

SOLUTIONS TO TOPIC G PROBLEMS

For problems 1-5 refer to the introduction video.

6) **Statement a is true.** When the concentrations of glucose and fructose are equal, then $Q = 1$ (because $Q = [\text{glucose}]/[\text{fructose}]$). However, K is greater than 1. Therefore, $Q < K$, so the reaction will appear to “go to the right.” In reality, it goes both ways, but the forward reaction is faster than the reverse reaction.

7) a) $K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$ b) $K_c = \frac{1}{[\text{O}_2]}$ c) $K = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]^2}{[\text{CO}_2]}$

8) a) For part a, $K_p = \frac{(P_{\text{NO}_2})^2}{(P_{\text{NO}})^2(P_{\text{O}_2})}$ For part b, $K_p = \frac{1}{P_{\text{O}_2}}$

b) $K_p = K_c (RT)^{\Delta n_{\text{gases}}}$ where Δn_{gases} is the change in the number of moles of gases in the balanced equation. For this reaction, $\Delta n_{\text{gases}} = 2 - 3 = -1$.

Substituting the given values gives $K_p = (2.8 \times 10^{11}) \times \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 473 \text{ K}\right)^{-1}$

The arithmetic is straightforward, but how will the units work? In general, both K_c and K_p are written with no units. However, in this formula the units will cancel correctly only if you include the unit that would match the original equilibrium constant expression. In this case, the unit of K_c will be $\text{M}^2/(\text{M}^2 \times \text{M})$, which simplifies to $1/\text{M} = \text{L/mol}$. We can include this in our formula...

$$\begin{aligned} K_p &= (2.8 \times 10^{11} \text{ L/mol}) \times \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 473 \text{ K}\right)^{-1} \\ &= (2.8 \times 10^{11} \text{ L/mol}) \times (38.81 \text{ L} \cdot \text{atm/mol})^{-1} \\ &= (2.8 \times 10^{11} \text{ L/mol}) \times 0.02576 \text{ mol/L} \cdot \text{atm} \\ &= 7.2 \times 10^9 \text{ atm}^{-1} \end{aligned}$$

When we write K_p , we leave out the unit, so $K_p = 7.2 \times 10^9$.

9) a) To determine whether this is an equilibrium mixture, we calculate Q and compare the result to K_c .

$$Q = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{0.0139 \text{ M}}{0.0381 \text{ M} \times 0.0593 \text{ M}} = 6.15$$

K_c is 6.17, so Q is essentially equal to K_c here. (The difference between 6.15 and 6.17 is not statistically meaningful, because the last digit is always uncertain.) **This mixture is at equilibrium.**

b) Again, we calculate Q and compare it to K_c :

$$Q = \frac{0.0455 \text{ M}}{0.0482 \text{ M} \times 0.289 \text{ M}} = 3.27$$

Q does not equal K_c , so **this mixture is not at equilibrium**. Since Q is smaller than K_c , **the reaction will go forward**.

c) Since the mixture does not contain any Cl_2 , **it is not at equilibrium**. The reaction cannot go forward, because there is no Cl_2 to react, so **the reaction will go backward**.

d) Before we calculate Q in this part, we must calculate the concentrations of the three chemicals. *You cannot use moles in any calculation that involves Q or K .*

$$[\text{PCl}_3] = 0.21 \text{ mol}/8.00 \text{ L} = 0.02625 \text{ M}$$

$$[\text{Cl}_2] = 0.48 \text{ mol}/8.00 \text{ L} = 0.060 \text{ M}$$

$$[\text{PCl}_5] = 0.39 \text{ mol}/8.00 \text{ L} = 0.04875 \text{ M}$$

$$Q = \frac{0.04875 \text{ M}}{0.02625 \text{ M} \times 0.060 \text{ M}} = 30.95$$

Q does not equal K_c , so **this mixture is not at equilibrium**. Since Q is larger than K_c , **the reaction will go backward**.

10) **Statement b is correct.**

11) a) Since the reaction is at equilibrium, we know that $Q = K_p$, so we can write:

$$\frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = 0.0489$$

Substituting the pressures of N_2 and H_2 gives us:

$$\frac{(P_{\text{NH}_3})^2}{(0.100 \text{ atm})(0.200 \text{ atm})^3} = 0.0489$$

Solving this equation gives $P_{\text{NH}_3} = 0.00625 \text{ atm}$. Note that the value of K_p always assumes that the pressures are in atmospheres, but K_p is written without units, so you must remember the correct unit.

b) Again, we can use $Q = K_p$, but now we must convert all of the pressures from torr to atm:

$$830 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.092 \text{ atm H}_2 \quad 42 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.05526 \text{ atm NH}_3$$

