

Additional Practice Problems for Chapter 14

1. Write the equilibrium constant expressions for the following:

- (a) $2 \text{NaHCO}_3(s) \rightleftharpoons \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)$
 (b) $2 \text{N}_2(g) + 6 \text{H}_2\text{O}(l) \rightleftharpoons 4 \text{NH}_3(g) + 3 \text{O}_2(g)$
 (c) $2 \text{C}_2\text{H}_4(g) + \text{O}_2(g) \rightleftharpoons 2 \text{CH}_3\text{CHO}(g)$ (note typo correction)
 (d) $\text{Ag}_2\text{SO}_4(s) \rightleftharpoons 2 \text{Ag}^+(aq) + \text{SO}_4^{2-}(aq)$
 (e) $\text{NH}_4\text{HS}(s) \rightleftharpoons \text{H}_2\text{S}(g) + \text{NH}_3(g)$

Answers: (a) $K_{\text{eq}} = P_{\text{CO}_2} P_{\text{H}_2\text{O}}$ (water in gas phase with partial pressure $P_{\text{H}_2\text{O}}$, so not pure)

(b) $K_{\text{eq}} = \frac{P_{\text{NH}_3}^4 P_{\text{O}_2}^3}{P_{\text{N}_2}^2}$ (water a pure condensed phase)

(c) $K_{\text{eq}} = \frac{P_{\text{CH}_3\text{CHO}}^2}{(P_{\text{C}_2\text{H}_4})^2 P_{\text{O}_2}}$

(d) $K_{\text{eq}} = [\text{Ag}^+][\text{SO}_4^{2-}]$

(e) $K_{\text{eq}} = P_{\text{H}_2\text{S}} P_{\text{NH}_3}$

2. Phosgene is a deadly gas whose use in warfare has been outlawed. The gas decomposes at elevated temperature:



$$K_{\text{eq}} = 8.3 \times 10^{-4} \text{ at } 352 \text{ }^\circ\text{C}$$

What are the pressures at equilibrium if a 2.55-L metal container is charged with 3.00 bar of phosgene at 25 °C and then heated to 352 °C?

Answer: Assume the equilibrium constant is pressure based, K_p . The temperatures in kelvins are: 25°C is 298.2 K and 352°C is 625.2 K with $P_2 = P_1(T_2/T_1)$ from the ideal gas law. The initial pressure of phosgene at the elevated pressure is $P_{\text{COCl}_2}^\circ = 3.00 \text{ bar}(625.2 \text{ K}/298.2 \text{ K}) = 6.290 \text{ bar}$.

	$\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$	
initial	P°	0 0
change	-x	+x +x
equilibrium	$P^\circ - x$	+x +x

with $P^\circ = 6.290 \text{ bar}$

With the equilibrium expression: $K_p = \frac{P_{\text{CO}} P_{\text{Cl}_2}}{P_{\text{COCl}_2}} = \frac{x^2}{P^\circ - x}$

Cross multiply to get quadratic form: $K_p P^\circ - K_p x = x^2$ or $x^2 + K_p x - K_p P^\circ = 0$

The quadratic formula for $ax^2 + bx + c = 0$ gives $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Applied to this problem: $x = \frac{-K_p \pm \sqrt{K_p^2 - 4K_p P^\circ}}{2}$

$$x = \frac{-8.3 \times 10^{-4} \text{ bar} \pm \sqrt{(8.3 \times 10^{-4} \text{ bar})^2 - 4(8.3 \times 10^{-4} \text{ bar})(6.290 \text{ bar})}}{2} = 0.07184 \text{ bar}$$

Checking the result with $K_p = \frac{x^2}{P^\circ - x} = \frac{(0.07184)^2}{6.290 - 0.07184} = 8.30 \times 10^{-4} \text{ bar}$

Since the K_p is given with two significant figures $P_{\text{CO}} = P_{\text{Cl}_2} = 0.72$ bar and $P_{\text{COCl}_2} = 6.290$ bar $- 0.07184$ bar = 6.22 bar. Remember to keep extra significant figures in intermediate calculations to avoid round off error.

