

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.

Water is the solute, and liquid nitrogen is the solvent, but the definition of mole fraction works the same. Use it to write the equation

$$X_{\text{H}_2\text{O}} = 1.00 \times 10^{-5} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{N}_2} + n_{\text{H}_2\text{O}}} = \frac{n_{\text{H}_2\text{O}}}{35.6972 + n_{\text{H}_2\text{O}}}$$

where 35.6972 is the number of moles of N_2 in 1.00 kg of N_2 (non-significant figures are carried along deliberately). Solving the equation for $n_{\text{H}_2\text{O}}$ is simplified by noting that $n_{\text{H}_2\text{O}}$ can be neglected in the denominator. Thus, the 1.00 kg of $\text{N}_2(l)$ contains 3.5697×10^{-4} mol of dissolved H_2O . This amounts to 0.00643 g of H_2O .

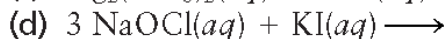
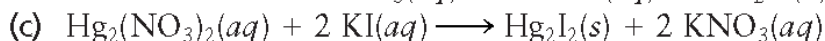
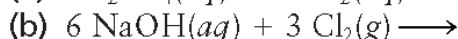
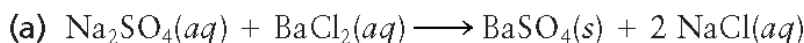
10. A perchloric acid solution is 60.0% HClO_4 by mass. It is simultaneously 9.20 M at 25°C .
- Compute the density of this solution.
 - What volume of this solution should be used in mixing 1.00 L of a 1.00 M perchloric acid solution?

a) Consider a 1 kg sample of the perchloric acid solution. It contains 600 g of HClO_4 . Dividing 600 g by $100.46 \text{ g mol}^{-1}$, the molar mass of HClO_4 , establishes that the solution contains 5.973 mol HClO_4 per kg. It simultaneously contains 9.20 mol of HClO_4 per liter (its molarity). Dividing the second of these two measures of composition by the first gives a density. To do the division, invert the divisor and multiply

$$\rho = \left(\frac{9.20 \text{ mol HClO}_4}{1 \text{ L solution}} \right) \times \left(\frac{1 \text{ kg solution}}{5.973 \text{ mol HClO}_4} \right) = 1.54 \text{ kg L}^{-1} = 1.54 \text{ g mL}^{-1}$$

b) To prepare 1.00 L of a solution that contains 1.00 mol of the solute requires 1.00 mol of the HClO_4 . The 9.20 M solution is quite concentrated: 1000 mL of it supplies 9.20 mol of HClO_4 . It follows that $1000/9.20 = 108.7 \text{ mL}$ of solution supplies 1.00 mol of solute.

14. Rewrite the following balanced equations as net ionic equations.

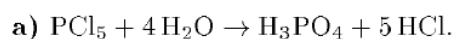


Net ionic equations omit all ions not specifically reacting:

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

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.



b)

$$n_{\text{PCl}_5} = \frac{PV}{RT} = \frac{(0.962 \text{ atm})(1.22 \text{ L})}{(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(215 + 273.15) \text{ K}} = 0.0293 \text{ mol PCl}_5$$

$$n_{\text{HCl}} = 0.0293 \text{ mol PCl}_5 \times \frac{5 \text{ mol HCl}}{1 \text{ mol PCl}_5} = 0.1465 \text{ mol HCl} = 0.146 \text{ mol HCl}$$

$$n_{\text{H}_3\text{PO}_4} = 0.0293 \text{ mol PCl}_5 \times \frac{1 \text{ mol H}_3\text{PO}_4}{1 \text{ mol PCl}_5} = 0.0293 \text{ mol H}_3\text{PO}_4$$

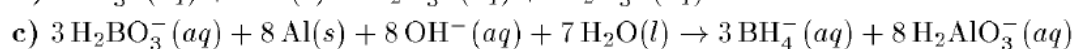
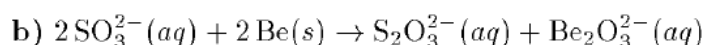
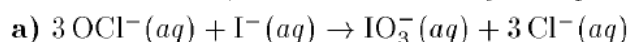
Both acids are collected in enough water so that the final volume of the solution is 697 mL