Substituting these values into Q gives us:

$$\frac{(0.05526 \text{ atm})^2}{(P_{N_2})(1.092 \text{ atm})^3} = 0.0489$$

Solving this equation gives **0.0480 atm**, or **36.4 torr**.

c) To do this part, we must start by converting K_p into K_c . To do so, we need to know the temperature in kelvins, and we need Δn_{gases} .

$$T = 256 + 273 = 529 \text{ K}$$

$$\Delta n_{\text{gases}} = 2 \text{ mol} - 4 \text{ mol} = -2 \text{ mol}$$

Substituting these values and the value of K_p into the equation relating K_p and K_c gives:

$$0.0489 = K_c(0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K} \times 529 \text{ K})^{-2}$$

$$0.0489 = K_c \times (43.4097)^{-2}$$

$$0.0489 = K_c \times 0.00053067$$

$$K_c = 92.147$$

Now we substitute the molarities of N_2 and H_2 into Q, and set $Q = K_c$:

$$\frac{(0.0300 \text{ M})^2}{(0.0100 \text{ M})[H_2]^3} = 92.147$$

Solving this equation gives $[H_2] = \mathbf{0.0992 \text{ M}}$.

d) If the concentrations of the three chemicals are all equal, the partial pressures must also be equal. You can prove this by taking the ideal gas law and dividing both sides by V:

$$P = \frac{n}{V}RT$$

and then recognizing that n/V is the molarity (moles per liter). Therefore, the pressure equals the concentration times RT , and RT is the same for all three gases.

Since the pressures are equal, let x be the pressure of each gas. Substituting x into Q and setting $Q = K_p$ gives:

$$\frac{x^2}{x \cdot x^3} = 0.0489$$

Solving this equation gives $x = 4.52$, so **the pressure of each gas is 4.52 atm**.

12) We start by calculating the initial concentration of N_2O_4 in the container. 1.00 g of N_2O_4 (molar mass = 92.02 g/mol) equals 0.010867 moles, so the initial concentration is $0.010867 \text{ mol}/5.00 \text{ L} = 0.0021734 \text{ M}$.

Next, we set up an ICE table. We know that the initial concentration of N_2O_4 is 0.0021734 M , the initial concentration of NO_2 is zero, and the final concentration of NO_2 is $6.68 \times 10^{-4} \text{ M} = 0.000668 \text{ M}$, so we have:

	N_2O_4	\rightarrow	$2 NO_2$
Initial M:	0.0021734		0 M
Change:	?		?
Ending M:	?		0.000668

We calculate the remaining values as follows:

- Since the initial molarity of NO_2 is 0 M and the final molarity is 0.000668 M, the change in the NO_2 molarity must be +0.000668 M.
- The change in the N_2O_4 concentration must be half as large as the change in the NO_2 concentration (from the balanced equation), and it must be negative, so it is $(-0.000668 \text{ M})/2 = -0.000334 \text{ M}$
- The final molarity of N_2O_4 is therefore $0.0021734 \text{ M} - 0.000334 \text{ M} = 0.0018394 \text{ M}$.

The final ICE table looks like this:

	N_2O_4	\rightarrow	2NO_2
Initial M:	0.0021734		0 M
Change:	-0.000334		+0.000668
Ending M:	0.0018394		0.000668

The final concentrations must satisfy $Q = K_c$, so we have:

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.000668 \text{ M})^2}{0.0018394 \text{ M}} = 2.426 \times 10^{-4}$$

We are also asked to calculate K_p , which we can do using the usual relationship. In this case, $T = 50 + 273 = 323 \text{ K}$ and $\Delta n_{\text{gases}} = 2 \text{ mol} - 1 \text{ mol} = 1 \text{ mol}$:

$$\begin{aligned} K_p &= (2.426 \times 10^{-4}) \times (0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K} \times 323 \text{ K})^1 \\ K_p &= (2.426 \times 10^{-4}) \times (26.505)^1 \\ K_p &= (2.426 \times 10^{-4}) \times 26.505 \\ K_p &= \mathbf{6.43 \times 10^{-3}} \end{aligned}$$

13) For this problem, you can take two approaches

Option 1: convert the final ammonia pressure to a molarity, calculate the initial molarities of N_2 and H_2 using the moles and volume, do the ICE table in molarities, calculate K_c , then calculate K_p .

Option 2: use the initial moles and volume to calculate initial pressures of N_2 and H_2 , do the ICE table in pressures, calculate K_p , then calculate K_c .

I'll show option 1 in detail, and summarize option 2 afterward.