3. A saturated solution of chloroform (CHCl_3) in water contains one drop of excess chloroform. If more liquid chloroform is added to this mixture, does the concentration of chloroform in the aqueous solution change? Explain your answer in molecular terms.

Answer: No, if the solution is saturated, then adding additional pure chloroform increases the amount of pure chloroform in the second immiscible layer. In other words, the newly added chloroform joins the original one-drop excess. The concentration of the solution remains constant. The concentration of a saturated solution is only a function of the temperature.

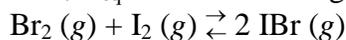
On a molecular level, the saturated concentration in the aqueous phase is dependent on the intermolecular forces. Chloroform is negligibly soluble in water. Call the solvent water component A. Call the solute chloroform component B. The A-A force in pure water are much stronger than the A-B or B-B forces because of hydrogen bonding in water. Adding more chloroform to the aqueous phase breaks A-A and B-B interactions and makes A-B interactions. The decrease in the number of A-A interactions is unfavorable, excluding additional solute from the aqueous phase.

4. A student mixes sodium chloride and water until the solid and the aqueous solution are at equilibrium. If more solid sodium chloride is added to this mixture, does the concentration of sodium chloride in the aqueous solution change? Explain your answer in molecular terms.

Answer: No, if the solution is saturated, then adding additional pure sodium chloride increases the amount of pure sodium chloride in the precipitate in the bottom of the beaker. In other words, the newly added sodium chloride joins the original solid that was in equilibrium initially. The concentration of the solution remains constant. The concentration of a saturated solution is only a function of the temperature.

On a molecular level, the saturated concentration in the aqueous phase is dependent on the intermolecular and ionic forces. Sodium chloride is strongly soluble in water. Call the solvent water component A. Adding more sodium chloride to the aqueous phase breaks A-A interactions and also the strong electrostatic interactions in the ionic solid between Na^+ and Cl^- ions. The formation of the solution is stabilized by ion-dipole interactions of water molecules with Na^+ ions and water molecules with Cl^- ions. At equilibrium, the A-A forces, the lattice energy, and the ion-dipole forces in solution are balanced. The decrease in the number of A-A interactions and the lattice energy is unfavorable upon additional transfer of Na^+ and Cl^- ions into the aqueous phase.

5. At 350 K, K_{eq} for the following reaction is 322:



Suppose the equilibrium partial pressure of bromine is 0.512 bar and that of iodine is 0.327 bar. What is the pressure of IBr?

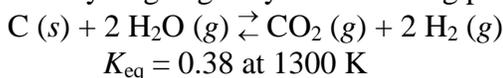
Answer: Assume the equilibrium constant is pressure based, K_p .

With the equilibrium expression: $K_p = \frac{P_{\text{IBr}}^2}{P_{\text{Br}_2} P_{\text{I}_2}} = \frac{P_{\text{IBr}}^2}{(0.512 \text{ bar})(0.327 \text{ bar})} = 322$.

Solving for P_{IBr} gives $P_{\text{IBr}} = 7.342 \text{ bar}$

Checking the result gives back $K_p = \frac{(7.342 \text{ bar})^2}{(0.512 \text{ bar})(0.327 \text{ bar})} = 322$.

6. Coal (solid carbon plus a collection of impurities) can be converted to a mixture of carbon dioxide and hydrogen gas by the following process:



At an industrial plant, a mixture of coal and water is placed inside a steel reaction vessel. When the mixture is heated to 1300 K, the equilibrium partial pressure of water is $2.80 \times 10^2 \text{ bar}$. Calculate the partial pressures of H_2 and CO_2 .

