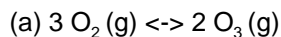
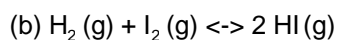


Solutions to:
Chemical Equilibrium Homework Problem Set
S.E. Van Bramer 1/9/96

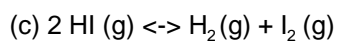
1. Write an expression for each of the equilibria



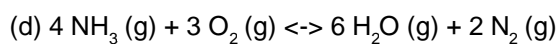
$$K_p = \frac{(P_{\text{O}_3})^2}{(P_{\text{O}_2})^3}$$



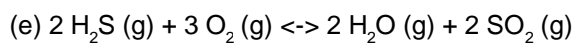
$$K_p = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2}) \cdot (P_{\text{I}_2})}$$



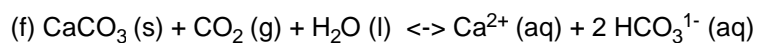
$$K_p = \frac{(P_{\text{H}_2}) \cdot (P_{\text{I}_2})}{(P_{\text{HI}})^2}$$



$$K_p = \frac{(P_{\text{H}_2\text{O}})^6 \cdot (P_{\text{N}_2})^2}{(P_{\text{NH}_3})^4 \cdot (P_{\text{O}_2})^3}$$



$$K_p = \frac{(P_{\text{H}_2\text{O}})^2 \cdot (P_{\text{SO}_2})^2}{(P_{\text{H}_2\text{S}})^2 \cdot (P_{\text{O}_2})^3}$$



$$K = \frac{(C_{\text{Ca}^{2+}}) \cdot (C_{\text{HCO}_3^{-1}})^2}{C_{\text{CO}_2}}$$

2. A 10 g sample of gaseous PCl_5 is introduced into a 3.0 L flask at 250 C. After the system comes to equilibrium the pressure in the flask is $1.136 \times 10^5 \text{ Pa}$.

The reaction is: $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

The initial amount of PCl_5 is:

$$\text{Initial_mass PCl}_5 := 10 \cdot \text{gm}$$

Convert this to moles:

$$\text{MW PCl}_5 := ((30.974) + (5) \cdot (35.453)) \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{Initial_mole PCl}_5 := \frac{\text{Initial_mass PCl}_5}{\text{MW PCl}_5}$$

$$\text{Initial_mole PCl}_5 = 0.04802 \cdot \text{mole}$$

From the equilibrium pressure and the ideal gas law determine the moles of gas at equilibrium.

$$P_{\text{total}} := 1.136 \cdot 10^5 \cdot \text{Pa}$$

$$V := 3 \cdot \text{liter}$$

$$T := (273.15 + 250) \cdot \text{K}$$

$$R := 8.314 \cdot \text{joule} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$$

$$n_{\text{total}} := \frac{P_{\text{total}} \cdot V}{R \cdot T}$$

$$n_{\text{total}} = 0.0784 \cdot \text{mole}$$

From the balanced equation the amount of each species at equilibrium is expressed as:

$$n_{\text{PCl}_5} = \text{Initial_mole PCl}_5 - X$$

$$n_{\text{PCl}_3} = X$$

$$n_{\text{Cl}_2} = X$$

So at equilibrium the total number of moles is:

$$n_{\text{total}} = \text{Initial_mole PCl}_5 - X + X + X$$

$$X := n_{\text{total}} - \text{Initial_mole PCl}_5$$

$$X = 0.0303 \cdot \text{mole}$$

And the amount of each species is:

$$n_{\text{PCl}_5} := \text{Initial_mole_PCl}_5 - X \qquad n_{\text{PCl}_5} = 0.0177 \cdot \text{mole}$$

$$n_{\text{PCl}_3} := X \qquad n_{\text{PCl}_3} = 0.0303 \cdot \text{mole}$$

$$n_{\text{Cl}_2} := X \qquad n_{\text{Cl}_2} = 0.0303 \cdot \text{mole}$$

The concentration of each species is:

$$C_{\text{PCl}_5} := \frac{n_{\text{PCl}_5}}{V} \qquad C_{\text{PCl}_5} = 0.0059 \cdot \text{mole} \cdot \text{liter}^{-1}$$

$$C_{\text{PCl}_3} := \frac{n_{\text{PCl}_3}}{V} \qquad C_{\text{PCl}_3} = 0.0101 \cdot \text{mole} \cdot \text{liter}^{-1}$$

$$C_{\text{Cl}_2} := \frac{n_{\text{Cl}_2}}{V} \qquad C_{\text{Cl}_2} = 0.0101 \cdot \text{mole} \cdot \text{liter}^{-1}$$