To begin, we calculate the initial molarities of N_2 and H_2 (which are equal):

$$\text{initial } [\text{H}_2] = \text{initial } [\text{N}_2] = 0.100 \text{ mol}/5.00 \text{ L} = 0.0200 \text{ M}$$

Next, we use the ideal gas law to calculate the final number of moles of NH_3 . The pressure of NH_3 is 0.0506 atm, the volume is 5.00 L, and the temperature is $300^\circ\text{C} = 573 \text{ K}$, so we have:

$$(0.0506 \text{ atm})(5.00 \text{ L}) = n(0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(573 \text{ K})$$

Solving for n gives $n = 0.0053806$ moles. The final molarity of ammonia is therefore:

$$0.0053806 \text{ mol}/5.00 \text{ L} = 0.0010761 \text{ M}$$

Now we set up an ICE table, which includes the initial molarities of all three gases and the final molarity of NH_3 :



Initial M:	0.0200	0.0200	0
Change:	?	?	?
Ending M:	?	?	0.0010761

Now, we recognize that the changes in the molarities must be in the ratio 1:3:2, to match the balanced equation. Therefore, we can replace the question marks in the “change” row with a variable, as shown on the next page:

	N_2	+	3 H_2	\rightarrow	2 NH_3
Initial M:	0.0200		0.0200		0
Change:	$-x$		$-3x$		$+2x$
Ending M:	?		?		0.0010761

Then we use the final and initial molarities of NH_3 to determine x :

$$0 + 2x = 0.0010761 \quad \text{so...} \quad x = 0.0005381$$

Now, we substitute this value of x into the entire “change” row:

	N_2	+	3 H_2	\rightarrow	2 NH_3
Initial M:	0.0200		0.0200		0
Change:	-0.0005381		$-3(0.0005381)$		$+2(0.0005381)$
Ending M:	?		?		0.0010761

And finally we do a bit of arithmetic to get the final concentrations of N_2 and H_2 , noting that $3(0.0005381) = 0.0016143$:

	N_2	+	3 H_2	\rightarrow	2 NH_3
Initial M:	0.0200		0.0200		0
Change:	-0.0005381		-0.0016143		$+0.0010761$
Ending M:	0.019462		0.018386		0.0010761

These final molarities must satisfy $Q = K_c$, so we can now calculate K_c :

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.0010761)^2}{(0.019462)(0.018386)^3} = 9.57$$

Finally, we calculate K_p . In this case, $T = 573 \text{ K}$ and $\Delta n_{\text{gases}} = 2 \text{ mol} - 4 \text{ mol} = -2 \text{ mol}$:

$$K_p = 9.57 \times (0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K}) \times 573 \text{ K}^{-2}$$

$$K_p = 9.57 \times (47.020)^{-2}$$

$$K_p = 9.57 \times 0.0004523$$

$$K_p = 0.00433$$

If you use option 2, you should get the following results:

Initial pressures of N_2 and $\text{H}_2 = 0.94041 \text{ atm}$

Completed ICE table (in atm):

	N_2	+	3 H_2	\rightarrow	2 NH_3
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Initial P (atm):	0.94041	0.94041	0
Change:	-0.0253	-0.0759	+0.0506
Ending P (atm):	0.91511	0.86451	0.0506

Substituting these values into Q gives $Q = K_p = 0.00433$ (the same answer we got using option 1). Then the usual method gives $K_c = 9.57$, again matching the answer we got using option 1.

- 14) a) We are given the initial concentration of PCl_5 , and we can assume that there is no PCl_3 and Cl_2 in the flask before the reaction occurs. We are also given K_c , so we do not need to convert the concentrations into pressures. Therefore, we can proceed directly to an ICE table:

	PCl_5	\rightarrow	PCl_3	+	Cl_2
Initial M:	0.100		0		0
Change:	$-x$		$+x$		$+x$
Ending M:	$0.100 - x$		x		x

The final concentrations must satisfy $Q = K_c$, so our next step is to set up the equilibrium constant expression:

$$\frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = K_c$$

so...
$$\frac{(x)(x)}{(0.100-x)} = 0.0168$$

Solving this equation gives two roots: $x = 0.03344$ and $x = -0.05024$. (See me, a chemistry tutor, or a math tutor if you need help solving this type of equation.) The negative root is physically meaningless, because it would mean that the concentrations of the products are negative numbers. Therefore, the positive root is correct, and the final concentrations of the gases are:

$$[\text{PCl}_5] = 0.100 - 0.03344 = \mathbf{0.0666 \text{ M}}$$

$$[\text{PCl}_3] = \mathbf{0.0334 \text{ M}}$$

$$[\text{Cl}_2] = \mathbf{0.0334 \text{ M}}$$

(Note on rounding: applying the significant figure rules to a problem like this is very difficult and very tedious, so as a general guideline, you should round your final answers to the same number of significant figures as K .)

