

$$20. \quad \text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{HBr}(\text{g}) \quad K_p = \frac{P_{\text{HBr}}^2}{(P_{\text{H}_2})(P_{\text{Br}_2})} = 3.5 \times 10^4$$

$$\text{a.} \quad \text{HBr} \rightleftharpoons 1/2 \text{H}_2 + 1/2 \text{Br}_2 \quad K'_p = \frac{(P_{\text{H}_2})^{1/2}(P_{\text{Br}_2})^{1/2}}{P_{\text{HBr}}} = \left(\frac{1}{K_p} \right)^{1/2} = \left(\frac{1}{3.5 \times 10^4} \right)^{1/2} = 5.3 \times 10^{-3}$$

$$\text{b.} \quad 2 \text{HBr} \rightleftharpoons \text{H}_2 + \text{Br}_2 \quad K''_p = \frac{(P_{\text{H}_2})(P_{\text{Br}_2})}{P_{\text{HBr}}^2} = \frac{1}{K_p} = \frac{1}{3.5 \times 10^4} = 2.9 \times 10^{-5}$$

$$\text{c.} \quad 1/2 \text{H}_2 + 1/2 \text{Br}_2 \rightleftharpoons \text{HBr} \quad K'''_p = \frac{P_{\text{HBr}}}{(P_{\text{H}_2})^{1/2}(P_{\text{Br}_2})^{1/2}} = (K_p)^{1/2} = 190$$

$$22. \quad K = \frac{[\text{NCl}_3]^2}{[\text{N}_2][\text{Cl}_2]^3} = \frac{(0.19)^2}{(1.4 \times 10^{-3})(4.3 \times 10^{-4})^3} = 3.2 \times 10^{11}$$

34. As in Exercise 13.33, determine Q for each reaction, and compare this value to K_p (2.4×10^3) to determine which direction the reaction shifts to reach equilibrium. Note that, for this reaction, $K = K_p$ since $\Delta n = 0$.

$$\text{a.} \quad Q = \frac{P_{\text{N}_2} \times P_{\text{O}_2}}{P_{\text{NO}}^2} = \frac{(0.11)(2.0)}{(0.010)^2} = 2.2 \times 10^3$$

$Q < K_p$ so the reaction shifts right to reach equilibrium.

$$\text{b.} \quad Q = \frac{(0.36)(0.67)}{(0.078)^2} = 4.0 \times 10^3 > K_p$$

Reaction shifts left to reach equilibrium.

$$\text{c.} \quad Q = \frac{(0.51)(0.18)}{(0.0062)^2} = 2.4 \times 10^3 = K_p; \text{ at equilibrium}$$



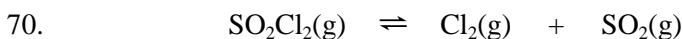
| | | | |
|---------|---|-------------|-------|
| Initial | 1.00 atm | 2.00 atm | 0 |
| | x atm of N_2 reacts to reach equilibrium | | |
| Change | $-x$ | $-3x$ | $+2x$ |
| equil. | $1.00 - x$ | $2.00 - 3x$ | $2x$ |

From set-up: $P_{\text{TOT}} = 2.00 \text{ atm} = P_{\text{N}_2} + P_{\text{H}_2} + P_{\text{NH}_3}$

$$2.00 \text{ atm} = (1.00 - x) + (2.00 - 3x) + 2x = 3.00 - 2x$$

$$x = 0.500 \text{ atm}; P_{\text{H}_2} = 2.00 - 3x = 2.00 - 3(0.500) = 0.50 \text{ atm}$$

58. When the volume of a reaction container is increased, the reaction itself will want to increase its own volume by shifting to the side of the reaction which contains the most molecules of gas. When the molecules of gas are equal on both sides of the reaction, then the reaction will remain at equilibrium no matter what happens to the volume of the container.
- Reaction shifts left (to reactants) since the reactants contain 4 molecules of gas compared to 2 molecules of gas on the product side.
 - Reaction shifts right (to products) since there are more product molecules of gas (2) than reactant molecules (1).
 - No change since there are equal reactant and product molecules of gas.
 - Reaction shifts right.
 - Reaction shifts right to produce more $\text{CO}_2(\text{g})$. One can ignore the solids and only concentrate on the gases because gases occupy a relatively large volume compared to solids. We make the same assumption when liquids are present (only worry about the gas molecules).
62.
 - shift to left
 - shift to right; The reaction is endothermic (heat is a reactant), thus an increase in temperature will shift the equilibrium to the right.
 - no effect
 - shift to right
 - shift to right; Because there are more gaseous product molecules than gaseous reactant molecules, the equilibrium will shift right with an increase in volume.
63. An endothermic reaction, where heat is a reactant, will shift right to products with an increase in temperature. The amount of $\text{NH}_3(\text{g})$ will increase as the reaction shifts right so the smell of ammonia will increase.