The partial pressure of each species is:

$$P_{\text{PCl}_5} := \frac{n_{\text{PCl}_5} \cdot R \cdot T}{V} \qquad P_{\text{PCl}_5} = 2.5646 \cdot 10^4 \cdot \text{Pa}$$

$$P_{\text{PCl}_3} := \frac{n_{\text{PCl}_3} \cdot R \cdot T}{V} \qquad P_{\text{PCl}_3} = 4.3977 \cdot 10^4 \cdot \text{Pa}$$

$$P_{\text{Cl}_2} := \frac{n_{\text{Cl}_2} \cdot R \cdot T}{V} \qquad P_{\text{Cl}_2} = 4.3977 \cdot 10^4 \cdot \text{Pa}$$

What is K_c for this system?

$$K_c := \frac{C_{\text{PCl}_3} \cdot C_{\text{Cl}_2}}{C_{\text{PCl}_5}} \qquad K_c = 0.0173 \cdot \text{mole} \cdot \text{liter}^{-1}$$

What is K_p for this system?

$$K_p := \frac{P_{\text{PCl}_3} \cdot P_{\text{Cl}_2}}{P_{\text{PCl}_5}} \qquad K_p = 7.541 \cdot 10^4 \cdot \text{Pa}$$

3. Using the equilibrium constant for PCl_5 from the previous problem, calculate the equilibrium pressure of each species under the following conditions:

a. 5 grams of PCl_5 is added to a 3.0 liter flask at 250 °C.

$$V := 3.00 \cdot \text{liter}$$

$$T = 523.15 \cdot \text{K}$$

$$\text{Mass}_{\text{PCl}_5} := 5 \cdot \text{gm}$$

$$\text{MW}_{\text{PCl}_5} = 208.239 \cdot \text{gm} \cdot \text{mole}^{-1}$$

$$n_{\text{initial}} := \frac{\text{Mass}_{\text{PCl}_5}}{\text{MW}_{\text{PCl}_5}} \quad n_{\text{initial}} = 0.024 \cdot \text{mole}$$

$$P_{\text{initial}} := \frac{n_{\text{initial}} \cdot R \cdot T}{V} \quad P_{\text{initial}} = 3.4812 \cdot 10^4 \cdot \text{Pa}$$

From the equilibrium expression with final pressures of:

$$P_{\text{PCl}_5} = P_{\text{initial}} - X$$

$$P_{\text{PCl}_3} = X$$

$$P_{\text{Cl}_2} = X$$

$$K_p = \frac{X \cdot X}{P_{\text{initial}} - X}$$

Rearrange to solve using the quadratic equation:

$$X^2 + K_p \cdot X - K_p \cdot P_{\text{initial}} = 0$$

Include values

$$X^2 + (7.541 \cdot 10^4 \cdot X) - (7.541 \cdot 10^4 \cdot 3.4812 \cdot 10^4) = 0$$

$$X^2 + (7.541 \cdot 10^4 \cdot X) - (2625172920.) = 0$$

$$X = \left(\begin{array}{l} 25909.77772499091268 \\ -101319.77772499091268 \end{array} \right)$$

Two roots from solving the quadratic equation, only the first is "real"

$$X := 25909.8 \cdot \text{Pa}$$

Gives equilibrium pressures of:

$$P_{\text{PCl}_5} := P_{\text{initial}} - X \quad P_{\text{PCl}_5} = 8.9017 \cdot 10^3 \cdot \text{Pa}$$

$$P_{\text{PCl}_3} := X \quad P_{\text{PCl}_3} = 2.591 \cdot 10^4 \cdot \text{Pa}$$

$$P_{\text{Cl}_2} := X \quad P_{\text{Cl}_2} = 2.591 \cdot 10^4 \cdot \text{Pa}$$

b. 25 grams of PCl_5 is added to a 6.0 liter flask at 250 °C.

