

Name: 陈稼霖
StudentID: 45875852

Problem 11.7. Water is slightly soluble in liquid nitrogen. At -196°C (the boiling point of liquid nitrogen), the mole fraction of water in a saturated solution is 1.00×10^{-5} . Compute the mass of water that can dissolve in 1.00 kg of boiling liquid nitrogen.

Solution: The number of moles of 1.00 kg nitrogen is

$$n_{N_2} = \frac{m_{N_2}}{1.00 \times 10^{-3} g \cdot kg^{-1} \times M_{N_2}} = \frac{1.00 kg}{1.00 \times 10^{-3} g \cdot kg^{-1} \times 28.0 g \cdot mol^{-1}} = 35.7 mol$$

The mass of water that can dissolve in 1.00 kg of boiling liquid nitrogen is

$$\begin{aligned} m_{H_2O} &= \frac{1.00 \times 10^{-5} n_{N_2}}{1.00 + 1.00 \times 10^{-5}} \times M(H_2O) = \frac{1.00 \times 10^{-5} \times 35.7 mol}{1.00 + 1.00 \times 10^{-5}} \times 18.0 g \cdot mol^{-1} \\ &= \underline{6.43 \times 10^{-3} g} \end{aligned}$$

□

Problem 11.10. A perchloric acid solution is 60.0% HClO_4 by mass. It is simultaneously 9.20 M at 25°C .

- Compute the density of this solution.
- What volume of this solution should be used in mixing 1.00 L of a 1.00 M perchloric acid solution?

Solution:

- Consider 1.00 L of this solution. The mass of HClO_4 in the solution is

$$m_{HClO_4} = c_{HClO_4} V_{solution} M_{HClO_4} = 9.20 mol \cdot L^{-1} \times 1.00 L \times 100.5 g \cdot mol^{-1} = 9.246 \times 10^2 g$$

The mass of the solution is

$$m_{solution} = \frac{m_{HClO_4}}{60.0\%} = \frac{9.246 \times 10^2 g}{60.0\%} = 1.54 \times 10^3 g = 1.54 kg$$

The density of this solution is

$$\rho_{solution} = \frac{m_{solution}}{V_{solution}} = \frac{1.54 kg}{1.00 L} = \underline{1.54 kg \cdot L^{-1}}$$

- The volume of this solution should be used in mixing 1.00 L of a 1.00 M perchloric acid solution is

$$V_i = \frac{c_f V_f}{c_i} = \frac{1.00 mol \cdot mol^{-1} \times 1.00 L}{9.20 mol \cdot mol^{-1} \times} = 0.109 L = \underline{109 mL}$$

□

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Problem 11.14. Rewrite the following balanced equations as net ionic equations.

- (a) $\text{Na}_2\text{SO}_4(\text{aq}) + \text{BaCl}_2(\text{aq}) \longrightarrow \text{BaSO}_4(\text{s}) + 2\text{NaCl}(\text{aq})$
- (b) $6\text{NaOH}(\text{aq}) + 3\text{Cl}_2(\text{g}) \longrightarrow \text{NaClO}_3(\text{aq}) + 5\text{NaCl}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$
- (c) $\text{Hg}_2(\text{NO}_3)_2(\text{aq}) + 2\text{KI}(\text{aq}) \longrightarrow \text{Hg}_2\text{I}_2(\text{s}) + 2\text{KNO}_3(\text{aq})$
- (d) $3\text{NaOCl}(\text{aq}) + \text{KI}(\text{aq}) \longrightarrow \text{NaIO}_3(\text{aq}) + 2\text{NaCl}(\text{aq}) + \text{KCl}(\text{aq})$

Solution:

- (a) $\text{SO}_4^{2-}(\text{aq}) + \text{Ba}^{2+}(\text{aq}) \longrightarrow \text{BaSO}_4(\text{s})$
- (b) $6\text{OH}^{-}(\text{aq}) + 3\text{Cl}_2(\text{g}) \longrightarrow \text{ClO}_3^{-}(\text{aq}) + 5\text{Cl}^{-}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$
- (c) $2\text{Hg}^{+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \longrightarrow \text{Hg}_2\text{I}_2(\text{s})$
- (d) $3\text{OCl}^{-}(\text{aq}) + \text{I}^{-}(\text{aq}) \longrightarrow \text{IO}_3^{-}(\text{aq}) + 3\text{Cl}^{-}(\text{aq})$ □

Problem 11.24. Phosphorus pentachloride reacts violently with water to give a mixture of phosphoric acid and hydrochloric acid.