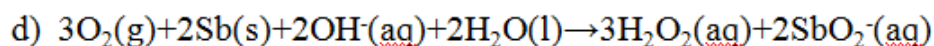
$$c_{\text{HCl}} = \frac{0.1465 \text{ mol}}{0.697 \text{ L}} = 0.210 \text{ mol L}^{-1} \quad c_{\text{H}_3\text{PO}_4} = \frac{0.0293 \text{ mol}}{0.697 \text{ L}} = 0.0420 \text{ mol L}^{-1}$$

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

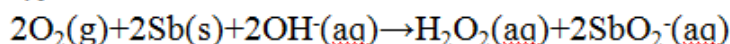
- (a) $\text{OCl}^-(aq) + \text{I}^-(aq) \longrightarrow \text{IO}_3^-(aq) + \text{Cl}^-(aq)$
- (b) $\text{SO}_3^{2-}(aq) + \text{Be}(s) \longrightarrow \text{S}_2\text{O}_3^{2-}(aq) + \text{Be}_2\text{O}_3^{2-}(aq)$
- (c) $\text{H}_2\text{BO}_3^-(aq) + \text{Al}(s) \longrightarrow \text{BH}_4^-(aq)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

In basic solution, OH^- and H_2O may take part either as reactants or as products.





或



⋮



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.

- Calculate the mole fraction of benzene in the solution.
- Calculate the total vapor pressure of the solution at 300 K.
- Calculate the mole fraction of benzene in the vapor in equilibrium with the solution.

a) The chemical amount of benzene ($M = 78.11 \text{ g mol}^{-1}$) in 50.0 g is 0.640 mol. The chemical amount of *n*-hexane ($M = 86.18 \text{ g mol}^{-1}$) is 0.580 mol. The mole fraction of benzene in the solution is

$$X_{\text{benzene}} = \frac{0.640 \text{ mol}}{(0.640 + 0.580) \text{ mol}} = 0.525$$

b) The total vapor pressure above the solution is

$$\begin{aligned} P_{\text{tot}} &= P_{\text{benzene}} + P_{\text{hexane}} \\ &= X_{\text{benzene}} P_{\text{benzene}}^{\circ} + X_{\text{hexane}} P_{\text{hexane}}^{\circ} \\ &= 0.525(0.1355 \text{ atm}) + (1 - 0.525)(0.2128 \text{ atm}) = 0.172 \text{ atm} \end{aligned}$$

c) $X_{\text{benzene}}(\text{vapor}) = 0.525(0.1355 \text{ atm})/0.172 \text{ atm} = 0.414$.

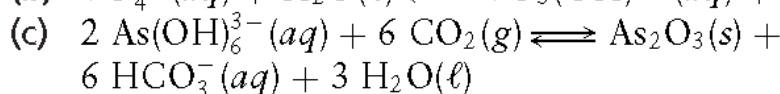
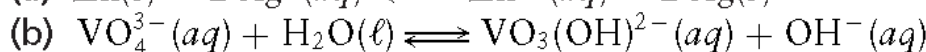
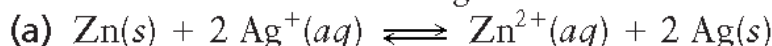
78. Ethylene glycol ($\text{CH}_2\text{OHCH}_2\text{OH}$) is used in antifreeze because, when mixed with water, it lowers the freezing point below 0°C . What mass percentage of ethylene glycol in water must be used to reduce the freezing point of the mixture to -5.0°C , assuming ideal solution behavior?

The molality of the required antifreeze solution of ethylene glycol is

$$m = -\frac{\Delta T}{K_f} = -\frac{(-5.0)}{1.86} = 2.69 \text{ mol kg}^{-1}$$

Such a solution has 2.69 mol of $\text{CH}_2\text{OHCH}_2\text{OH}$ ($M = 62.07 \text{ g mol}^{-1}$) dissolved in 1000 g of water. This chemical amount of ethylene glycol equals 167 g. There is thus 167 g of ethylene glycol for every 1167 g of solution. The percentage by mass of the ethylene glycol in the solution is $167/1167 \times 100\% = 14.3\%$. Note the assumption that ethylene glycol neither dissociates into two or more particles nor associates in aqueous solution (in addition to the assumption of ideal solution behavior).