$$V := 6.00 \cdot \text{liter}$$

$$\text{Mass}_{\text{PCl}_5} := 25 \cdot \text{gm}$$

$$n_{\text{initial}} := \frac{\text{Mass}_{\text{PCl}_5}}{\text{MW}_{\text{PCl}_5}} \qquad n_{\text{initial}} = 0.1201 \cdot \text{mole}$$

$$P_{\text{initial}} := \frac{n_{\text{initial}} \cdot R \cdot T}{V} \qquad P_{\text{initial}} = 8.7029 \cdot 10^4 \cdot \text{Pa}$$

From the equilibrium expression with final pressures of:

$$P_{\text{PCl}_5} = P_{\text{initial}} - X$$

$$P_{\text{PCl}_3} = X$$

$$P_{\text{Cl}_2} = X$$

$$K_p = \frac{X \cdot X}{P_{\text{initial}} - X}$$

Rearrange to solve using the quadratic equation:

$$X^2 + K_p \cdot X - K_p \cdot P_{\text{initial}} = 0$$

Include values

$$X^2 + (7.541 \cdot 10^4 \cdot X) - (7.541 \cdot 10^4 \cdot 8.7029 \cdot 10^4) = 0$$

$$X^2 + (7.541 \cdot 10^4 \cdot X) - (6562856890.) = 0$$

$$X = \left(\begin{array}{l} 51651.163273721639799 \\ -127061.1632737216398 \end{array} \right)$$

Two roots from solving the quadratic equation, only the first is "real"

$$X := 51651 \cdot \text{Pa}$$

Gives equilibrium pressures of:

$$P_{\text{PCl}_5} := P_{\text{initial}} - X$$

$$P_{\text{PCl}_5} = 3.5378 \cdot 10^4 \cdot \text{Pa}$$

$$P_{\text{PCl}_3} := X$$

$$P_{\text{PCl}_3} = 5.1651 \cdot 10^4 \cdot \text{Pa}$$

$$P_{\text{Cl}_2} := X$$

$$P_{\text{Cl}_2} = 5.1651 \cdot 10^4 \cdot \text{Pa}$$

c. 5 grams of PCl_3 and 5 grams of Cl_2 is added to a 3.0 liter flask at 250 °C.

$$V := 3.0 \cdot \text{liter}$$

Initial PCl_3 :

$$\text{Mass}_{\text{PCl}_3} := 5 \cdot \text{gm}$$

$$\text{MW}_{\text{PCl}_3} := (30.9738 + 3 \cdot 35.4527) \cdot \text{gm} \cdot \text{mole}^{-1}$$

$$n_{\text{PCl}_3} := \frac{\text{Mass}_{\text{PCl}_3}}{\text{MW}_{\text{PCl}_3}}$$

$$n_{\text{PCl}_3} = 0.0364 \cdot \text{mole}$$

$$P_{\text{PCl}_3_initial} := \frac{n_{\text{PCl}_3} \cdot R \cdot T}{V}$$

$$P_{\text{PCl}_3_initial} = 5.2785 \cdot 10^4 \cdot \text{Pa}$$

Initial Cl_2 :

$$\text{Mass}_{\text{Cl}_2} := 5 \cdot \text{gm}$$

$$\text{MW}_{\text{Cl}_2} := (2 \cdot 35.4527) \cdot \text{gm} \cdot \text{mole}^{-1}$$

$$n_{\text{Cl}_2} := \frac{\text{Mass}_{\text{Cl}_2}}{\text{MW}_{\text{Cl}_2}}$$

$$n_{\text{Cl}_2} = 0.0705 \cdot \text{mole}$$

$$P_{\text{Cl}_2_initial} := \frac{n_{\text{Cl}_2} \cdot R \cdot T}{V}$$

$$P_{\text{Cl}_2_initial} = 1.0224 \cdot 10^5 \cdot \text{Pa}$$

The Equilibrium Pressure of each species is:

$$P_{\text{PCl}_5} = X$$

$$P_{\text{PCl}_3} = P_{\text{PCl}_3_initial} - X$$

$$P_{\text{Cl}_2} = P_{\text{Cl}_2_initial} - X$$

So the equilibrium expression is:

$$K_p = \frac{(P_{\text{PCl}_3_initial} - X) \cdot (P_{\text{Cl}_2_initial} - X)}{X}$$

