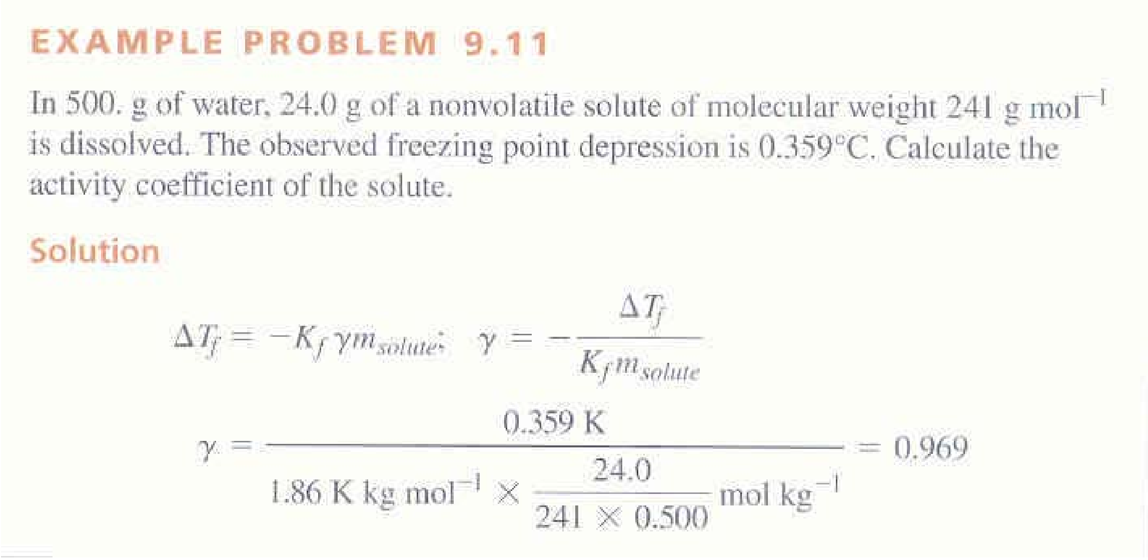
$$a_{solute}^{molality} = \frac{P_{solute}}{k_H^{molality}} \quad \text{with } a_{solute}^{molality} \to m_{solute} \text{ as } m_{solute} \to 0 \quad (9.57)$$

$$\gamma_{solute}^{molality} = \frac{a_{solute}^{molality}}{m_{solute}} \quad \text{with } \gamma_{solute}^{molality} \to 1 \text{ as } m_{solute} \to 0 \quad (9.58)$$

The colligavite properties refer to the solvent properties in a dilute solution. So, Raoult's law ss applies. Equations (9.33), (9.35), and (9.41)(Derived for ideal solution) can be used with activities replacing concentrations, ie m → a = γ m or a = γ c.

$$\begin{aligned} \Delta T_f &= -K_f \gamma m_{solute} \\ \Delta T_b &= K_b \gamma m_{solute} \\ \pi &= \gamma c_{solute} RT \end{aligned} \qquad (9.59)$$

The activity coefficient is defined wrt molality for the boiling point elevation (ΔT_b) and freezing point depression (ΔT_f), and wrt molarity for the osmotic pressure (π). Equations (9.59) provides a useful way to determine activity coefficients as shown in Example Problem 9.11.



EXAMPLE PROBLEM 9.11

In 500. g of water, 24.0 g of a nonvolatile solute of molecular weight 241 g mol^{-1} is dissolved. The observed freezing point depression is 0.359°C. Calculate the activity coefficient of the solute.

Solution

$$\Delta T_f = -K_f \gamma m_{solute}; \quad \gamma = -\frac{\Delta T_f}{K_f m_{solute}}$$

$$\gamma = \frac{0.359\text{ K}}{1.86\text{ K kg mol}^{-1} \times \dfrac{24.0}{241 \times 0.500}\text{ mol kg}^{-1}} = 0.969$$

Scan Example 9.11 here

9.12 HENRY'S LAW AND THE SOLUBILITY OF GASES IN A SOLVENT

The ideal dilute solution model can be applied to the solubility of gases in liquid solvents. An example for this type of solution equilibrium is the amount of N_2 absorbed by water. One of the components of the solution is a liquid and the other is a gas. The equilibrium of interest between the solution and the vapor phase is

$$N_2(aqueous) \rightleftarrows N_2(vapor) \qquad (9.60)$$

The chemical potential of the dissolve N_2 is given by

$$\mu_{N_2}^{solution} = \mu_{N_2}^{*H}(vapor) + RT\ln a_{solute} \qquad (9.61)$$

In this case, a Henry's law standard state is the appropriate choice, because the nitrogen is sparingly soluble in water. The mole fraction of N_2 in solution, x_{N_2}, is given by