- (a) Write a balanced chemical equation for this reaction.
- (b) Determine the concentration (in moles per liter) of each of the acids that result from the complete reaction of 1.22 L of phosphorus pentachloride (measured at 215°C and 0.962 atm pressure) with enough water to give a solution volume of 697 mL.

Solution:

- (a) $\text{PCl}_5 + 4\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_4 + 5\text{HCl}$
- (b) The number of moles of Phosphorus pentachloride is

$$n_{\text{PCl}_5} = \frac{PV}{RT} = \frac{0.962\text{atm} \times 1.22\text{L}}{0.0821\text{L} \cdot \text{atm} \cdot \text{mol}^{-1}\text{K}^{-1} \times 488\text{K}} = 0.0293\text{mol}$$

The numbers of moles of phosphoric acid and hydrochloric acid are

$$n_{\text{H}_3\text{PO}_4} = n_{\text{PCl}_5} = 0.0293\text{mol}$$

and

$$n_{\text{HCl}} = 5n_{\text{PCl}_5} = 5 \times 0.0293\text{mol} = 0.1465\text{mol}$$

The concentration of phosphoric acid and hydrochloric acid are

$$c_{\text{H}_3\text{PO}_4} = \frac{n_{\text{H}_3\text{PO}_4}}{V_{\text{solution}}} = \frac{0.0293\text{mol}}{0.697\text{L}} = \underline{0.0420\text{mol} \cdot \text{L}^{-1}}$$

and

$$c_{\text{HCl}} = \frac{n_{\text{HCl}}}{V_{\text{solution}}} = \frac{0.1465\text{mol}}{0.697\text{L}} = \underline{0.210\text{mol} \cdot \text{L}^{-1}}$$

□

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Problem 11.34. Complete and balance the following equations for reactions taking place in basic solution.

- (a) $\text{OCl}^-(\text{aq}) + \text{I}^-(\text{aq}) \longrightarrow \text{IO}_3^-(\text{aq}) + \text{Cl}^-(\text{aq})$
- (b) $\text{SO}_3^{2-}(\text{aq}) + \text{Be}(\text{s}) \longrightarrow \text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{Be}_2\text{O}_3^{2-}(\text{aq})$
- (c) $\text{H}_2\text{BO}_3^-(\text{aq}) + \text{Al}(\text{s}) \longrightarrow \text{BH}_4^-(\text{aq}) + \text{H}_2\text{AlO}_3^-(\text{aq})$
- (d) $\text{O}_2(\text{g}) + \text{Sb}(\text{s}) \longrightarrow \text{H}_2\text{O}_2(\text{aq}) + \text{SbO}_2^-(\text{aq})$
- (e) $\text{Sn}(\text{OH})_6^{2-}(\text{aq}) + \text{Si}(\text{s}) \longrightarrow \text{HSnO}_2^-(\text{aq}) + \text{SiO}_3^{2-}(\text{aq})$

Solution:

- (a) $3\text{OCl}^-(\text{aq}) + \text{I}^-(\text{aq}) \longrightarrow \text{IO}_3^-(\text{aq}) + 3\text{Cl}^-(\text{aq})$
- (b) $2\text{SO}_3^{2-}(\text{aq}) + 2\text{Be}(\text{s}) \longrightarrow \text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{Be}_2\text{O}_3^{2-}(\text{aq})$
- (c) $3\text{H}_2\text{BO}_3^-(\text{aq}) + 8\text{Al}(\text{s}) + 8\text{OH}^-(\text{aq}) + 7\text{H}_2\text{O}(\text{l}) \longrightarrow 3\text{BH}_4^-(\text{aq}) + 8\text{H}_2\text{AlO}_3^-(\text{aq})$
- (d) $3\text{O}_2(\text{g}) + 2\text{Sb}(\text{s}) + 2\text{OH}^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 3\text{H}_2\text{O}_2(\text{aq}) + 2\text{SbO}_2^-(\text{aq})$
- (e) $2\text{Sn}(\text{OH})_6^{2-}(\text{aq}) + \text{Si}(\text{s}) \longrightarrow 2\text{HSnO}_2^-(\text{aq}) + \text{SiO}_3^{2-}(\text{aq}) + 5\text{H}_2\text{O}(\text{l})$ □

Problem 11.64. At 300 K, the vapor pressure of pure benzene (C_6H_6) is 0.1355 atm and the vapor pressure of pure n-hexane (C_6H_{14}) is 0.2128 atm. Mixing 50.0 g of benzene with 50.0 g of n-hexane gives a solution that is nearly ideal.