Substitute known values:

$$7.541 \cdot 10^4 = \frac{(5.2785 \cdot 10^4 - X) \cdot (1.0224 \cdot 10^5 - X)}{X}$$

Expand the expression:

$$7.541 \cdot 10^4 = \frac{(5396738400.0 - 155025.0 \cdot X + X^2)}{X}$$

Rearrange and set equal to zero:

$$7.541 \cdot 10^4 \cdot X = (5396738400.0 - 155025.0 \cdot X + X^2)$$

$$5396738400.0 - 155025.0 \cdot X + X^2 - 7.541 \cdot 10^4 \cdot X = 0$$

$$5396738400.0 - 230435.0 \cdot X + X^2 = 0$$

$$X = \left(\begin{array}{l} 203977.47919248291487 \\ 26457.520807517085132 \end{array} \right)$$

Solve using the quadratic equation, only the second root is meaningful. The first root is too large and would result in a negative pressure of the products.

$$X := 26457 \cdot \text{Pa}$$

This gives equilibrium pressures of:

$$P_{\text{PCl}_5} := X$$

$$P_{\text{PCl}_5} = 2.6457 \cdot 10^4 \cdot \text{Pa}$$

$$P_{\text{PCl}_3} := P_{\text{PCl}_3, \text{initial}} - X$$

$$P_{\text{PCl}_3} = 2.6328 \cdot 10^4 \cdot \text{Pa}$$

$$P_{\text{Cl}_2} := P_{\text{Cl}_2, \text{initial}} - X$$

$$P_{\text{Cl}_2} = 7.5779 \cdot 10^4 \cdot \text{Pa}$$

Check the solution:

$$\frac{P_{\text{PCl}_3} \cdot P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = 7.5411 \cdot 10^4 \cdot \text{Pa}$$

$$K_p = 7.541 \cdot 10^4 \cdot \text{Pa}$$

4. For the reaction $\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})$ at 973 K the equilibrium constant, K_c , is 9.00. Calculate the equilibrium concentrations of all the species present when:

(a). 1.00 mol of SO_2 and 1.00 mol of NO_2 are injected into a 1.00 L container at 973 K:

The container volume is:

$$\text{volume} := 1.00 \cdot \text{liter}$$

The initial concentration (I_M) for each species is:

$$I_{M \text{SO}_2} := \frac{1.00 \cdot \text{mole}}{\text{volume}} \quad I_{M \text{SO}_2} = 1 \cdot \frac{\text{mole}}{\text{liter}}$$

$$I_{M \text{NO}_2} := \frac{1.00 \cdot \text{mole}}{\text{volume}} \quad I_{M \text{NO}_2} = 1 \cdot \frac{\text{mole}}{\text{liter}}$$

$$I_{M \text{SO}_3} := \frac{0.00 \cdot \text{mole}}{\text{volume}} \quad I_{M \text{SO}_3} = 0 \cdot \frac{\text{mole}}{\text{liter}}$$

$$I_{M \text{NO}} := \frac{0.00 \cdot \text{mole}}{\text{volume}} \quad I_{M \text{NO}} = 0 \cdot \frac{\text{mole}}{\text{liter}}$$

The Equilibrium concentration (E_M) for each species, where X is the moles that react:

$$E_{M \text{SO}_2} = I_{M \text{SO}_2} - X$$

$$E_{M \text{SO}_3} = I_{M \text{SO}_3} + X$$

$$E_{M \text{NO}_2} = I_{M \text{NO}_2} - X$$

$$E_{M \text{NO}} = I_{M \text{NO}} + X$$

The expression for K_c is:

$$K_C = \frac{(E_{M \text{SO}_3}) \cdot (E_{M \text{NO}})}{(E_{M \text{SO}_2}) \cdot (E_{M \text{NO}_2})}$$

Then substitute the expressions for the initial concentrations into the expression to yield:

$$K_C = \frac{(I_{M \text{SO}_3} + X) \cdot (I_{M \text{NO}} + X)}{(I_{M \text{SO}_2} - X) \cdot (I_{M \text{NO}_2} - X)}$$

