

### Problem Set 3 Solutions (For January 27)

1. First, we convert the temperature from °C to K units, and the pressure from torr to atm units:

$$T/K = t/^{\circ}\text{C} + 273.15 = 20 + 273.15 \quad \text{so} \quad T = 293.15 \text{ K}$$

$$P/\text{atm} = \frac{(P/\text{torr})}{760} = \frac{8.0 \times 10^{-7}}{760} = 1.05 \times 10^{-9} \quad \text{or} \quad P = 1.05 \times 10^{-9} \text{ atm}$$

We know  $V = 1.0 \text{ L}$ , and we can find  $n$ , the number of moles of gas in the volume:

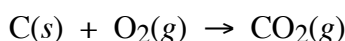
$$n = \frac{PV}{RT} = \frac{(1.05 \times 10^{-9} \text{ atm})(1.0 \text{ L})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(293.15 \text{ K})} = 4.38 \times 10^{-11} \text{ mol}$$

That's not very many moles, but it is a lot of molecules:

$$N = nN_A = (4.38 \times 10^{-11} \text{ mol})(6.02 \times 10^{23} \text{ mol}^{-1}) = 2.6 \times 10^{13}$$

(The average density of ordinary matter in the Universe is about one atom per cubic centimeter, or  $10^3$  per liter,  $10^{10}$  times less than this pretty good vacuum.)

2. First things first:  $0.631 \text{ g of C is } 0.631/12.011 \text{ g mol}^{-1} = 0.0525 \text{ mol C}$ . Now, what happens to C when it is burned in  $\text{O}_2$ , assuming  $\text{CO}_2$  is the only product? The answer is the simple, balanced reaction



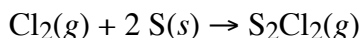
The reaction stoichiometry tells us that  $0.0525 \text{ mol of C}(s)$  will yield  $0.0525 \text{ mol CO}_2(g)$  when burned. Moreover, the combustion will require  $0.0525 \text{ mol O}_2(g)$ . How many moles of  $\text{O}_2$  do we have to begin with?  $P = 3.75 \text{ atm}$ ,  $V = 425 \text{ mL} = 0.425 \text{ L}$ , and  $T = 20.0 \text{ }^{\circ}\text{C} = 293.15 \text{ K}$ . Thus

$$n_{\text{O}_2} = \frac{PV}{RT} = \frac{(3.75 \text{ atm})(0.425 \text{ L})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(293.15 \text{ K})} = 0.0663 \text{ mol}$$

and we have more than enough  $\text{O}_2$  to do the job. When the reaction is over, all the  $\text{C}(s)$  is gone, and we have a gaseous mixture of  $0.0525 \text{ mol CO}_2$  and  $(0.0663 - 0.0525) \text{ mol} = 0.0138 \text{ mol O}_2$ . The mole fractions are  $\chi(\text{CO}_2) = (0.0525 \text{ mol})/(0.0663 \text{ mol}) = 0.792$  and  $\chi(\text{O}_2) = 1 - 0.792$  (this is a binary mixture, so the mole fractions add to 1) =  $0.208$ . The final temperature, we're told, is  $2.0 \text{ }^{\circ}\text{C}$  higher, or  $T = 295.15 \text{ K}$  at the end. The final pressure is computed from a total number of moles  $n = 0.0663 \text{ mol}$  and the final  $T$  and  $V$  values:

$$P = \frac{nRT}{V} = \frac{(0.0663 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(295.15 \text{ K})}{(0.425 \text{ L})} = 3.78 \text{ atm}$$