- (a) Calculate the mole fraction of benzene in the solution.
- (b) Calculate the total vapor pressure of the solution at 300 K.
- (c) Calculate the mole fraction of benzene in the vapor in equilibrium with the solution.

Solution:

- (a) The number of moles of benzene and n-hexane is

$$n_{\text{C}_6\text{H}_6} = \frac{m_{\text{C}_6\text{H}_6}}{M_{\text{C}_6\text{H}_6}} = \frac{50.0\text{g}}{78.1\text{g} \cdot \text{mol}^{-1}} = 0.640\text{mol}$$

and

$$n_{\text{C}_6\text{H}_{14}} = \frac{m_{\text{C}_6\text{H}_{14}}}{M_{\text{C}_6\text{H}_{14}}} = \frac{50.0\text{g}}{86.2\text{g} \cdot \text{mol}^{-1}} = 0.580\text{mol}$$

The mole fraction of benzene in the solution is

$$X_{\text{C}_6\text{H}_6} = \frac{n_{\text{C}_6\text{H}_6}}{n_{\text{C}_6\text{H}_6} + n_{\text{C}_6\text{H}_{14}}} = \frac{0.640\text{mol}}{0.640\text{mol} + 0.580\text{mol}} = \underline{0.525}$$

- (b) The total vapor pressure of the solution at 300 K is

$$\begin{aligned} P &= X_{\text{C}_6\text{H}_6} P_{\text{C}_6\text{H}_6} + X_{\text{C}_6\text{H}_{14}} P_{\text{C}_6\text{H}_{14}} \\ &= 0.525 \times 0.1355\text{atm} + (1 - 0.525) \times 0.2128\text{atm} \\ &= \underline{0.172\text{atm}} \end{aligned}$$

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(c) The mole fraction of benzene in the vapor in equilibrium with the solution is

$$X_{\text{benzene in vapor}} = \frac{X_{C_6H_6} P_{C_6H_6}}{P} = \frac{0.525 \times 0.1355 \text{ atm}}{0.172 \text{ atm}} = \underline{0.414}$$

□

Problem 11.78. Ethylene glycol ($\text{CH}_2\text{OHCH}_2\text{OH}$) is used in antifreeze because, when mixed with water, it lowers the freezing point below 0°C . What mass percentage of ethylene glycol in water must be used to reduce the freezing point of the mixture to -5.0°C , assuming ideal solution behavior?

Solution: The freezing-point depression constant of water is $K_f = 1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}$. Molality of ethylene glycol in water must be used to reduce the freezing point of the mixture to -5.0°C is

$$\text{molality of Ethylene glycol} = \frac{\Delta T_f}{K_f} = -\frac{(273.0 - 268.0) \text{ K}}{1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}} = 2.69 \text{ mol} \cdot \text{kg}^{-1}$$

The corresponding mass percentage of ethylene glycol in water is

$$\begin{aligned} \text{mass percentage of ethylene glycol} &= \frac{2.69 \text{ mol} \cdot \text{kg}^{-1} \times 1.00 \text{ kg} \times 0.0621 \text{ kg} \cdot \text{mol}^{-1}}{2.69 \text{ mol} \cdot \text{kg}^{-1} \times 1.00 \text{ kg} \times 0.0621 \text{ kg} \cdot \text{mol}^{-1} + 1.00 \text{ kg}} \times 100\% \\ &= \underline{14.3\%} \end{aligned}$$

□

Problem 14.11. Using the law of mass action, write the equilibrium expression for each of the following reactions.