Now let's put in the numbers from above (ignoring units):

$$9.00 = \frac{(0.0 + X) \cdot (0.0 + X)}{(1.0 - X) \cdot (1.0 - X)}$$

Then expand and rearrange the equations:

$$9.00 = \frac{X^2}{(1.0 - 2.0 \cdot X + X^2)}$$

And set equal to zero:

$$9.00 \cdot (1.0 - 2.0 \cdot X + X^2) - X^2 = 0$$

Multiply out to form for using the quadratic equation:

$$9. - 18. \cdot X + 8. \cdot X^2 = 0$$

Solves for two possible values of X: $\begin{pmatrix} 1.5 \\ .75 \end{pmatrix}$

These solutions for X may be found using the quadratic equation where:

For the equation $9. - 18. \cdot X + 8. \cdot X^2 = 0$

$$X = \frac{-b + \sqrt{b^2 - 4 \cdot a \cdot c}}{2 \cdot a} \quad \text{And} \quad X = \frac{-b - \sqrt{b^2 - 4 \cdot a \cdot c}}{2 \cdot a}$$

Where

$$a := 8$$

$$b := -18$$

$$c := 9$$

This gives two possible values for X from the above equations.

First

$$X := \frac{-b + \sqrt{b^2 - 4 \cdot a \cdot c}}{2 \cdot a}$$

$$X = 1.5$$

Second

$$X := \frac{-b - \sqrt{b^2 - 4 \cdot a \cdot c}}{2 \cdot a}$$

$$X = 0.75$$

Finally, Recall the initial conditions:

$$I_{M_{SO_2}} = 1 \cdot \frac{\text{mole}}{\text{liter}}$$

$$I_{M_{NO}} = 0 \cdot \frac{\text{mole}}{\text{liter}}$$

$$I_{M_{NO_2}} = 1 \cdot \frac{\text{mole}}{\text{liter}}$$

$$I_{M_{SO_3}} = 0 \cdot \frac{\text{mole}}{\text{liter}}$$

From the initial conditions, one solution for X is not Physically reasonable and we pick:

$$X := 0.75 \cdot \frac{\text{mole}}{\text{liter}}$$

The expressions for the equilibrium concentrations is:

$$E_M_{\text{SO}_2} := I_M_{\text{SO}_2} - X$$

$$E_M_{\text{SO}_3} := I_M_{\text{SO}_3} + X$$

$$E_M_{\text{NO}_2} := I_M_{\text{NO}_2} - X$$

$$E_M_{\text{NO}} := I_M_{\text{NO}} + X$$

And this gives equilibrium concentrations of:

$$E_M_{\text{SO}_2} = 0.25 \cdot \frac{\text{mole}}{\text{liter}}$$

$$E_M_{\text{SO}_3} = 0.75 \cdot \frac{\text{mole}}{\text{liter}}$$

$$E_M_{\text{NO}_2} = 0.25 \cdot \frac{\text{mole}}{\text{liter}}$$

$$E_M_{\text{NO}} = 0.75 \cdot \frac{\text{mole}}{\text{liter}}$$

(b). 1.00 mol of SO_2 and 1.00 mol of NO_2 are injected into a 2.00 L container at 973 K (some steps will be skipped here, but solve the same as a:

The container volume is:

$$\text{volume} := 2.00 \cdot \text{liter}$$

The initial concentration (I_M) for each species is:

$$I_{M \text{SO}_2} := \frac{1.00 \cdot \text{mole}}{\text{volume}} \quad I_{M \text{SO}_2} = 0.5 \cdot \frac{\text{mole}}{\text{liter}}$$

$$I_{M \text{NO}_2} := \frac{1.00 \cdot \text{mole}}{\text{volume}} \quad I_{M \text{NO}_2} = 0.5 \cdot \frac{\text{mole}}{\text{liter}}$$

$$I_{M \text{SO}_3} := \frac{0.00 \cdot \text{mole}}{\text{volume}} \quad I_{M \text{SO}_3} = 0 \cdot \frac{\text{mole}}{\text{liter}}$$

$$I_{M \text{NO}} := \frac{0.00 \cdot \text{mole}}{\text{volume}} \quad I_{M \text{NO}} = 0 \cdot \frac{\text{mole}}{\text{liter}}$$

The expression for K_c is:

$$K_C = \frac{(I_{M \text{SO}_3} + X) \cdot (I_{M \text{NO}} + X)}{(I_{M \text{SO}_2} - X) \cdot (I_{M \text{NO}_2} - X)}$$

Now let's put in the numbers from above (ignoring units):

$$9.00 = \frac{(0.0 + X) \cdot (0.0 + X)}{(0.5 - X) \cdot (0.5 - X)}$$

Then expand, rearrange, and set equal to zero:

$$2.25 - 9 \cdot X + 8 \cdot X^2 = 0$$

Solves for two possible values of X: $\begin{pmatrix} .75 \\ .375 \end{pmatrix}$

These solutions for X may be found using the quadratic equation where:

$$\text{Where } a := 8 \quad b := -9 \quad c := 2.25$$

This gives two possible values for X from the above equations.

First

$$X := \frac{-b + \sqrt{b^2 - 4 \cdot a \cdot c}}{2 \cdot a} \quad X = 0.75$$

Second

$$X := \frac{-b - \sqrt{b^2 - 4 \cdot a \cdot c}}{2 \cdot a} \quad X = 0.375$$

Finally, Recall the initial conditions:

$$\begin{aligned} I_{M_{SO_2}} &= 0.5 \cdot \frac{\text{mole}}{\text{liter}} & I_{M_{NO}} &= 0 \cdot \frac{\text{mole}}{\text{liter}} \\ I_{M_{NO_2}} &= 0.5 \cdot \frac{\text{mole}}{\text{liter}} & I_{M_{SO_3}} &= 0 \cdot \frac{\text{mole}}{\text{liter}} \end{aligned}$$

From the initial conditions, one solution for X is not Physically reasonable and we pick:

$$X := 0.375 \cdot \frac{\text{mole}}{\text{liter}}$$

The expressions for the equilibrium concentrations is:

$$\begin{aligned} E_{M_{SO_2}} &:= I_{M_{SO_2}} - X & E_{M_{SO_3}} &:= I_{M_{SO_3}} + X \\ E_{M_{NO_2}} &:= I_{M_{NO_2}} - X & E_{M_{NO}} &:= I_{M_{NO}} + X \end{aligned}$$

And this gives equilibrium concentrations of:

$$\begin{aligned} E_{M_{SO_2}} &= 0.125 \cdot \frac{\text{mole}}{\text{liter}} & E_{M_{SO_3}} &= 0.375 \cdot \frac{\text{mole}}{\text{liter}} \\ E_{M_{NO_2}} &= 0.125 \cdot \frac{\text{mole}}{\text{liter}} & E_{M_{NO}} &= 0.375 \cdot \frac{\text{mole}}{\text{liter}} \end{aligned}$$

(c). 1.00 mol of SO_3 and 1.00 mol of NO are injected into a 1.00 L container at 973 K. (Notice in this example the products are given for the initial conditions. (some steps will be skipped here, but solve the same as a:

The container volume is:

$$\text{volume} := 1.00\text{-liter}$$

The initial concentration (I_M) for each species is:

$$I_M_{\text{SO}_2} := \frac{0.0 \cdot \text{mole}}{\text{volume}} \quad I_M_{\text{SO}_2} = 0 \cdot \frac{\text{mole}}{\text{liter}}$$

$$I_M_{\text{NO}_2} := \frac{0.0 \cdot \text{mole}}{\text{volume}} \quad I_M_{\text{NO}_2} = 0 \cdot \frac{\text{mole}}{\text{liter}}$$

$$I_M_{\text{SO}_3} := \frac{1.0 \cdot \text{mole}}{\text{volume}} \quad I_M_{\text{SO}_3} = 1 \cdot \frac{\text{mole}}{\text{liter}}$$

$$I_M_{\text{NO}} := \frac{1.0 \cdot \text{mole}}{\text{volume}} \quad I_M_{\text{NO}} = 1 \cdot \frac{\text{mole}}{\text{liter}}$$

The expression for K_c is:

$$K_C = \frac{(I_M_{\text{SO}_3} + X) \cdot (I_M_{\text{NO}} + X)}{(I_M_{\text{SO}_2} - X) \cdot (I_M_{\text{NO}_2} - X)}$$

Now let's put in the numbers from above (ignoring units):

$$9.00 = \frac{(1.0 + X) \cdot (1.0 + X)}{(0.0 - X) \cdot (0.0 - X)}$$

Then expand and rearrange:

$$9.00 = \frac{(1.0 + 2.0 \cdot X + X^2)}{X^2}$$

Set this expression equal to zero for the quadratic:

$$8 \cdot X^2 - 1 - 2 \cdot X = 0$$

Solves for two possible values of X:

$$\begin{pmatrix} .5 \\ -.25 \end{pmatrix}$$

These solutions for X may be found using the quadratic equation where:

Where $a := 8$ $b := -2$ $c := -1$

This gives two possible values for X from the above equations.

First

$$X := \frac{-b + \sqrt{b^2 - 4 \cdot a \cdot c}}{2 \cdot a} \qquad X = 0.5$$

Second

$$X := \frac{-b - \sqrt{b^2 - 4 \cdot a \cdot c}}{2 \cdot a} \qquad X = -0.25$$

Finally, Recall the initial conditions:

$$I_{M_{SO_2}} = 0 \cdot \frac{\text{mole}}{\text{liter}} \qquad I_{M_{NO}} = 1 \cdot \frac{\text{mole}}{\text{liter}}$$

$$I_{M_{NO_2}} = 0 \cdot \frac{\text{mole}}{\text{liter}} \qquad I_{M_{SO_3}} = 1 \cdot \frac{\text{mole}}{\text{liter}}$$

From the initial conditions, one solution for X is not Physically reasonable and we pick:

$$X := -0.25 \cdot \frac{\text{mole}}{\text{liter}}$$

The expressions for the equilibrium concentrations is:

$$E_{M_{SO_2}} := I_{M_{SO_2}} - X \qquad E_{M_{SO_3}} := I_{M_{SO_3}} + X$$

$$E_{M_{NO_2}} := I_{M_{NO_2}} - X \qquad E_{M_{NO}} := I_{M_{NO}} + X$$

And this gives equilibrium concentrations of:

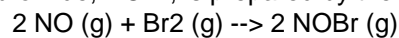
$$E_{M_{SO_2}} = 0.25 \cdot \frac{\text{mole}}{\text{liter}} \qquad E_{M_{SO_3}} = 0.75 \cdot \frac{\text{mole}}{\text{liter}}$$

$$E_{M_{NO_2}} = 0.25 \cdot \frac{\text{mole}}{\text{liter}} \qquad E_{M_{NO}} = 0.75 \cdot \frac{\text{mole}}{\text{liter}}$$

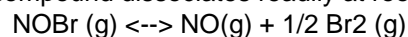
Notice: these are the same equilibrium values as for part a. Does this make sense?

Solution to Chapter 16, question 73 from: Kotz & Treichel, *Chemistry & Chemical Reactivity*, 3rd ed. 1996, Saunders, page 793.

Nitrosyl bromide, NOBr, is prepared by the direct reaction of NO and Br₂.



But the compound dissociates readily at room temperature.



(a) If you mix 3.50 g of NO and 9.67 g of Br₂, how many grams of NOBr can be prepared?

Amounts given (initial)

$$\text{Mass}_{\text{NO}} := 3.50 \cdot \text{gm}$$

$$\text{Mass}_{\text{Br}_2} := 9.67 \cdot \text{gm}$$

$$\text{MW}_{\text{NO}} := (14.00674 + 15.9994) \cdot \text{gm} \cdot \text{mole}^{-1}$$

$$\text{MW}_{\text{Br}_2} := (2 \cdot 79.904) \cdot \text{gm} \cdot \text{mole}^{-1}$$

$$n_{\text{NO}} := \frac{\text{Mass}_{\text{NO}}}{\text{MW}_{\text{NO}}} \quad n_{\text{NO}} = 0.1166 \cdot \text{mole}$$

$$n_{\text{Br}_2} := \frac{\text{Mass}_{\text{Br}_2}}{\text{MW}_{\text{Br}_2}} \quad n_{\text{Br}_2} = 0.0605 \cdot \text{mole}$$

Determine the limiting reagent

If all NO reacts

$$n_{\text{Br}_2 \text{ required}} := \frac{1}{2} \cdot n_{\text{NO}}$$

$$n_{\text{Br}_2 \text{ required}} = 0.0583 \cdot \text{mole}$$

Since sufficient Br₂ is available for all the NO to react, NO is the limiting reagent.

Amount of NOBr prepared

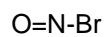
$$n_{\text{NOBr}} := n_{\text{NO}}$$

$$\text{MW}_{\text{NOBr}} := (14.00674 + 15.9994 + 79.904) \cdot \text{gm} \cdot \text{mole}^{-1}$$

$$\text{Mass}_{\text{NOBr}} := n_{\text{NOBr}} \cdot \text{MW}_{\text{NOBr}}$$

$$\text{Mass}_{\text{NOBr}} = 12.8202 \cdot \text{gm}$$

(b) If N is the central atom of nitrosyl bromide, draw the electron dot structure for the molecule.



You have to add non-bonding electrons to fill the valence for each atom.

(c) What is the electron pair geometry of NOBr?

O - trigonal planar

N - trigonal planar

Br - tetrahedral

What is the molecular geometry?

N - bent

Is the molecule polar?

Yes, look at the geometry and the electronegativities.

(d) Some NOBr is placed in a flask at 25 C and allowed to dissociate. The total pressure at equilibrium is 190 mm Hg, and the compound is found to be 34% dissociated. What is the value of K_p ?

Start by setting up an equilibrium table. There are lots of blanks, but it will help you see where to start. The question states that "some" NOBr is placed in a flask. You do not know what the initial amount is or the size of the flask, so use "X" for the initial pressure of NOBr in the flask. The other piece of information that is relevant at this point is that 34% of the NOBr dissociates. This gives us an expression for the amount of change (34% of X).

	NOBr (g)	\leftrightarrow	NO(g)	+	1/2 Br ₂ (g)
Initial	X		0		0
Change	- 34%·X		+ 34%·X		+ $\frac{1}{2}$ ·(34%·X)
Final	X - 0.34·X		0.34·X		0.17·X

Now, from the relationships that are found in the equilibrium table we can write an equilibrium expression.

$$K_p = \frac{P_{\text{NO}} \cdot P_{\text{Br}_2}^{\frac{1}{2}}}{P_{\text{NOBr}}}$$

Substitute in the appropriate equations from the equilibrium table to get:

$$K_p = \frac{(0.34 \cdot X) \cdot (0.17 \cdot X)^{\frac{1}{2}}}{(X - 0.34 \cdot X)}$$

Notice how many variables there are in this expression.

Now we have a single equation, but it contains two variables. So there is no "solution" to this equation. To solve for two variables (K_p and X), we need two equations. So look back at the original problem to see what other information is provided.

The question states that the "total pressure at equilibrium is 190 mmHg". Is there any way to relate that to what is happening and the variables that we are using?

Recall that we have expressions for the equilibrium pressure of each species. Based upon the concept of "partial pressure", the total pressure is the sum of the pressure for each species present. So that:

$$P_{\text{total}} = P_{\text{NOBr}} + P_{\text{NO}} + P_{\text{Br}}$$

Now substitute in the above expressions:

$$P_{\text{total}} = (X - 0.34 \cdot X) + (0.34 \cdot X) + (0.17 \cdot X)$$

This is another equation with two variables, but we know what P_{total} is at equilibrium. So we can write:

$$190 \cdot \text{torr} = (X - 0.34 \cdot X) + (0.34 \cdot X) + (0.17 \cdot X)$$

Since torr=mmHg, and Mathcad uses torr for pressure units.

Which solves as:

$$190 \cdot \text{torr} = (.66 \cdot X) + (0.34 \cdot X) + (0.17 \cdot X)$$

$$190 \cdot \text{torr} = 1.17 \cdot X$$

$$X := \frac{190 \cdot \text{torr}}{1.17}$$

$$X = 162.3932 \cdot \text{torr}$$

Now we have a value for X , so it is possible to solve for K_p :

$$K_p := \frac{(0.34 \cdot X) \cdot (0.17 \cdot X)^{\frac{1}{2}}}{(X - 0.34 \cdot X)}$$

$$K_p = 2.7067 \cdot \text{torr}^{\frac{1}{2}}$$

$$K_p = 0.0982 \cdot \text{atm}^{\frac{1}{2}}$$

Normally 1 atmosphere is used as the "standard state", so K_p is given with all pressures in atmospheres. Just be certain that you indicated the units YOU use to solve the problem.

Take a careful look at the problem solving techniques used to answer this question. It is a great example.