3. Here, we're dealing with the net reaction

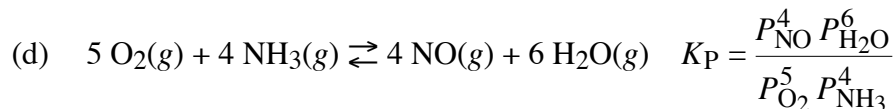
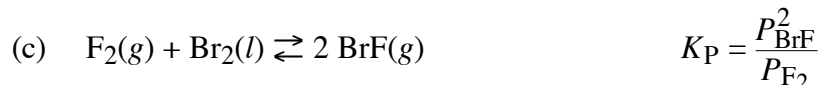
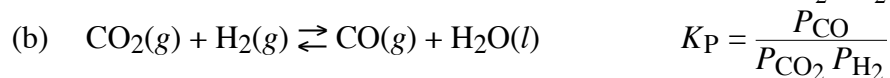
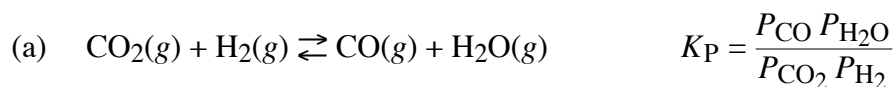


Let's see which reactant is in excess. We know we have  $0.052 \text{ mol Cl}_2$ , and we know we have  $0.258 \text{ g S}(s)$ .  $0.258 \text{ g S}(s)$  is  $0.258 \text{ g}/32.06 \text{ g mol}^{-1} = 0.00805 \text{ mol S}$ , far less than the amount of  $\text{Cl}_2$ . Since each mole of  $\text{S}_2\text{Cl}_2$  product requires  $2 \text{ mol S}$ , and since  $\text{S}$  is the limiting reagent, we can make only  $0.00805/2 \text{ mol} = 0.00403 \text{ mol S}_2\text{Cl}_2$  and we will use up all the  $\text{S}(s)$ . We will use up only  $0.00403 \text{ mol of Cl}_2$ , since the stoichiometry is 1 to 1 between  $\text{Cl}_2$  and  $\text{S}_2\text{Cl}_2$ . At the end, we will have a gas mixture consisting of  $0.00403 \text{ mol S}_2\text{Cl}_2$  and  $(0.052 - 0.00403) \text{ mol} = 0.048 \text{ mol Cl}_2$  (to two significant figures). The total number of moles of gas, however, will be what it was at the start:  $0.052 \text{ mol}$ , because every mole of  $\text{Cl}_2$  that was consumed was replaced by one mole of  $\text{S}_2\text{Cl}_2$ . All this gas will be at  $300 \text{ K}$  in the total volume of  $2.00 \text{ L}$ ; so, the pressure will be

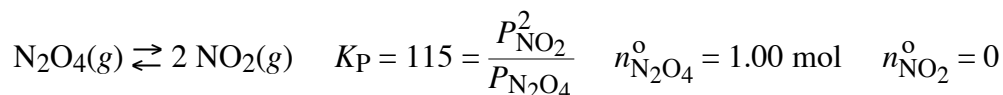
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$$P = \frac{nRT}{V} = \frac{(0.052 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(300 \text{ K})}{(2.00 \text{ L})} = 0.64 \text{ atm}$$

4. These are pretty straightforward. Note that in (b) and (c), the pure liquids *do not appear* in the equilibrium constant expression.



5. Let's work this using the "extent of reaction" methodology. Here's what we know:



Now let's write the equilibrium constant expression in terms of mole fractions and the total pressure:

$$K_P = 115 = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{\chi_{\text{NO}_2}^2 P_{\text{tot}}^2}{\chi_{\text{N}_2\text{O}_4} P_{\text{tot}}} = \frac{\chi_{\text{NO}_2}^2}{\chi_{\text{N}_2\text{O}_4}} P_{\text{tot}}$$

Next, we turn mole fractions into ratios of number of moles of each gas and total number of moles:

$$K_P = 115 = \frac{\chi_{\text{NO}_2}^2}{\chi_{\text{N}_2\text{O}_4}} P_{\text{tot}} = \frac{\left(\frac{n_{\text{NO}_2}}{n_{\text{tot}}}\right)^2}{\left(\frac{n_{\text{N}_2\text{O}_4}}{n_{\text{tot}}}\right)} P_{\text{tot}} = \frac{n_{\text{NO}_2}^2}{n_{\text{N}_2\text{O}_4} n_{\text{tot}}} P_{\text{tot}}$$