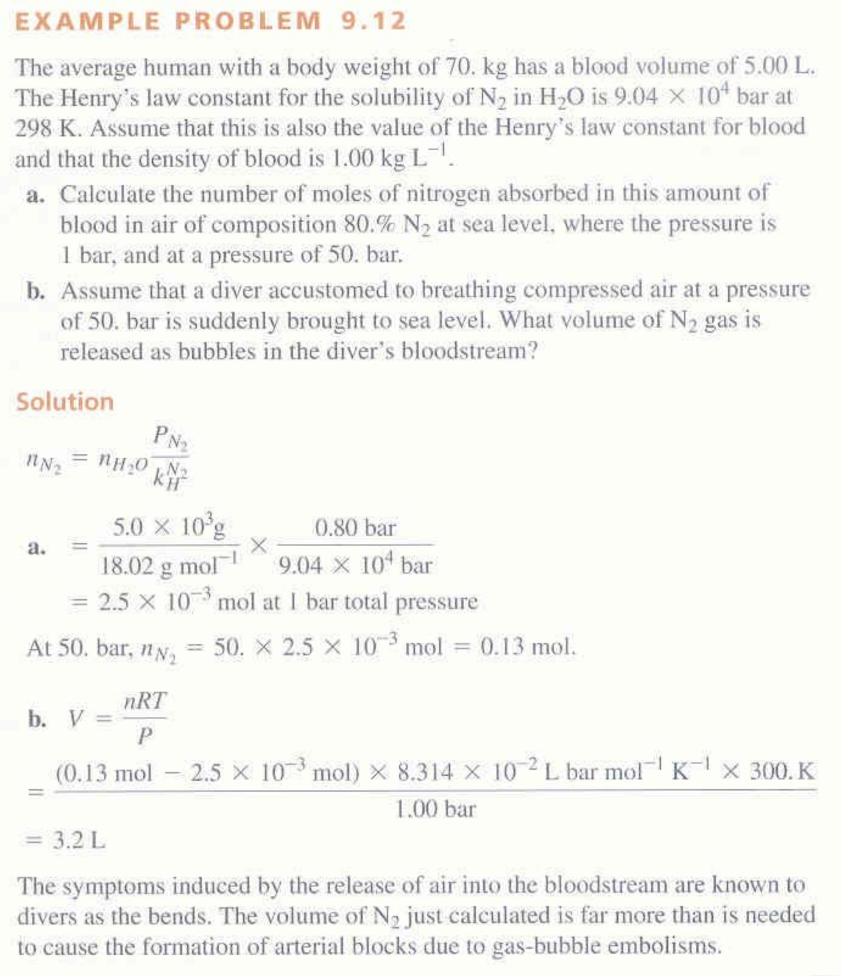
$$x_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{H_2O}} \approx \frac{n_{N_2}}{n_{H_2O}} \qquad (9.62)$$

The amount of dissolved gas is given by

$$n_{N_2} = n_{H_2O} x_{N_2} = n_{H_2O} \frac{P_{N_2}}{k_H^{N_2}} \qquad (9.63)$$

Note concentration=activity in ideal dilute solution.

Example Problem 9.12 shows how Equation (9.63) is used to model the dissolution of a gas in a liquid.



EXAMPLE PROBLEM 9.12

The average human with a body weight of 70. kg has a blood volume of 5.00 L. The Henry's law constant for the solubility of N_2 in H_2O is 9.04×10^4 bar at 298 K. Assume that this is also the value of the Henry's law constant for blood and that the density of blood is 1.00 kg L^{-1}.

a. Calculate the number of moles of nitrogen absorbed in this amount of blood in air of composition 80.% N_2 at sea level, where the pressure is 1 bar, and at a pressure of 50. bar.

b. Assume that a diver accustomed to breathing compressed air at a pressure of 50. bar is suddenly brought to sea level. What volume of N_2 gas is released as bubbles in the diver's bloodstream?

Solution

$$n_{N_2} = n_{H_2O} \frac{P_{N_2}}{k_H^{N_2}}$$

a. $$= \frac{5.0 \times 10^3 \text{g}}{18.02 \text{ g mol}^{-1}} \times \frac{0.80 \text{ bar}}{9.04 \times 10^4 \text{ bar}}$$

$$= 2.5 \times 10^{-3} \text{ mol at 1 bar total pressure}$$

At 50. bar, $n_{N_2} = 50. \times 2.5 \times 10^{-3} \text{ mol} = 0.13 \text{ mol}$.

b. $$V = \frac{nRT}{P}$$

$$= \frac{(0.13 \text{ mol} - 2.5 \times 10^{-3} \text{ mol}) \times 8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 300. \text{ K}}{1.00 \text{ bar}}$$

$$= 3.2 \text{ L}$$

The symptoms induced by the release of air into the bloodstream are known to divers as the bends. The volume of N_2 just calculated is far more than is needed to cause the formation of arterial blocks due to gas-bubble embolisms.