| | | | | |
|---------|-----------|------|------|--|
| Initial | P_0 | 0 | 0 | $P_0 = \text{initial pressure of } \text{SO}_2\text{Cl}_2$ |
| Change | $-x$ | $+x$ | $+x$ | |
| Equil. | $P_0 - x$ | x | x | |
| | | | | |

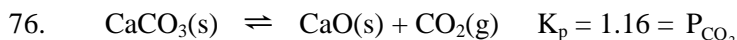
$$P_{\text{total}} = 0.900 \text{ atm} = P_0 + x + x + x = P_0 + 3x$$

$$\frac{x}{P_0} \times 100 = 12.5, \quad P_0 = 8.00 \text{ atm}$$

$$\text{Solving: } 0.900 = P_0 + 3x = 9.00x, \quad x = 0.100 \text{ atm}$$

$$x = 0.100 \text{ atm} = P_{\text{Cl}_2} = P_{\text{SO}_2}; \quad P_0 + x = 8.00 + 0.100 = 8.10 \text{ atm} = P_{\text{SO}_2\text{Cl}_2}$$

$$K_p = \frac{P_{\text{Cl}_2} \times P_{\text{SO}_2}}{P_{\text{SO}_2\text{Cl}_2}} = \frac{(0.100)^2}{8.10} = 1.43 \times 10^{-2} \text{ atm}$$



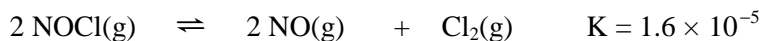
Some of the 20.0 g of CaCO_3 will react to reach equilibrium. The amount that reacts is the quantity of CaCO_3 required to produce a CO_2 pressure of 1.16 atm (from the K_p expression).

$$n_{\text{CO}_2} = \frac{P_{\text{CO}_2} V}{RT} = \frac{1.16 \text{ atm} \times 10.0 \text{ L}}{\frac{0.08206 \text{ L atm}}{\text{K mol}} \times 1073 \text{ K}} = 0.132 \text{ mol CO}_2$$

$$\text{mass CaCO}_3 \text{ reacted} = 0.132 \text{ mol CO}_2 \times \frac{1 \text{ mol CaCO}_3}{\text{mol CO}_2} \times \frac{100.09 \text{ g}}{\text{mol CaCO}_3} = 13.2 \text{ g CaCO}_3$$

$$\text{mass \% CaCO}_3 \text{ reacted} = \frac{13.2 \text{ g}}{20.0 \text{ g}} \times 100 = 66.0\%$$

79. There is a little trick we can use to solve this problem in order to avoid solving a cubic equation. Because K for this reaction is very small, the dominant reaction is the reverse reaction. We will let the products react to completion by the reverse reaction, then we will solve the forward equilibrium problem to determine the equilibrium concentrations. Summarizing these steps in a table:



Before 0 2.0 M 1.0 M

Let 1.0 mol/L Cl_2 react completely.

(K is small, reactants dominate.)

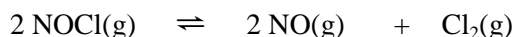
| | | | | | |
|--|----------|---|-----|-----|------------------------|
| Change | +2.0 | ← | 2.0 | 1.0 | React completely |
| After | 2.0 | | 0 | 0 | New initial conditions |
| 2x mol/L of NOCl reacts to reach equilibrium | | | | | |
| Change | 2x | → | +2x | +x | |
| Equil. | 2.0 - 2x | | 2x | x | |

$$K = 1.6 \times 10^{-5} = \frac{(2x)^2(x)}{(2.0 - 2x)^2} \approx \frac{4x^3}{2.0^2} \quad (\text{assuming } 2.0 - 2x \approx 2.0)$$

$$x^3 = 1.6 \times 10^{-5}, \quad x = 2.5 \times 10^{-2}; \quad \text{Assumption good by the 5\% rule (2x is 2.5\% of 2.0).}$$

$$[\text{NOCl}] = 2.0 - 0.050 = 1.95 \text{ M} \approx 2.0 \text{ M}; \quad [\text{NO}] = 0.050 \text{ M}; \quad [\text{Cl}_2] = 0.025 \text{ M}$$

Note: If we do not break this problem into two parts (a stoichiometric part and an equilibrium part), we are faced with solving a cubic equation. The set-up would be:

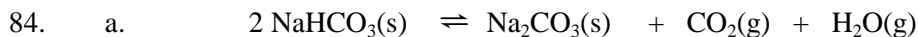


| | | | | |
|---------|------|---|----------|---------|
| Initial | 0 | | 2.0 M | 1.0 M |
| Change | +2.0 | ← | 2y | y |
| Equil. | 2y | | 2.0 - 2y | 1.0 - y |

$$1.6 \times 10^{-5} = \frac{(2.0 - 2y)^2(1.0 - y)}{(2y)^2} \quad \text{If we say that } y \text{ is small to simplify the problem, then:}$$

$$1.6 \times 10^{-5} = \frac{2.0^2}{4y^2}; \quad \text{We get } y = 250. \text{ This is impossible!}$$