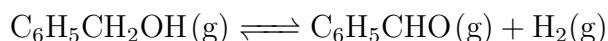
- (a) $\text{Zn(s)} + 2 \text{Ag}^+(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2 \text{Ag(s)}$
(b) $\text{VO}_4^{3-}(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{VO}_3(\text{OH})^{2-}(\text{aq}) + \text{OH}^-(\text{aq})$
(c) $2 \text{As(OH)}_6^{3-}(\text{aq}) + 6 \text{CO}_2(\text{g}) \rightleftharpoons \text{As}_2\text{O}_3(\text{s}) + 6 \text{HCO}_3^-(\text{aq}) + 3 \text{H}_2\text{O(l)}$

Solution:

- (a) $K = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$
(b) $K = \frac{[\text{VO}_3(\text{OH})^{2-}][\text{OH}^-]}{[\text{VO}_4^{3-}]}$
(c) $K = \frac{[\text{HCO}_3^-]^6}{[\text{As(OH)}_6^{3-}]^2 (\text{PCO}_2)^6}$

□

Problem 14.27. The dehydrogenation of benzyl alcohol to make the flavoring agent benzaldehyde is an equilibrium process described by the equation



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At 523 K, the value of its equilibrium constant is $K = 0.558$.

- (a) Suppose 1.20 g of benzyl alcohol is placed in a 2.00-L vessel and heated to 523 K. What is the partial pressure of benzaldehyde when equilibrium is attained?
(b) What fraction of benzyl alcohol is dissociated into products at equilibrium?

Solution:

- (a) The initial number of moles of $C_6H_5CH_2OH$ is

$$n_{C_6H_5CH_2OH} = \frac{m_{C_6H_5CH_2OH}}{M_{C_6H_5CH_2OH}} = \frac{1.20g}{108g \cdot mol^{-1}} = 0.0111mol$$

The initial partial pressure of $C_6H_5CH_2OH$ is

$$P_{C_6H_5CH_2OH} = \frac{n_{C_6H_5CH_2OH}RT}{V} = \frac{0.0111mol \times 0.0821L \cdot atm \cdot mol^{-1} \cdot K^{-1} \times 523K}{2.00L} = 0.238atm$$

Suppose the change of partial pressure of $C_6H_5CH_2OH$ is x , then

	$C_6H_5CH_2OH(g)$	\rightleftharpoons	$C_6H_5CHO(g)$	+	$H_2(g)$
Initial, atm	0.238		0		0
Change, atm	$-x$		x		x
Equilibrium, atm	$0.238 - x$		x		x

The equilibrium constant of this process can be write as

$$K = \frac{P_{C_6H_5CHO}P_{H_2}}{P_{C_6H_5CH_2OH}} = \frac{x^2}{0.238 - x} = 0.558$$

We solve the equation and get the partial pressure of benzaldehyde when equilibrium is attained

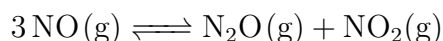
$$P_{C_6H_5CHO} = x = \underline{0.180atm}$$

- (b) The fraction of benzyl alcohol that is dissociated into products at equilibrium is

$$fraction = \frac{0.180atm}{0.238atm} \times 100\% = \underline{75.6\%}$$

□

Problem 14.53. Explain the effect of each of the following stresses on the position of the following equilibrium:



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The reaction as written is exothermic.

- (a) $\text{N}_2\text{O}(\text{g})$ is added to the equilibrium mixture without change of volume or temperature.
- (b) The volume of the equilibrium mixture is reduced at constant temperature.
- (c) The equilibrium mixture is cooled.
- (d) Gaseous argon (which does not react) is added to the equilibrium mixture while both the total gas pressure and the temperature are kept constant.
- (e) Gaseous argon is added to the equilibrium mixture without changing the volume.

Solution:

- (a) The addition of $\text{N}_2\text{O}(\text{g})$ increases the concentration of the product, which forces the reaction to proceed in the direction to reduce the concentration of N_2O . Therefore, the reaction proceeds to the left.
- (b) The reduction of volume increases the pressure of the system, which forces the reaction to proceed in the direction to decrease the pressure of the system. Therefore, the reaction proceeds to the right.
- (c) The cooling of the system forces the reaction to proceed in the direction to increase the temperature of the system. Considering the reaction is exothermic, the reaction proceeds to the right.
- (d) The argon does not react but the addition of gaseous argon enlarge the volume of the system. The reaction should proceed in the direction to keep the total gas pressure constant. Therefore, the reaction proceed to the left.
- (e) As argon does not react and the addition of gaseous argon does not change temperature or the partial pressure of the reactant and the product, the stress has no effect on the equilibrium. □