Example 9.12 here

9.13 CHEMICAL EQUILIBRIUM IN SOLUTION

Brief Review

$$\alpha A+\beta B\rightarrow\gamma C+\delta D \tag{6.54}$$

α, β < 0

γ, δ > 0

$$\mu_i\equiv\frac{\partial G}{\partial n_i})_{T,P,n_j\neq n_i} \tag{6.37}$$

→ $dG=\mu_i dn_i$ @ T, P = constant

Gibbs energy change of the reaction is given by

$$\triangle G_R=\triangle G_R^o+\gamma RT\ln\frac{P_C}{P^o}+\delta RT\ln\frac{P_D}{P^o}-\alpha RT\ln\frac{P_A}{P^o}-\beta RT\ln\frac{P_B}{P^o}$$

$$=\triangle G_R^o+RT\ln\frac{(\frac{P_C}{P^o})^\gamma(\frac{P_D}{P^o})^\delta}{(\frac{P_A}{P^o})^\alpha(\frac{P_B}{P^o})^\beta} \tag{6.56}$$

At standard state (P = 1bar):

$$\triangle G_R^o=\gamma\mu_C^o(T)+\delta\mu_D^o(T)-\alpha\mu_A^o(T)-\beta\mu_B^o(T)=\sum_i v_i\triangle G_{f,i}^o \tag{6.57}$$

$$Q_P=\frac{(\frac{P_C}{P^o})^\gamma(\frac{P_D}{P^o})^\delta}{(\frac{P_A}{P^o})^\alpha(\frac{P_B}{P^o})^\beta} \tag{6.58}$$

Q_P = Reaction quotient of pressure

Then Eq (6.56) is written as

$$\triangle G_R=\triangle G_R^o+RT\ln Q_P \tag{6.59}$$

Note: $\triangle G_R$ is separated into two terms: Only one term depends on the partial pressure of reactants and products.

If $\triangle G_R < 0$ reaction will spontaneously move to the right.

If $\triangle G_R > 0$ reaction will spontaneously move to the left.

At equilibrium

$\triangle G_R = 0$ and

$$\begin{aligned}\triangle G_R^o &= -RT\ln Q_P \\ &= -RT\ln K_P\end{aligned}$$

$$\ln K_P = -\frac{\triangle G_R^o}{RT} \qquad (6.60)$$

$K \equiv$ Thermodynamic equilibrium constant

For a reaction between solutes in a solution @ equilibrium:

$$\sum_j v_j \mu_j (solution)_{equilibrium} = 0 \qquad (9.64)$$

Eq (9.64) can be broken into standard state chemical potential and a concentration dependent term. Assume Henry's law ($x_i \rightarrow a_i$) standard state for each solute (See eq 9.53), then (64) becomes

$$\sum_j v_j \mu_j^{*H}(solution) + RT\sum_j \ln(a_i^{eq})^{v_j} = 0 \qquad (9.65)$$

Then using $dG = \mu_i dn_i$

$$\triangle G^o_{reaction} = -RT\sum_j \ln(a_i^{eq})^{v_j} = -RT\ln K \qquad (9.66)$$