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



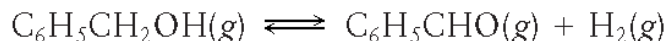
Pure solids and liquids are omitted from the expressions because their activities equal 1.

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

In all three parts, the concentrations of the solutes divided by the standard state concentration (1 M) approximates the activity of the solute. Also, the partial pressures of the gases divided by the standard-state pressure (1 atm) approximate the activity of the gas. This allows rewriting the answers as

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

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



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?

a) Calculate the chemical amount of the gaseous $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$. Then use the ideal-gas law to calculate its initial partial pressure. Abbreviate the formula of benzyl alcohol as BzOH ¹

$$n_{\text{BzOH}} = 1.20 \text{ g BzOH} \times \left(\frac{1 \text{ mol BzOH}}{108 \text{ g BzOH}} \right) = 0.0111 \text{ mol BzOH}$$

$$P_{\text{BzOH}} = \frac{n_{\text{BzOH}}RT}{V} = \frac{(0.0111 \text{ mol})(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(523 \text{ K})}{2.00 \text{ L}} = 0.238 \text{ atm}$$

The following three-line table shows how the partial pressures of benzyl alcohol and its products change as equilibrium is approached

	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}(g)$	\rightleftharpoons	$\text{C}_6\text{H}_5\text{CHO}(g) + \text{H}_2(g)$
Init. pressure (atm)	0.238		0 0
Change in pressure (atm)	$-x$		$+x$ $+x$
Equil. pressure (atm)	$0.238 - x$		x x

Substitute the final pressures in the mass-action expression

$$\frac{P_{\text{C}_6\text{H}_5\text{CHO}}P_{\text{H}_2}}{P_{\text{BzOH}}} = 0.558 = \frac{(x)(x)}{(0.238 - x)} \quad \text{from which} \quad x^2 + 0.558x - 0.133 = 0$$

Use the quadratic formula to solve for x

$$x = \frac{-(0.558) \pm \sqrt{(0.558)^2 - 4(1)(-0.133)}}{2(1)} = \frac{-0.558 \pm 0.918}{2}$$

$$x = 0.180 \quad \text{and} \quad x = -0.738$$

Disregard the solution $x = -0.738$ because it leads to impossible partial pressures for all three gases. The answer is $P_{\text{C}_6\text{H}_5\text{CHO}} = \boxed{0.180 \text{ atm}}$.

b) The fraction of the benzyl alcohol dissociated at equilibrium equals the amount dissociated divided by the initial amount. These amounts are respectively proportional to the decrease in partial pressure of the benzyl alcohol and the initial partial pressure of the benzyl alcohol. Hence

$$f = \frac{\text{amount of BzOH dissociated}}{\text{original amount of BzOH}} = \frac{0.180 \text{ atm}}{0.238 \text{ atm}} = \boxed{0.756}$$

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



The reaction as written is exothermic.

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

Chemical systems always tend toward equilibrium.² If a stress is applied to a system at equilibrium, the system reacts to minimize the stress and to reach a new equilibrium.

a) The stress is the addition of $\text{N}_2\text{O}(g)$. The system reacts to decrease the concentration of N_2O . The reaction proceeds from right to left until a new equilibrium is reached.

b) The stress is the reduction in volume. The partial pressures of all the compounds will momentarily rise. The equilibrium will then shift in such a way as to reduce the number of molecules of gas (chemical amount of gas) in the container and reduce the total pressure. There are three moles of gas on the reactant side of the equation and two moles of gas on the product side. The equilibrium will thus shift from left to right.

c) The reaction is exothermic. Cooling the mixture shifts the equilibrium from left to right (to favor the products).

d) In order to maintain a constant pressure, the volume of the system must have increased. Thus, the reaction will shift from right to left.

e) The partial pressures of the reacting gases are unchanged by the addition of an inert gas, and the equilibrium law is independent of total pressure. There is no effect on the position of the equilibrium.