To solve this equation, we cannot make any simplifying assumptions; we have to solve a cubic equation. If you don't have a graphing calculator, this is difficult. Alternatively, we can use some chemical common sense and solve the problem as illustrated above.



| | | | | |
|---|---|---|----|----|
| Initial | ! | ! | 0 | 0 |
| NaHCO ₃ (s) decomposes to form x atm each of CO ₂ (g) and H ₂ O(g) at equilibrium. | | | | |
| Change | ! | → | +x | +x |
| Equil. | ! | ! | x | x |

$$0.25 = K_P = P_{\text{CO}_2} \times P_{\text{H}_2\text{O}}, \quad 0.25 = x^2, \quad x = P_{\text{CO}_2} = P_{\text{H}_2\text{O}} = 0.50 \text{ atm}$$

$$\text{b. } n_{\text{CO}_2} = \frac{PV}{RT} = \frac{(0.50 \text{ atm})(1.00 \text{ L})}{(0.08206 \text{ L atm / mol} \cdot \text{K})(398 \text{ K})} = 1.5 \times 10^{-2} \text{ mol CO}_2$$

Mass of Na₂CO₃ produced:

$$1.5 \times 10^{-2} \text{ mol CO}_2 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{\text{mol CO}_2} \times \frac{105.99 \text{ g Na}_2\text{CO}_3}{\text{mol Na}_2\text{CO}_3} = 1.6 \text{ g Na}_2\text{CO}_3$$

Mass of NaHCO₃ reacted:

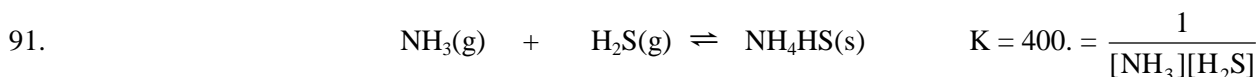
$$1.5 \times 10^{-2} \text{ mol CO}_2 \times \frac{2 \text{ mol NaHCO}_3}{1 \text{ mol CO}_2} \times \frac{84.01 \text{ g NaHCO}_3}{\text{mol}} = 2.5 \text{ g NaHCO}_3$$

Mass of NaHCO₃ remaining = 10.0 - 2.5 = 7.5 g

$$\text{c. } 10.0 \text{ g NaHCO}_3 \times \frac{1 \text{ mol NaHCO}_3}{84.01 \text{ g NaHCO}_3} \times \frac{1 \text{ mol CO}_2}{2 \text{ mol NaHCO}_3} = 5.95 \times 10^{-2} \text{ mol CO}_2$$

When all of the NaHCO₃ has been just consumed, we will have $5.95 \times 10^{-2} \text{ mol CO}_2$ gas at a pressure of 0.50 atm (from a).

$$V = \frac{nRT}{P} = \frac{(5.95 \times 10^{-2} \text{ mol})(0.08206 \text{ L atm/mol} \cdot \text{K})(398 \text{ K})}{(0.50 \text{ atm})} = 3.9 \text{ L}$$



| | | | |
|--|---|---|---|
| Initial | $\frac{2.00 \text{ mol}}{5.00 \text{ L}}$ | $\frac{2.00 \text{ mol}}{5.00 \text{ L}}$ | — |
| x mol/L of NH ₃ reacts to reach equilibrium | | | |
| Change | -x | -x | — |
| Equil. | 0.400 - x | 0.400 - x | — |

$$K = 400. = \frac{1}{(0.400 - x)(0.400 - x)}, \quad 0.400 - x = \left(\frac{1}{400.} \right)^{1/2} = 0.0500$$

$$x = 0.350 \text{ M}; \text{ mol NH}_4\text{HS}(\text{s}) \text{ produced} = 5.00 \text{ L} \times \frac{0.350 \text{ mol NH}_3}{\text{L}} \times \frac{1 \text{ mol NH}_4\text{HS}}{\text{mol NH}_3} = 1.75 \text{ mol}$$

Total mol NH₄HS(s) = 2.00 mol initially + 1.75 mol produced = 3.75 mol total

$$3.75 \text{ mol NH}_4\text{HS} \times \frac{51.12 \text{ g NH}_4\text{HS}}{\text{mol NH}_4\text{HS}} = 192 \text{ g NH}_4\text{HS}$$

$$[\text{H}_2\text{S}]_e = 0.400 \text{ M} - x = 0.400 \text{ M} - 0.350 \text{ M} = 0.050 \text{ M H}_2\text{S}$$

$$P_{\text{H}_2\text{S}} = \frac{n_{\text{H}_2\text{S}} RT}{V} = \frac{n_{\text{H}_2\text{S}}}{V} \times RT = \frac{0.050 \text{ mol}}{\text{L}} \times \frac{0.08206 \text{ L atm}}{\text{K mol}} \times 308 \text{ K} = 1.3 \text{ atm}$$