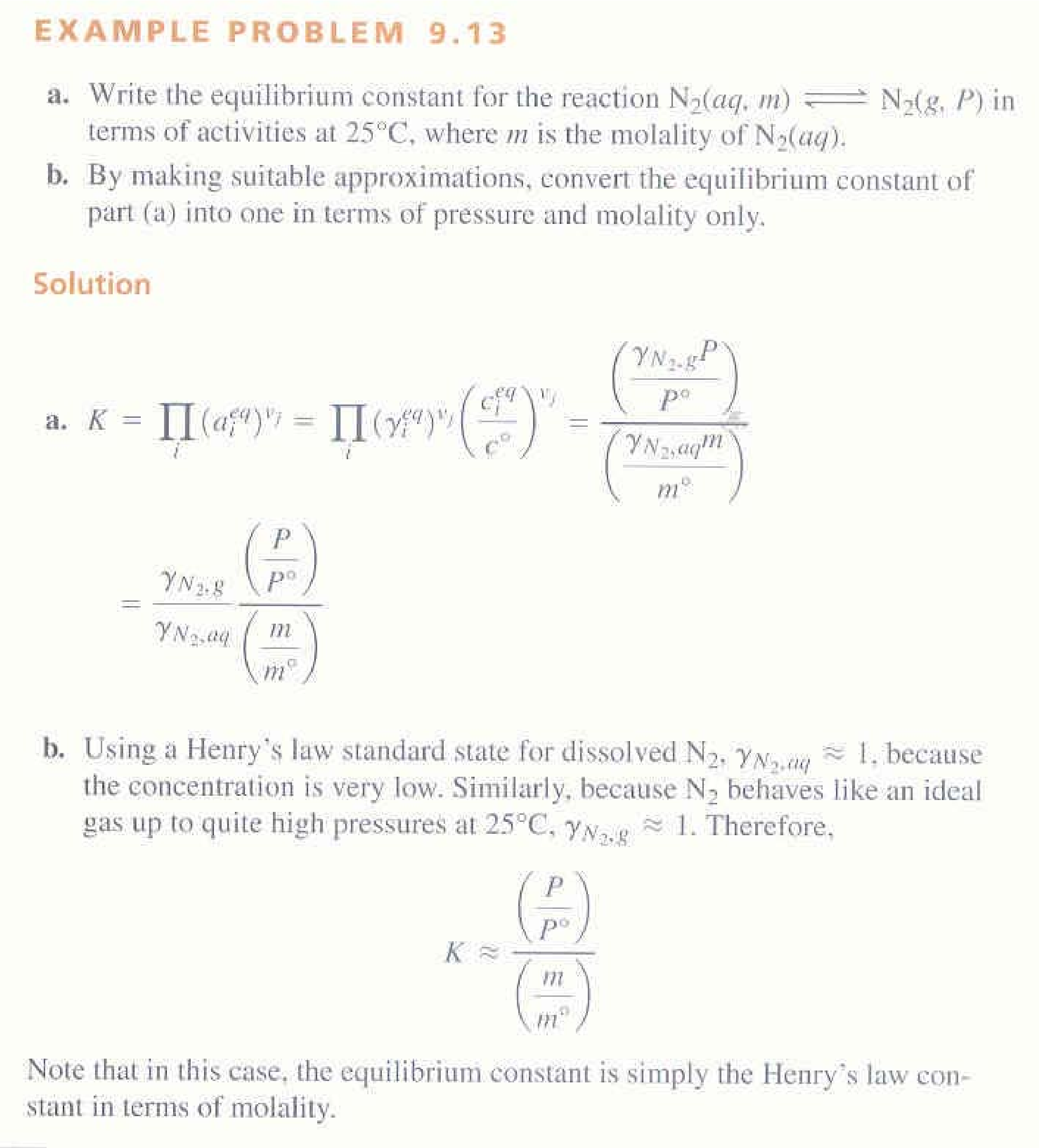
The equlibrium constant in terms of activity is given by

$$K = \prod_i (a_i^{eq})^{v_j} = \prod_i (\gamma_i^{eq})^{v_j} (\frac{c_i^{eq}}{c^o})^{v_j} \qquad (9.67)$$

Note c^o is introduced for dimensionless concentration (eq 6.72).

An equilibrium constant in terms of molarity or molarity can be defined by setting all activity coefficients = 1 ($\gamma_i = 1$) in (9.67). (Reasonable for dilute solution using Henry's law standard state)

$$K = \prod_i (\gamma_i^{eq})^{v_j} (\frac{c_i^{eq}}{c^o})^{v_j} \approx \prod_i (\frac{c_i^{eq}}{c^o})^{v_j} \qquad (9.68)$$



EXAMPLE PROBLEM 9.13

- **a.** Write the equilibrium constant for the reaction $N_2(aq, m) \rightleftharpoons N_2(g, P)$ in terms of activities at 25°C, where m is the molality of $N_2(aq)$.
- **b.** By making suitable approximations, convert the equilibrium constant of part (a) into one in terms of pressure and molality only.

Solution

a. $$K = \prod_i (a_i^{eq})^{v_j} = \prod_i (\gamma_i^{eq})^{v_j} \left(\frac{c_i^{eq}}{c^\circ}\right)^{v_j} = \frac{\left(\frac{\gamma_{N_2,g} P}{P^\circ}\right)}{\left(\frac{\gamma_{N_2,aq} m}{m^\circ}\right)}$$

$$= \frac{\gamma_{N_2,g}}{\gamma_{N_2,aq}} \frac{\left(\frac{P}{P^\circ}\right)}{\left(\frac{m}{m^\circ}\right)}$$

b. Using a Henry's law standard state for dissolved N_2, $\gamma_{N_2,aq} \approx 1$, because the concentration is very low. Similarly, because N_2 behaves like an ideal gas up to quite high pressures at 25°C, $\gamma_{N_2,g} \approx 1$. Therefore,

$$K \approx \frac{\left(\frac{P}{P^\circ}\right)}{\left(\frac{m}{m^\circ}\right)}$$

Note that in this case, the equilibrium constant is simply the Henry's law constant in terms of molality.

Scan Example 9.13 here