- b) In this case, we have nonzero concentrations of all three chemicals in the reaction, so we must start by figuring out which way the reaction will go. We do this by calculating Q and comparing it to K_c .

$$Q = \frac{(0.200)(0.300)}{0.100} = 0.600$$

This is larger than K_c , so the reaction will go backward. The ICE table looks like this:

	PCl_5	\leftarrow	PCl_3	+	Cl_2
Initial M:	0.100		0.200		0.300
Change:	$+x$		$-x$		$-x$
Ending M:	$0.100 + x$		$0.200 - x$		$0.300 - x$

The final concentrations must satisfy $Q = K_c$. Note that even though the reaction went backward, we can still use the same equilibrium constant expression.

$$\frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = K_c$$

so... $\frac{(0.200-x)(0.300-x)}{(0.100+x)} = 0.0168$

Solving this equation for x gives two roots, $x = 0.1665$ and $x = 0.3503$. In this case, only the first root is physically meaningful; the second root gives negative concentrations for PCl_3 and Cl_2 .

Therefore, the final concentrations are:

$$\begin{aligned} [\text{PCl}_5] &= 0.100 + 0.1665 = \mathbf{0.266 \text{ M}} \\ [\text{PCl}_3] &= 0.200 - 0.1665 = \mathbf{0.0335 \text{ M}} \\ [\text{Cl}_2] &= 0.300 - 0.1665 = \mathbf{0.133 \text{ M}} \end{aligned}$$

Note: if you are not comfortable with the idea that you can use the original Q expression, it's also okay to write the reaction in reverse and to modify Q and K_c accordingly. When you reverse a reaction, both Q and K "flip over", so you'll get:

$$\frac{(0.100+x)}{(0.200-x)(0.300-x)} = \frac{1}{0.0168}$$

Solving this equation gives you the same answers we got above.

15) a) In this problem, we start with the product of the reaction (HI), so the reaction obviously must "go backward." Since we are given K_p and the initial pressure of HI , we should do our stoichiometry using pressures. All K_p values are calculated using pressures in atm, so we must also use atm.

	H_2	+	I_2	\leftarrow	2 HI
Initial P (atm):	0		0		3.00
Change:	$+x$		$+x$		$-2x$
Ending P (atm):	x		x		$3.00 - 2x$

These final pressures must satisfy the equilibrium condition $Q_p = K_p$:

$$\frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})} = \frac{(3.00-2x)^2}{(x)(x)} = 0.513$$

Solving this equation gives two roots, $x = 1.1045$ and $x = 2.3369$. We can discard the second value, because it will give us a negative pressure of HI ($3.00 - 2(2.3369) = -1.6738$). Therefore, the final pressures of H_2 and I_2 in the equilibrium mixture (rounding to three significant figures) will be **1.10 atm**, and the final pressures of HI will be $3.00 - 2(1.1045) = \mathbf{0.791 \text{ atm}}$.

b) Here, we have a mixture of all three chemicals, so we must begin by figuring out which way the reaction will go. As in problem 9 part b, we do this by calculating Q and comparing it to K_p .

$$Q = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})} = \frac{(0.0310 \text{ atm})^2}{(0.433 \text{ atm})(0.0471 \text{ atm})} = 0.0471$$

Q is smaller than K_p , so the reaction will go forward. Now we can set up an ICE table:

	H_2	+	I_2	→	2 HI
Initial P (atm):	0.433		0.0471		0.0310
Change:	$-x$		$-x$		$+2x$
Ending P (atm):	$0.433 - x$		$0.0471 - x$		$0.0310 + 2x$

These final pressures must satisfy the equilibrium condition $Q_p = K_p$:

$$\frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})} = \frac{(0.0310+2x)^2}{(0.433-x)(0.0471-x)} = 0.513$$

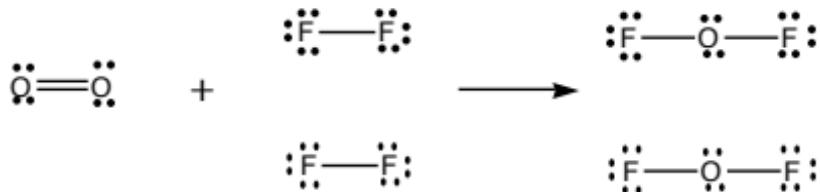
Solving this equation gives two roots, $x = 0.02136176$ and $x = -0.1275537$. We can discard the second value, because it will give us a negative pressure of HI . Therefore, the final pressures will be:

$$\text{H}_2: 0.433 - 0.02136176 = \mathbf{0.412 \text{ atm}}$$

$$\text{I}_2: 0.0471 - 0.02136176 = \mathbf{0.0257 \text{ atm}}$$

$$\text{HI: } 0.0310 + 2(0.02136176) = \mathbf{0.0737 \text{ atm}}$$

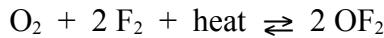
- 16) a) Adding F_2 (a reactant) drives the reaction **to the right**, to remove some of the additional F_2 .
- b) Adding O_2 (a reactant) drives the reaction to the right, to remove some of the additional O_2 : $\text{O}_2(\text{g}) + 2 \text{F}_2(\text{g}) \rightarrow 2 \text{OF}_2(\text{g})$. When the reaction goes forward, it also consumes F_2 , so **the partial pressure of F_2 decreases**.
- c) Increasing the volume of a gas-phase equilibrium drives the reaction toward the side with more moles of gases. In this case, there are three moles of gaseous reactants and only two moles of gaseous products, so the reaction shifts **to the left**.
- d) Decreasing the volume of a gas-phase equilibrium drives the reaction toward the side with fewer moles of gas, so the reaction shifts to the right: $\text{O}_2(\text{g}) + 2 \text{F}_2(\text{g}) \rightarrow 2 \text{OF}_2(\text{g})$. This direction makes OF_2 , so **the mass of OF_2 increases**.
- e) To determine the effect of temperature, we need to know ΔH for the reaction. Here are the structures of the reactants and products and the relevant bond energies:



Bond energy values: $\text{O}=\text{O}$ 495 kJ/mol, $\text{F}-\text{F}$ 154 kJ/mol, $\text{O}-\text{F}$ 190 kJ/mol.

$$\text{So } \Delta\text{H} = (1 \text{ mol} \times 495 \text{ kJ/mol}) + (2 \text{ mol} \times 154 \text{ kJ/mol}) - (4 \text{ mol} \times 190 \text{ kJ/mol}) = 43 \text{ kJ}$$

The value of ΔH is positive, so the reaction is endothermic as we read from left to right. We can rewrite the reaction including “heat” as a reactant:



Now we can solve the problem. When we increase the temperature, we add heat. By Le Châtelier’s Principle, the reaction will go in the direction that consumes heat. Based on the chemical equation, this is the forward direction, so the reaction goes **to the right**.

17) Changing the temperature (**part e**) changes the numerical value of K . In all other cases, we changed Q , but not K . *The value of any equilibrium constant only depends on temperature.*

18) a) NH_4Cl does not appear in the reaction quotient, because it is a solid. Therefore, changing the amount of NH_4Cl in the mixture does not change the value of Q . The mixture was originally at equilibrium ($Q = K$), and since we did not change the value of Q , then $Q = K$ still. Therefore, adding NH_4Cl did not disturb the equilibrium, and it will not affect the reaction. The mass of NH_3 in the mixture **will not change**. (In general, adding a solid reactant or product does not disturb an equilibrium.)

b) When we add NH_3 , the equilibrium shifts to the left to remove some of the added NH_3 .

$$\text{NH}_4\text{Cl}(\text{s}) \leftarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$$

When the reaction goes backward, it also uses HCl , so **the mass of HCl decreases**.

c) When we add HCl , the equilibrium shifts to the left to remove some of the added HCl .



When the reaction goes backward, it makes NH_4Cl , so **the mass of NH_4Cl increases**.

- 19) a) To begin, we must recognize that the HCl is completely dissociated, so we are actually adding H^+ and Cl^- ions to the equilibrium mixture.

Now, neither H^+ nor Cl^- appears in the balanced equation. Therefore, we ask ourselves “is there anything in the equilibrium mixture that would react with H^+ or Cl^- ?” The answer is yes: OH^- will react with H^+ to form water. Therefore, *adding H^+ is equivalent to decreasing the concentration of OH^- ions in the mixture*. This disturbs the original equilibrium.

Finally, we ask ourselves how the original reaction will respond to this disturbance. As we decrease the concentration of OH^- , the **reaction responds by going to the right**, to increase the concentration of OH^- and counteract the disturbance.

- b) To begin, we must recognize that the MgCl_2 is completely dissociated, so we are actually adding Mg^{2+} and Cl^- ions to the equilibrium mixture.

Again, neither Mg^{2+} nor Cl^- appears in the balanced equation, so we ask ourselves whether anything in the equilibrium mixture would react with one of these ions. The answer is yes: OH^- will react with Mg^{2+} , to form insoluble $\text{Mg}(\text{OH})_2$. Therefore, *adding Mg^{2+} is equivalent to decreasing the concentration of OH^- ions in the mixture*. As in part a, **the reaction responds by going to the right**.

- c) To begin, we must recognize that the NH_4NO_3 is completely dissociated, so we are actually adding NH_4^+ and NO_3^- ions to the mixture. In this case, NH_4^+ is a product in the original reaction. Therefore, as we add NH_4^+ ions, **the reaction responds by going to the left**, to reduce the concentration of NH_4^+ and counteract the disturbance.

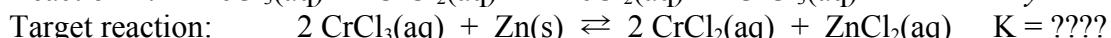
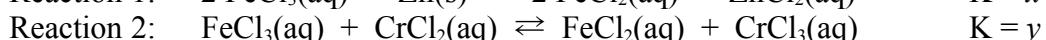
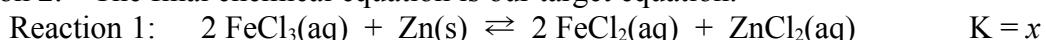
- 20) a) We can produce the chemical equation in part a by multiplying the original chemical equation by $\frac{1}{2}$. (In other words, we are multiplying all of the coefficients in the original equation by $\frac{1}{2}$.) When we multiply a chemical equation by n , the equilibrium constant for the new equation is the original K raised to the n power, so the new equilibrium constant is

$$(6.7 \times 10^{10})^{\frac{1}{2}} = 2.6 \times 10^5$$

- b) We can produce the chemical equation in part b by reversing the original chemical equation and multiplying it by 2. When we reverse a reaction, the new equilibrium constant is the reciprocal of the original one, so the new equilibrium constant is:

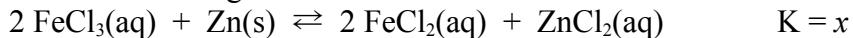
$$\left(\frac{1}{6.7 \times 10^{10}} \right)^2 = 2.2 \times 10^{-22}$$

- 21) Let's begin by labeling the chemical equations. Call the first two equations “reaction 1” and “reaction 2.” The final chemical equation is our target equation.



We need to find a way to combine reactions 1 and 2 so that when we add them, we produce the target reaction. The correct combination is:

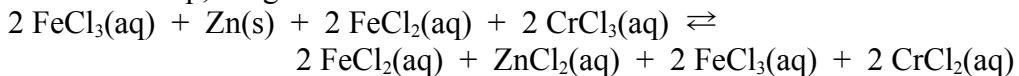
Leave reaction 1 unchanged:



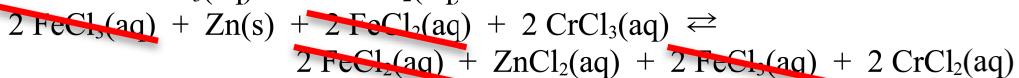
Reverse reaction 2 and multiply it by 2:



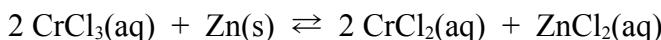
When we add these up, we get:



We can cancel 2 $\text{FeCl}_3(\text{aq})$ and 2 $\text{FeCl}_2(\text{aq})$ from both sides:



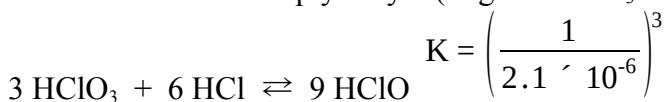
Which leaves us with:



This is our target reaction. Therefore, the equilibrium constant for this reaction is $x \cdot (1/y^2)$, which equals x/y^2 .

22) You must find some way to manipulate the three reactions whose K values you know, so they add up to the “target reaction.” Here is the correct combination:

Reverse reaction #2 and multiply it by 3 (to get 3 HClO_3 on the left side):



Multiply reaction #3 by 2 (to get 2 HClO_4 on the right side):



Reverse reaction #1 and multiply it by 8 (to cancel out all of the HCl and H_2O):



When you add these three equations, you get the target reaction, because you can cancel out 8 HCl, 8 H_2O , and 8 HClO from both sides. Therefore, K for the target reaction is:

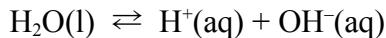
$$\left(\frac{1}{2.1 \cdot 10^{-6}} \right)^3 \cdot (7.9 \cdot 10^{-8})^2 \cdot \left(\frac{1}{6.2 \cdot 10^{-2}} \right)^8 = 3.1 \cdot 10^{12}$$