Now we introduce the extent of reaction variable and our initial amounts:

$$x = \frac{n_{\text{N}_2\text{O}_4}^0 - n_{\text{N}_2\text{O}_4}}{1} = 1.00 \text{ mol} - n_{\text{N}_2\text{O}_4} = \frac{n_{\text{NO}_2} - n_{\text{NO}_2}^0}{2} = \frac{n_{\text{NO}_2}}{2}$$

so that

$$n_{\text{N}_2\text{O}_4} = 1.00 \text{ mol} - x \quad n_{\text{NO}_2} = 2x \quad n_{\text{tot}} = n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2} = 1.00 \text{ mol} + x$$

We substitute these expressions into our  $K_P$  expression above and find

$$K_P = 115 = \frac{n_{\text{NO}_2}^2}{n_{\text{N}_2\text{O}_4} n_{\text{tot}}} P_{\text{tot}} = \frac{(2x)^2}{(1.00 \text{ mol} - x)(1.00 \text{ mol} + x)} P_{\text{tot}} = \frac{4x^2}{1.00 \text{ mol}^2 - x^2} P_{\text{tot}}$$

We thus need to solve the final expression for  $x$  with  $P_{\text{tot}} = 1.00 \text{ atm}$ . (But remember: this  $P_{\text{tot}}$  is in an equilibrium constant expression, so it has no units if the pressure is expressed in the standard units, which it is here!) Multiplying things out with  $P_{\text{tot}} = 1$  gives us the quadratic expression we can easily solve:

$$4x^2 = 115(1.00 \text{ mol}^2 - x^2) \quad \text{or} \quad 119x^2 = 115 \text{ mol}^2 \quad \text{or} \quad x = \sqrt{115/119} \text{ mol} = 0.983 \text{ mol}$$

Now we use this value for  $x$  to find the final amounts of both species (and, while we're at it,  $n_{\text{tot}}$ ):

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$$n_{\text{N}_2\text{O}_4} = 0.017 \text{ mol} \quad n_{\text{NO}_2} = 1.966 \text{ mol} \quad n_{\text{tot}} = n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2} = 1.983 \text{ mol}$$

and the final partial pressures:

$$P_{\text{N}_2\text{O}_4} = \frac{0.017 \text{ mol}}{1.983 \text{ mol}} 1.00 \text{ atm} = 8.57 \times 10^{-3} \text{ atm} \quad P_{\text{NO}_2} = \frac{1.966 \text{ mol}}{1.983 \text{ mol}} 1.00 \text{ atm} = 0.991 \text{ atm}$$

As a final check, we can substitute these final pressures back into the equilibrium constant expression and see that they yield the value  $K_P = 115$  that we expect:

$$K_P = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{(0.991)^2}{8.57 \times 10^{-3}} = 115 \text{ (to three significant figures)}$$

This was a long calculation, but one that followed a series of very simple algebraic steps: we turned partial pressures into (mole fractions) $\times$ (total pressure), then turned mole fractions into (amounts)/(total amount), then used the extent of reaction expressions and the initial amounts to express each individual amount and the total amount into quantities having only one unknown:  $x$ . We solved for  $x$  and used its value to work backwards through this series of expressions to recover the final partial pressures we wanted.

If the volume of the container was increased at constant  $T$ ,  $K_P$  would not change (it depends *only* on  $T$ ), but the total pressure would go down. We still have to satisfy the  $K_P$  expression, and we saw that it can be written in terms of mole fractions and  $P_{\text{tot}}$ . So as  $P_{\text{tot}}$  goes *down*, the *mole fractions much change, too!* Our friend Le Châtelier would say that to counteract the falling pressure, the reaction equilibrium will respond in any way it can to try and counteract that pressure drop: the reaction moves to the right, generating more  $\text{NO}_2$ , a move that will in fact increase the number of gaseous molecules, because each  $\text{N}_2\text{O}_4$  that disappears produces two  $\text{NO}_2$  molecules.