Answer: Assume the equilibrium constant is pressure based, K_p . The equilibrium expression is:

$$K_p = \frac{P_{\text{CO}_2} P_{\text{H}_2}^2}{P_{\text{H}_2\text{O}}^2}$$

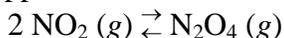
However, starting with only reactants, $P_{\text{H}_2} = 2 P_{\text{CO}_2}$ giving:

$$K_p = \frac{P_{\text{CO}_2} (2 P_{\text{CO}_2})^2}{(2.80 \times 10^2 \text{ bar})^2} = \frac{4 P_{\text{CO}_2}^3}{(2.80 \times 10^2 \text{ bar})^2} = 0.38$$

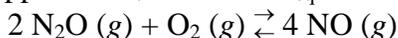
Solving for P_{CO_2} gives: $P_{\text{CO}_2} = 19.5 \text{ bar}$ and $P_{\text{H}_2} = 39.1 \text{ bar}$

Checking the result gives back: $K_p = (19.5 \text{ bar})(39.1 \text{ bar})^2 / (2.8 \times 10^2 \text{ bar})^2 = 0.380 \text{ bar}$

7. *Delete-material not covered until Chapter 17*--Using tabulated standard thermodynamic data from Appendix B, calculate K_{eq} for the reaction of NO_2 to form N_2O_4 at 298 K and at 525 K:



8. *Delete-material not covered until Chapter 17*--Using tabulated standard thermodynamic data from Appendix B, calculate K_{eq} for the following reaction at 298 K and at 825 K:



9. Write the equilibrium reaction and equilibrium constant expression for each of the following processes:

- Trimethylamine, $(\text{CH}_3)_3\text{N}$, a weak base, is added to water.
- Hydrofluoric acid, HF, a weak acid, is added to water.
- Solid calcium sulfate, CaSO_4 , a sparingly soluble salt, is added to water.

10. Predict the effect of each of the following changes on the equilibrium position of the reaction in Example 14-12:

- The partial pressure of NO_2 is cut in half.
- The volume of the reactor is doubled.
- A total of 10.0 bar of Ar gas is added to the reactor.

11. Predict the effect each of the following changes will have on the equilibrium position of the reaction in Example 14-11:

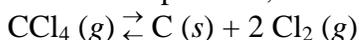
- (a) Some sodium benzoate is dissolved in the solution.
- (b) An additional 1.0 L of water is added to the solution.
- (c) Some NaCl is dissolved in the solution.

Answer:

12. Use the appropriate data from Appendix B to calculate K_{sp} for LiCl at 25 °C and 100 °C. Is LiCl more or less soluble at high temperature than at low temperature?

Answer:

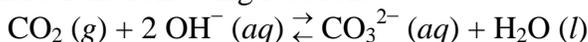
13. At elevated temperature, carbon tetrachloride decomposes to its elements:



At 700 K, if the initial pressure of CCl_4 is 1.00 bar, the total pressure at equilibrium is 1.35 bar. Use these pressures to calculate K_{eq} at 700 K.

Answer:

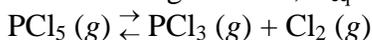
14. Consider the following reaction:



- (a) Write the equilibrium constant expression for this reaction.
- (b) What will happen to the pressure of CO_2 in this equilibrium system if some Na_2CO_3 solid is dissolved in the solution?
- (c) What will happen to the pressure of CO_2 in this equilibrium system if some HCl gas is bubbled through the solution?

Answer:

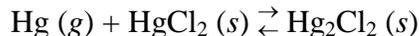
15. For the following reaction, K_{eq} is 1.83×10^{-3} at 390. K:



If 2.00 g of PCl_5 is placed in a 3.00-L bulb at 390. K, what is the equilibrium pressure of Cl_2 (1 atm = 1.013 bar)?