- 23) a) When we know the concentration of H^+ ions is related to the concentration of OH^- ions by the ion product of water: $[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$. Substituting in the concentration of H^+ , we get:

$$(0.315) \cdot [\text{OH}^-] = 1.0 \times 10^{-14}$$

Solving this equation gives $[\text{OH}^-] = 3.2 \times 10^{-14} \text{ M}$

- b) The hydroxide ions come from the self-ionization of water:



- c) The pH is given by the following formula: $\text{pH} = -\log_{10}[\text{H}^+]$. Therefore:

$$\text{pH} = -\log(0.315) = 0.50$$

When you calculate a pH, report it to two decimal places. We do not cover the significant figure rules for logarithms in Chem 101A.

- 24) a) We can convert the pH back into an H^+ concentration using the equation $[\text{H}^+] = 10^{-\text{pH}}$. Therefore:

$$[\text{H}^+] = 10^{-2.88} = 1.3 \times 10^{-3} \text{ M} \quad (\text{rounded from } 1.3183 \times 10^{-3} \text{ M})$$

When you convert a pH back into an H^+ concentration, report two significant figures. However, if you use this number in further calculations, carry it out to additional places and round your final answer to two sig figs.

- b) To calculate the concentration of OH^- , use the ion product equation:

$$(1.3183 \times 10^{-3}) \cdot [\text{OH}^-] = 1.0 \times 10^{-14}$$

Solving this equation gives $[\text{OH}^-] = 7.6 \times 10^{-12} \text{ M}$.

- c) This is a solution of HCl , which dissociates into equal numbers of H^+ and Cl^- ions. Therefore, the concentration of Cl^- equals the concentration of H^+ : $1.3 \times 10^{-3} \text{ M}$.

- 25) First, we recognize that $\text{Ba}(\text{OH})_2$ dissociates into one Ba^{2+} ion and two OH^- ions. Therefore, the concentration of OH^- in this solution is $2 \times (7.4 \times 10^{-4} \text{ M}) = 1.48 \times 10^{-3} \text{ M}$.

Next, we use the ion product equation to calculate the concentration of H^+ ions in this solution:

$$[\text{H}^+] \cdot (1.48 \times 10^{-3}) = 1.0 \times 10^{-14}$$

Solving this equation gives $[\text{H}^+] = 6.757 \times 10^{-12} \text{ M}$.

Finally, we calculate the pH, using the equation $\text{pH} = -\log_{10}[\text{H}^+]$:

$$\text{pH} = -\log_{10}(6.757 \times 10^{-12}) = 11.17$$

- 26) a) The chemical equation is $\text{HClO(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{ClO}^-(\text{aq})$

$$K_a = \frac{[\text{H}^+][\text{ClO}^-]}{[\text{HClO}]}$$

The K_a expression is

- b) The chemical equation is $\text{H}_2\text{C}_4\text{H}_4\text{O}_4(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HC}_4\text{H}_4\text{O}_4^-(\text{aq})$

$$K_a = \frac{[\text{H}^+][\text{HC}_4\text{H}_4\text{O}_4^-]}{[\text{H}_2\text{C}_4\text{H}_4\text{O}_4]}$$

The K_a expression is

c) The chemical equation is $\text{NH}_4^+(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{NH}_3(\text{aq})$

$$K_a = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]}$$

The K_a expression is

d) The chemical equation is $\text{H}_2\text{PO}_4^-(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$

$$K_a = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

The K_a expression is

27) We can start by setting up an ICE table for the ionization of H_3PO_3 .

	H_3PO_3	\longrightarrow	H^+	+	H_2PO_3^-
Initial M:	0.464		~0		0
Change:	$-x$		$+x$		$+x$
End M:	$0.464 - x$		x		x

All of the equilibrium concentrations appear to be unknown. But we actually know the equilibrium concentration of H^+ , because we are given the pH of the solution!

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-1.11} = 0.0776 \text{ M}$$

So $x = 0.0776$. Substituting this into the expressions in the table gives us:

$$[\text{H}^+] = 0.0776 \text{ M}$$

$$[\text{H}_2\text{PO}_3^-] = 0.0776 \text{ M}$$

$$[\text{H}_3\text{PO}_3] = 0.464 - 0.0776 = 0.3864 \text{ M}$$

$$K_a = \frac{[\text{H}^+][\text{H}_2\text{PO}_3^-]}{[\text{H}_3\text{PO}_3]} = \frac{(0.0776)(0.0776)}{(0.3864)} = 1.6 \times 10^{-2}$$

28) As in problem 12, we start by setting up an ICE table for the dissociation of HCO_2H .

	HCO_2H	\longrightarrow	H^+	+	HCO_2^-
Initial M:	0.27		~0		0
Change:	$-x$		$+x$		$+x$
End M:	$0.27 - x$		x		x

The final concentrations must satisfy the acid ionization equilibrium (the “ K_a reaction”):

$$\text{HCO}_2\text{H}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HCO}_2^-(\text{aq}) \quad K_a = \frac{[\text{H}^+][\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]}$$

Substituting in the expressions from our table and the given value of K_a gives us:

$$\frac{x \cdot x}{0.27 - x} = 1.8 \times 10^{-4}$$

Solving this directly (you'll get a quadratic equation) gives two roots, $x = 0.006882$ and $x = -0.007062$. The negative root is physically meaningless, because it gives negative concentrations of the products. Therefore, the positive root is the correct value.

$$[\text{H}^+] = 0.006882 \text{ M} \quad \text{pH} = -\log_{10}(0.006882) = \mathbf{2.16}$$

If you use the approximation method described in the textbook to do the algebra, you will get $x = 0.00697$, which is within the 5% cutoff (5% of 0.27 is 0.0135) and is therefore an acceptable approximation. Using $[\text{H}^+] = 0.00697 \text{ M}$ gives $\text{pH} = 2.16$, which is the same as the exact solution (the two pH values only differ in the third decimal place and beyond).

29) a) These solutions have the same molarity, so the solution that contains the strong acid will have the higher concentration of H^+ ions. However, a higher concentration of H^+ gives a lower pH, so the solution with the weaker acid has the higher pH. From the table, the K_a of HNO_2 is 4.0×10^{-4} , making it a weak acid, while HCl is a strong acid. Therefore, **0.1 M HNO_2 has the higher pH.**

b) This is similar to part a. HClO ($K_a = 3.5 \times 10^{-8}$) is a weaker acid than HF ($K_a = 7.2 \times 10^{-4}$), so **0.1 M HClO has the higher pH.**

c) HCN is a weak acid, so 0.1 M HCN will be an acidic solution and will have a pH below 7. NaCN is an ionic compound and dissociates completely in water, giving Na^+ and CN^- ions. Na^+ is neither acidic nor basic, but CN^- is a base – it is the conjugate base of HCN . Therefore, the pH of 0.1 M NaCN must be higher than 7. As a result, **0.1 M NaCN has the higher pH.**

30) A conjugate acid-base pair consists of two substances whose formulas differ by just one hydrogen ion; the conjugate acid contains one more hydrogen ion than the conjugate base does. In this question, you are asked for the formulas of the conjugate bases, so the compounds you are given are functioning as acids. To write the formula of the conjugate base, remove one H^+ from the formula of the acid.

- a) Removing H^+ from $\text{HC}_3\text{H}_5\text{O}_3$ gives $\text{C}_3\text{H}_5\text{O}_3^-$.
- b) Removing H^+ from N_2H_5^+ gives N_2H_4 .
- c) Removing H^+ from H_2O gives OH^- .
- d) Removing H^+ from HCO_3^- gives CO_3^{2-} .
- e) Removing H^+ from H_2SO_4 gives HSO_4^- .

31) In this question, you are asked for the formulas of the conjugate acids, so the compounds you are given are functioning as bases. To write the formula of the conjugate acid, add one H^+ to the formula of the base.

- a) Adding H^+ to NH_3 gives NH_4^+ .
- b) Adding H^+ to HSO_3^- gives H_2SO_3 .
- c) Adding H^+ to H_2O gives H_3O^+ .
- d) Adding H^+ to PO_4^{3-} gives HPO_4^{2-} .

- 32) a) HNO_2 is the acid (it loses H^+) and H_2O is the base (it gains H^+).
b) HSO_4^- is the acid (it loses H^+) and H_2PO_4^- is the base (it gains H^+).

33) For any acid-base reaction, the equilibrium will always favor the side with the weaker acid. Therefore, to solve this problem, we must identify the acid on each side, and then check K_a values to see which acid is weaker.

a) On the reactant side, the acid is $\text{HC}_3\text{H}_5\text{O}_3$, which has a K_a of 1.38×10^{-4} . On the product side, the acid is HCN , which has a K_a of 6.2×10^{-10} . The K_a of HCN is the smaller of the two, so HCN is the weaker acid. Therefore, **the equilibrium favors the products**.

b) On the reactant side, the acid is HOCl , while on the product side, the acid is H_2O . Water is a weaker acid than HOCl (the effective K_a of water is 1.0×10^{-14}), so **the equilibrium favors the products**.