Answer:

16. Using tabulated thermodynamic data from Appendix B, compute (a) K_{eq} at 298 K; (b) the temperature at which the equilibrium pressure is 1.00 bar; and (c) K_{eq} at 1050 K for the following reaction:

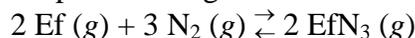


Answer:

17. At 1020 °C, K_{eq} for the conversion of $\text{CO}_2 (g)$ to $\text{CO} (g)$ by solid graphite, $\text{C} (s)$, is 167.5. A 1.00-L, high-pressure chamber containing excess graphite powder is charged with 0.494 mol each of CO_2 and CO and then is heated to 1020 °C. What is the equilibrium total pressure (1 atm = 1.013 bar)?

Answer:

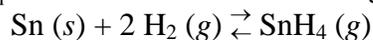
18. A chemist claims to have discovered a new gaseous element, effluvium (Ef), which reacts with atmospheric nitrogen to form effluvium nitride:



In a container initially containing N_2 at 1.00 bar pressure and Ef gas at 0.75 bar, the total gas pressure at equilibrium, according to the chemist's measurements, is 0.85 bar. Compute K_{eq} for this reaction.

Answer:

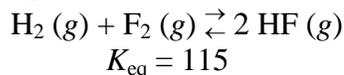
19. $K_{\text{eq}} = 1.1 \times 10^{-33}$ for the following reaction at 298 K:



Find the equilibrium pressure of $\text{SnH}_4 (g)$ in a container at 298 K containing 10.0 g of $\text{Sn} (s)$ and 2.00×10^2 bar of H_2 . What volume of container is expected to contain a single molecule of SnH_4 (1 atm = 1.013 bar)?

Answer:

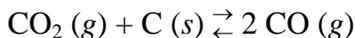
20. Hydrogen fluoride is a highly reactive gas. It has many industrial uses, but the most familiar property of HF is its ability to react with glass. As a result, HF is used to etch glass and frost the inner surfaces of light bulbs. Hydrogen fluoride gas must be stored in stainless steel containers, and aqueous solutions must be stored in plastic bottles. Hydrogen fluoride can be produced from H_2 and F_2 :



In a particular experiment, 3.00 bar each of H_2 and F_2 are added to a 1.50-L flask. Calculate the equilibrium partial pressures of all species.

Answer:

21. (a) A container contains CO_2 at $P = 0.464$ bar. When graphite is added to the container, some CO_2 is converted to CO , and at equilibrium, the total pressure is 0.746 bar. Compute K_{eq} for the reaction:



(b) Suppose that the equilibrium system is compressed to one third its initial volume. Find the new equilibrium pressure.

Answer:

22. When 1.00 mol of gaseous HI is sealed in a 1.00-L flask at 225°C , it decomposes until the equilibrium amount of I_2 present is 0.182 moles:



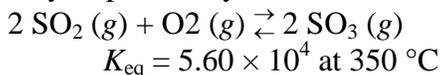
(a) Use these data to calculate K_{eq} for this reaction at 225°C .

(b) Using standard thermodynamic data from Appendix D, estimate K_{eq} at 625°C .

(c) Using the result of (b), calculate the equilibrium partial pressures of all reagents under these conditions (1 atm = 1.013 bar).

Answer:

23. The key step in the synthesis of sulfuric acid is the combustion of SO_2 to give sulfur trioxide:



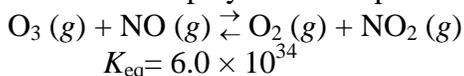
(a) Sulfur dioxide and oxygen are mixed initially at 0.350 and 0.762 bar, respectively, at 350°C . What are the partial pressures of the three gases when the mixture reaches equilibrium?

(b) Use thermodynamic data (see Appendix B) to calculate K_{eq} for the sulfur trioxide reaction at 298 K. Based on this result, should this industrial synthesis be run at a higher or lower temperature than 350°C to improve the yield?

(c) Suggest reasons why this reaction is run industrially at 700 K.

Answer:

24. One reaction that plays a role in photochemical smog is the following:



Automobile engines produce both O_3 and NO . If the morning rush hour results in an atmosphere containing 1.5 ppm NO and 6.5 ppb O_3 , calculate the equilibrium partial pressures of the three pollutants (O_2 is 21% of the atmosphere).

Answer: