

(a)  $Q_c = \frac{[AB]^2}{[A_2][B_2]} = \frac{(6)^2}{(1)(1)} = 36$

↑  
these are numbers of molecules in the picture, rather than molarities, but since ~~there are~~ this is a unitless  $K_{eq}$  ( $\Delta n_{gas} = 0$ ) it won't matter.

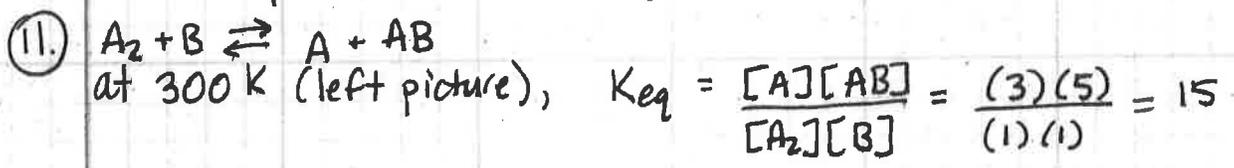
This is not at equilibrium since  $Q_c = 36$  but  $K_c = 1.5$  ( $Q \neq K$ ). since  $Q > K$ , the reaction will have to proceed toward reactants / (to the left) / in reverse direction

(b)  $Q_c = \frac{3^2}{(3)(2)} = \frac{9}{6} = 1.5$

$Q_c = K_c = 1.5$  so this rxn is at equilibrium.

(c)  $Q_c = \frac{2^2}{(3)(3)} = \frac{4}{9} \approx 0.44$

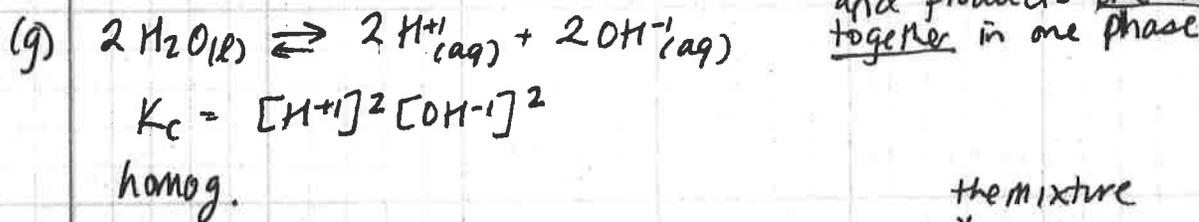
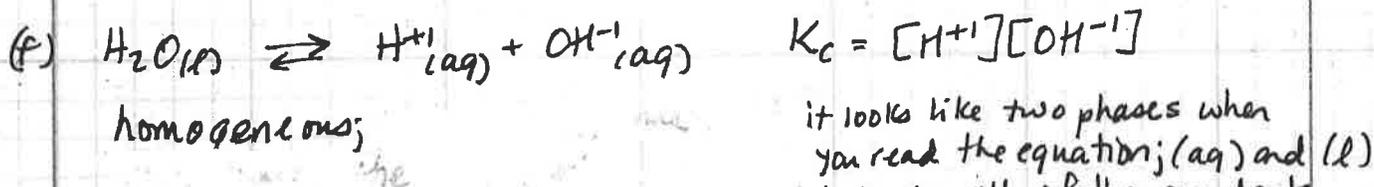
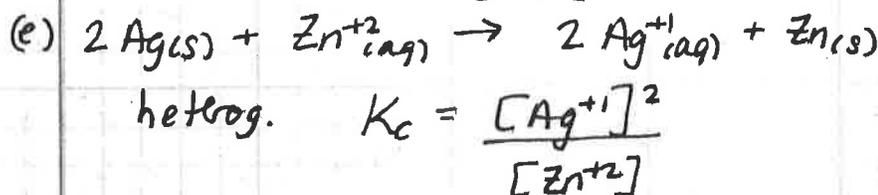
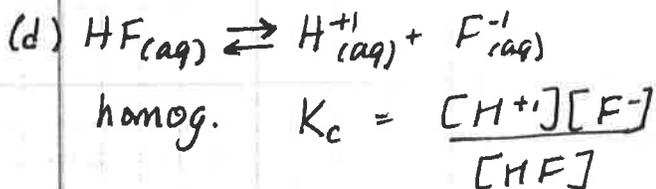
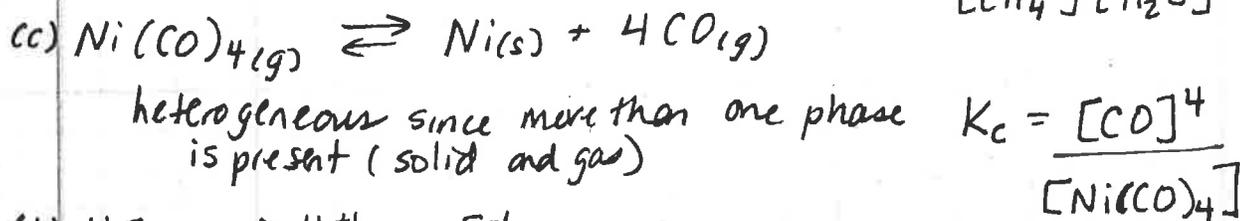
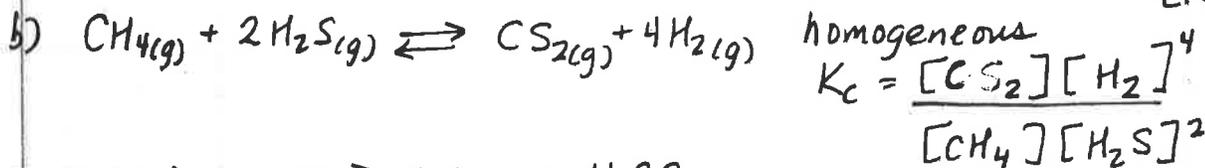
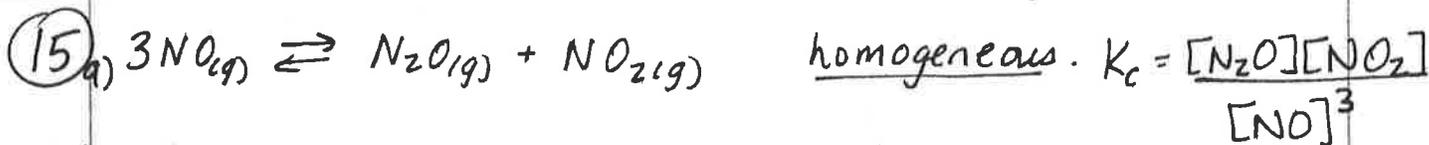
$Q_c < K_c$  so this rxn must proceed toward products / to the right / in the forward direction.



at 500 K (right picture)

$K_{eq} = \frac{[A][AB]}{[A_2][B]} = \frac{(1)(3)}{(3)(3)} = \frac{1}{3} \approx .33..$

$K_{eq} = 15 @ 300 K$   
 $K_{eq} = 0.33 @ 500 K$  } since  $K_{eq}$  decreases as temperature increases, the rxn must be exothermic.



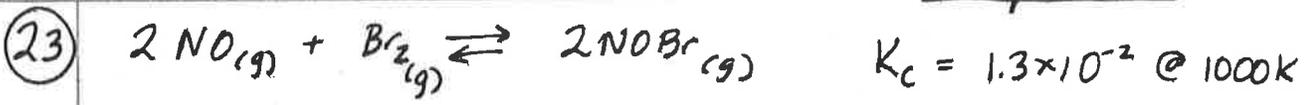
(17) When the rxn reaches equilibrium, will it contain mostly reactants or mostly products?

If  $K_{eq} < 1$  then reactants are favored (equilibrium lies to the left) so there will be more reactants.

if  $K_{eq} > 1$  then products are favored (eqm lies to right) so there will be more products (eqm lies to right).

(a)  $K_c = 1.5 \times 10^{-10}$   
 $1.5 \times 10^{-10} < 1$  so there will be mostly reactants.

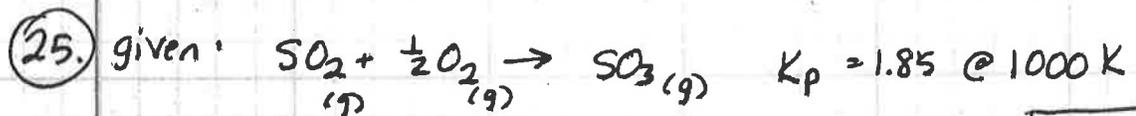
(b)  $K_p = 2.5 \times 10^9$  so mostly products since  $K > 1$



(a) at 1000K, the rxn favors NO and Br<sub>2</sub> (the reactants) (or "equilibrium lies to the left") since  $K_c < 1$   
 (so  $\frac{[\text{NOBr}]^2}{[\text{NO}]^2[\text{Br}_2]} = 1.3 \times 10^{-2}$ )

(b) calculate  $K_c$  for  $2 \text{NOBr} \rightleftharpoons 2 \text{NO} + \text{Br}_2$   
 this is just the original rxn, except reversed. ( $K_c = \frac{[\text{NO}]^2[\text{Br}_2]}{[\text{NOBr}]^2}$ )  
 $K_{\text{reverse}} = \frac{1}{K_{\text{forward}}} = \frac{1}{1.3 \times 10^{-2}} = 76.92 \rightarrow \boxed{77}$

(c) calculate  $K_c$  for  $\text{NOBr} \rightleftharpoons \text{NO} + \frac{1}{2} \text{Br}_2$   
 this is the original rxn except reversed and divided by 2.  
 $K = \left( \frac{1}{1.3 \times 10^{-2}} \right)^{1/2} = 8.7706 \rightarrow \boxed{8.8}$  ( $K_c = \frac{[\text{NO}][\text{Br}_2]^{1/2}}{[\text{NOBr}]}$ )



(a) find  $K_p$  of  $\text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2} \text{O}_2$   $K_p = \frac{1}{1.85} = \boxed{0.541}$

(b) find  $K_p$  of  $2 \text{SO}_2 + \text{O}_2 \rightarrow 2 \text{SO}_3$   $K_p = (1.85)^2 = \boxed{3.42}$

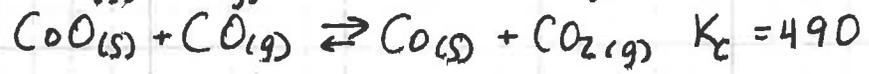
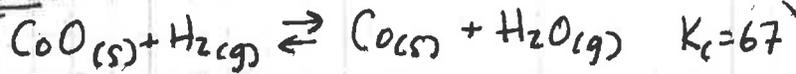
(c) find  $K_c$  for the rxn in (b)

$K_p = K_c (RT)^{\Delta n}$  so  $K_c = K_p (RT)^{-\Delta n}$

$\Delta n$  for the rxn in (b) =  $2 - 3 = -1$   $K_c = (3.4225) (0.0821 \cdot 1000)^{-(-1)}$

$K_c = \boxed{281}$

27. given:



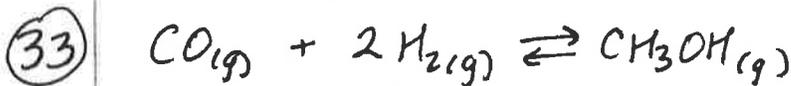
calculate  $K_c$  of  $\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$

leave the first rxn as is:  $\text{CoO} + \text{H}_2 \rightleftharpoons \text{Co} + \text{H}_2\text{O}$   $K_c = 67$

reverse the second rxn:  $\text{Co} + \text{CO}_2 \rightleftharpoons \text{CoO} + \text{CO}$   $K_c = \left( \frac{1}{490} \right)$

The two rxns now add up to our goal rxn,  $\rightarrow \text{H}_2 + \text{CO}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$

so we need to multiply the  $K_c$  values together:  $K_c = 67 \left( \frac{1}{490} \right) = \boxed{0.14}$  .1367  $\downarrow$



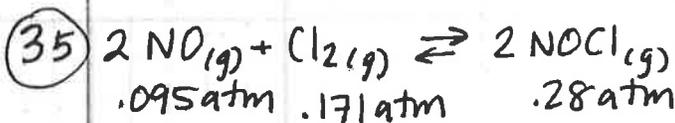
.170 mole      .302 mole      .0406 mole

← these amounts are present at equilibrium in a 2.00 L vessel. calculate  $K_c$

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{(\frac{.0406 \text{ mole}}{2.00L})}{(\frac{.170 \text{ mole}}{2.00L})(\frac{.302 \text{ mole}}{2.00L})^2}$$

$$K_c = \frac{.0203 M}{(0.850 M)(.151 M)^2} = 10.474 M^{-2} \rightarrow \boxed{K_c = 10.5}$$

↑ except that all of the molarities are divided by a "reference molarity" of 1.00 M so we get rid of the units...



.095 atm   .171 atm   .28 atm

← these are the partial pressures @ eqm @ 500.0K. calculate  $K_p$ .

(a)  $K_p = \frac{P_{NOCl}^2}{P_{NO}^2 \cdot P_{Cl_2}} = \frac{(.28 \text{ atm})^2}{(.095 \text{ atm})^2 (.171 \text{ atm})}$

$$K_p = 50.80106 \text{ atm}^{-1} \rightarrow \boxed{K_p = 51}$$

(again... you divide each pressure by a std pressure of 1 atm and get rid of units...

(b) if  $V = 5.00 L$ , calculate  $K_c$  (still at 500.0K)

{ if you really want to use the 5.00 L, you could use it to solve for moles of each gas ( $n = \frac{PV}{RT}$ ) but then you'd have to divide all your moles by 5.00 L to get molarities for  $K_c$ ... so the 5.00 L cancels...

you could do it this way:  $P = \frac{nRT}{V} = \frac{n}{V}RT = MRT$

so  $M = \frac{P}{RT}$       so  $M_{NOCl} = [NOCl] = \frac{.28 \text{ atm}}{(.0821 \frac{L \cdot atm}{mol \cdot K})(500.0K)} = .006821 M$

similarly,  $M_{NO} = [NO] = .002314 M$

$M_{Cl_2} = [Cl_2] = .0041656 M$

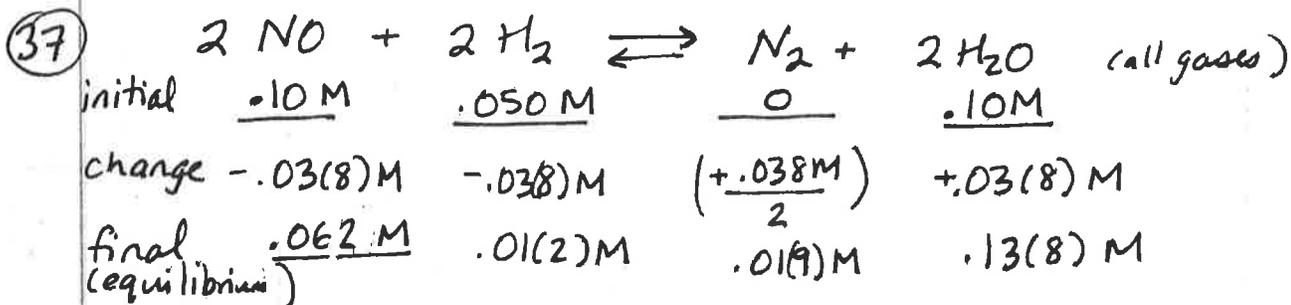
so  $K_c = \frac{[NOCl]^2}{[NO]^2 [Cl_2]} = \frac{(.006821)^2}{(.002314)^2 (.0041656)} = 2085.87 \rightarrow \underline{\underline{K_c = 2100}}$

OR (!!! Do this way !!!)

$K_p = K_c (RT)^{\Delta n}$

so  $K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{50.80106 \text{ atm}^{-1}}{(.0821 \frac{L \cdot atm}{mol \cdot K})(500K)}^{-1}$

$$K_c = 2085.38 \frac{1}{\text{mole}} \rightarrow \boxed{K_c = 2100}$$



(a) The underlined values in the above chart were given.

(The "initial" values were actually given as moles but the total volume was 1.0 L, so I changed them to molarities so they would have same units as the given .062 M value. also we'll need molarity values anyway once we calculate  $K_{eq}$ .)

$.10 \text{ M} - .062 \text{ M} = .03(8) \text{ M}$ , so NO's molarity was reduced by .038 M.  $\text{H}_2$ 's molarity has to be reduced by the same amt (acc. to stoichiometry) and  $\text{H}_2\text{O}$  must increase by the same amt (also acc to stoich.)

$\text{N}_2$  ~~also~~ increases half as much as  $\text{H}_2\text{O}$  increases due to the  $1/2$  mole ratio.

So eqm molarities:

$[\text{NO}] = .062$
$[\text{H}_2] = .012 \rightarrow .01 \text{ M}$
$[\text{N}_2] = .019 \rightarrow .02 \text{ M}$
$[\text{H}_2\text{O}] = .138 \rightarrow .14 \text{ M}$

(b) 
$$K_c = \frac{[\text{N}_2][\text{H}_2\text{O}]^2}{[\text{NO}]^2[\text{H}_2]^2} = \frac{(.019)(.138)^2}{(.062)^2(.012)^2} = 653.68$$

$K_c = 700$

39. Into a 2.000 L vessel at 500 K: .2000 mole CO<sub>2</sub>, .1000 mole H<sub>2</sub>, .1600 mole H<sub>2</sub>O

(a) calculate initial partial pressures:

$$P = \frac{nRT}{V} \quad P_{CO_2} = \frac{(2000 \text{ mole})(.0821 \frac{\text{L}\cdot\text{atm}}{\text{mole}\cdot\text{K}})(500 \text{ K})}{2.000 \text{ L}} = 4.105 \text{ atm}$$

$$P_{H_2} = \frac{(.1000)(.0821)(500)}{2.000} \text{ atm} = 2.0525 \text{ atm} \rightarrow \underline{2 \text{ atm}}$$

$$P_{H_2O} = \frac{(0.1600)(.0821)(500)}{2.000} \text{ atm} = 3.284 \text{ atm} \rightarrow \underline{3 \text{ atm}}$$

4 atm  
(or 4.11 if using 500. K)  
↑

(b) at eqm, P<sub>H<sub>2</sub>O</sub> = 3.51 atm. calculate p<sub>CO<sub>2</sub></sub>, P<sub>H<sub>2</sub></sub>, P<sub>CO</sub> @ eqm.

	$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$				
Initial	<u>4.105 atm</u>	<u>2.0525 atm</u>	0	<u>3.284 atm</u>	underlined values given/found in (a)
Δ	<u>-0.226</u>	<u>-0.226</u>	<u>+0.226</u>	<u>+0.226</u>	
EQM	<u>3.879</u>		<u>.226</u>	<u>3.51 atm</u>	

$$(c) K_p = \frac{P_{CO} \cdot P_{H_2O}}{P_{CO_2} \cdot P_{H_2}} = \frac{(0.226)(3.51)}{(3.879)(1.8265)} = 0.11196 \rightarrow \boxed{0.1 = K_p}$$

$$(d) K_p = K_c(RT)^{\Delta n} \quad K_c = K_p(RT)^{-\Delta n}$$

$$\Delta n_{gas} = 2 - 2 = 0 \quad \text{so } \boxed{K_p = K_c = 0.1}$$

$$\text{so } K_c = K_p(RT)^0$$

40.  $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$

Initial	<u>1.500 atm</u>	<u>1.00 atm</u>	← underlined values were given
Δ	<u>+(.48(8)/2)</u>	<u>-.48(8) atm</u>	
EQM	<u>1.74(4) atm</u>	<u>0.512 atm</u>	

(a)  $P_{N_2O_4} = \boxed{1.74 \text{ atm}}$  at equilibrium

$$(b) K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{(0.512)^2}{(1.744)} = 0.15031 \rightarrow \boxed{0.150 = K_p}$$

$$(c) K_p = K_c(RT)^{\Delta n} \quad K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{.15031}{(.0821)(298)^1} = \boxed{0.00614 = K_c}$$

- 43 (a) how is the reaction quotient ( $Q$ ) different from the equilibrium constant ( $K$ )?

The reaction quotient ( $Q$ ) is the ratio of product concentrations (or pressures) to reactant concentrations (or pressures) for whatever amounts of reactants and products are in the flask at a particular moment (the rxn may or may not be at equilibrium.)

The equilibrium constant ( $K$ ) is the ratio of product conc'n/Pressure to reactant conc'n/pressure when at equilibrium.

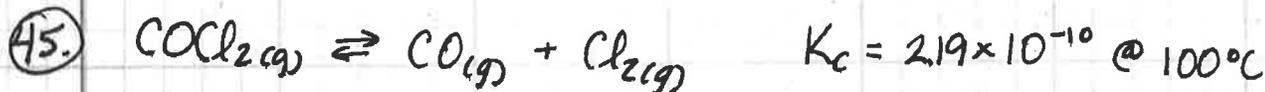
(you must plug in equilibrium pressures or concentrations to evaluate  $K_{eq}$ .)

- (b) If  $Q < K$ , the ratio of products is too low to be at eqm;  
reactants

The rxn must proceed in the forward direction (to the right) to reach eqm.

(if  $Q > K$ , there are too many products per reactants, so reaction must shift left)

- (c) If  $Q = K$ , the reaction is at equilibrium.



(a)  $[\text{COCl}_2] = 2.00 \times 10^{-3} \text{ M}$   
 $[\text{CO}] = 3.3 \times 10^{-6} \text{ M}$   
 $[\text{Cl}_2] = 6.62 \times 10^{-6} \text{ M}$

$$Q_c = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = \frac{(3.3 \times 10^{-6})(6.62 \times 10^{-6})}{(2.00 \times 10^{-3})} = 1.1 \times 10^{-8}$$

(b)

$$Q_c = \frac{(1.1 \times 10^{-9})(2.25 \times 10^{-6})}{(4.50 \times 10^{-2})}$$

$$Q_c = 5.5 \times 10^{-12}$$

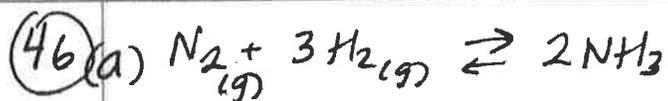
$Q < K$  so must shift right to reach eqm.

$$Q = 1.1 \times 10^{-8}, K = 2.19 \times 10^{-10}$$

$Q > K$  so it is not at eqm.  
must shift left to reach eqm.

(c)  $Q_c = \frac{(1.48 \times 10^{-6} \text{ M})(1.48 \times 10^{-6} \text{ M})}{(0.0100 \text{ M})} = 2.19 \times 10^{-10}$

$Q = K$  so the rxn is at eqm!

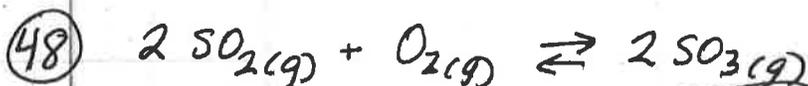


$$K_p = 4.51 \times 10^{-5} @ 450^\circ C$$

which way must it shift if  $P_{NH_3} = 98 \text{ atm}$ ,  $P_{N_2} = 45 \text{ atm}$ ,  
 $P_{H_2} = 55 \text{ atm}$ ?

$$Q_p = \frac{P_{NH_3}^2}{P_{N_2} \cdot P_{H_2}^3} = \frac{(98)^2}{(45)(55)^3} = \underline{1.3 \times 10^{-3}}$$

$Q > K$  so there must shift left  
(proceed toward reactants)  
to reach eqm.



0.135 atm    0.455 atm

?? atm  
at eqm?

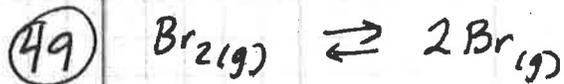
$$K_p = 0.345 @ 900K$$

$$K_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 \cdot P_{O_2}}$$

$$P_{SO_3}^2 = K_p \cdot P_{SO_2}^2 \cdot P_{O_2}$$

$$P_{SO_3}^2 = (0.345)(0.135)^2(0.455) = 0.002861$$

$$P_{SO_3} = (0.002861)^{1/2} = \boxed{0.0535 \text{ atm}}$$



$$K_c = .00104 \text{ at } 1285^\circ C$$

0.245 g  
in 0.200 L  
vessel  
(at eqm)

↑  
find mass in  
vessel at eqm.

$$K_c = \frac{[Br]^2}{[Br_2]}$$

$$[Br] = (K_c [Br_2])^{1/2}$$

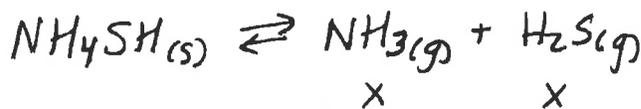
$$[Br_2] = \frac{(0.245 \text{ g}) \left( \frac{1 \text{ mole}}{159.808 \text{ g}} \right)}{0.200 \text{ L}} = 0.0076654 \text{ M}$$

$$\text{so, } [Br] = ((0.00104)(0.0076654))^{1/2}$$

$$[Br] = 0.0028235 \text{ M}$$

$$(0.0028235 \frac{\text{mol}}{\text{L}})(0.200 \text{ L}) \left( \frac{79.904 \text{ g}}{\text{mole}} \right) = \boxed{0.0451 \text{ grams of Br}}$$

54.



$$K_c = 1.2 \times 10^{-4} \text{ at } 218^\circ\text{C}$$

these have to be the same at equilibrium (or at any time) since the flask started out with only solid  $\text{NH}_4\text{SH}$ , and  $\text{NH}_3$  and  $\text{H}_2\text{S}$  are 1:1 by stoichiometry.

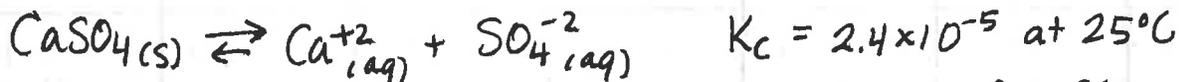
$$K_c = [\text{NH}_3][\text{H}_2\text{S}]$$

$$1.2 \times 10^{-4} = x^2$$

$$x = (1.2 \times 10^{-4})^{1/2} = 0.01095$$

$$[\text{NH}_3] = [\text{H}_2\text{S}] = 0.011 \text{ M}$$

55.



(a) find  $[\text{Ca}^{2+}]$  and  $[\text{SO}_4^{2-}]$  in a saturated solution of  $\text{CaSO}_4$

$$K_c = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (x)(x) = x^2$$

$$2.4 \times 10^{-5} = x^2$$

$$x = (2.4 \times 10^{-5})^{1/2} = 0.00489898$$

$$[\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = 0.0049 \text{ M}$$

(The calcium and sulfate ions must have same conc'n acc to stoichiometry, since they both started at zero...)

(b) minimum mass of  $\text{CaSO}_4$  needed to form a saturated solution with volume of 1.4 L

$$\left( \frac{0.004899 \text{ moles Ca}^{2+}}{\text{L}} \right) \left( \frac{1 \text{ mole CaSO}_4}{1 \text{ mole Ca}^{2+}} \right) (1.4 \text{ L}) \left( \frac{136.1406 \text{ g}}{\text{mole}} \right) = 0.93 \text{ g CaSO}_4$$



How will eqm mixture be affected if you:

(a) Add  $\text{O}_2(g)$ .

This will make the rxn shift right in order to restore the value of  $K_{eq}$ ; more  $\text{SO}_3$  will be produced, and the  $\text{SO}_2$  concentration will decrease

(b) heat up the mixture. (this would increase the temperature...)

This rxn is exothermic, so adding heat will cause the  $K_{eq}$  to decrease, so the rxn will shift left;  
 $[\text{SO}_2]$  and  $[\text{O}_2]$  will increase,  $[\text{SO}_3]$  will decrease.

(c) The volume of the rxn vessel is doubled.

This would cause the pressure of all 3 gases to decrease by a factor of 2, since pressure is inversely prop. to volume. So the rxn will shift left, toward the side with more gas molecules (3 vs 2). so more  $\text{SO}_2$  and  $\text{O}_2$  will be produced, and  $\text{SO}_3$  will be used up/ decrease.

$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$
 at eqm. if all molarities decrease by a factor of 2, the numerator will decrease by a factor of  $2^2=4$  and denm. will decrease by factor of  $2^3=8$ . So the value for  $Q$  will increase by a factor of 2, so that  $Q > K$  and rxn must shift left!

(d) a catalyst is added:  
no effect.

(The fwd and reverse rxns will increase by the same factor, but the  $K_{eq}$  will remain the same. It is still at eqm)

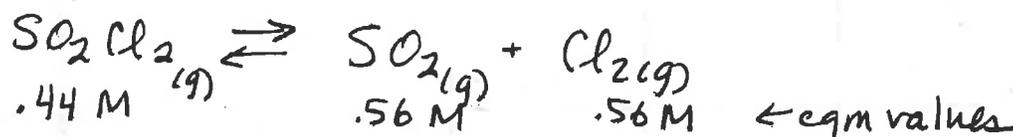
(e) Increase Total pressure by adding a noble gas: no effect.  
 The Noble gas is not involved in  $K_{eq}$ , and does not change any partial pressures (or molarities) of  $\text{SO}_3$ ,  $\text{SO}_2$ , or  $\text{O}_2$  (and does not affect temperature)

(f)  $\text{SO}_3$  is removed: The rxn will need to shift right to make more  $\text{SO}_3$ , which will cause  $\text{SO}_2$  and  $\text{O}_2$  to decrease.  
 (when  $\text{SO}_3$  is removed,  $Q$  will decrease to below  $K$ )

72 (a) 2.00 mole of  $\text{SO}_2\text{Cl}_2$  in a 2.00 L flask at 303 K.  
 56% of  $\text{SO}_2\text{Cl}_2$  decomposes to  $\text{SO}_2$  and  $\text{Cl}_2$ .  
 Calculate  $K_c$ !  $[\text{SO}_2\text{Cl}_2] = \frac{2.00 \text{ mole}}{2.00 \text{ L}} = 1.00 \text{ M}$  at beginning.

$$[\text{SO}_2\text{Cl}_2]_{\text{eqm}} = (1.00 \text{ M}) - (1.00 \text{ M})(0.56) = 0.44 \text{ M}$$

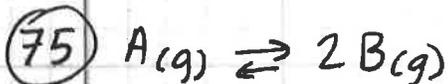
$$\left\{ \begin{aligned} [\text{SO}_2] &= [\text{Cl}_2] = 0.56(1.00 \text{ M}) = 0.56 \text{ M} \end{aligned} \right.$$



$$K_c = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]} = \frac{(0.56)(0.56)}{(0.44)} = 0.71273 \rightarrow \boxed{0.71}$$

or you could do a table:

	$\text{SO}_2\text{Cl}_2$	$\rightleftharpoons$	$\text{SO}_2$	$+$	$\text{Cl}_2$
Initial	1.00		0		0
$\Delta$	<u>-0.56</u>		<u>+0.56</u>		<u>+0.56</u>
EQM	0.44		0.56		0.56



Initial	<u>0.75</u>	0
$\Delta$	-0.39	+2(0.39)
EQM	<u>0.36</u>	0.78

↑  
 these are all partial pressures in atm.

← given pressures (in atm) are underlined

$$P_{\text{TOTAL}} \text{ at eqm} = P_A + P_B$$

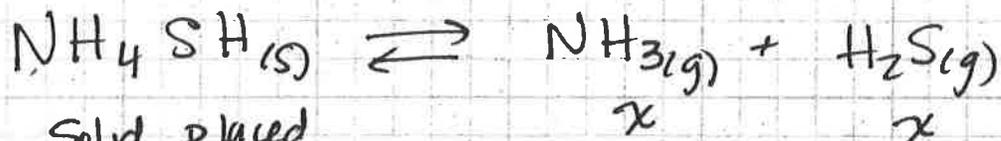
$$P_{\text{TOTAL}} = 0.36 \text{ atm} + 0.78 \text{ atm}$$

(a)  $\boxed{P_{\text{TOTAL}} = 1.14 \text{ atm}}$

(b)  $K_p = \frac{(P_B)^2}{(P_A)} = \frac{(0.78)^2}{(0.36)} = 1.69 \rightarrow \boxed{1.7 = K_p}$  (b)

## Chapter 15

(79)



Solid placed  
into evacuated  
flask @ 24°C

$P_{\text{TOTAL}} @ \text{EQM} = 0.614 \text{ atm}$   
Calculate  $K_p$ !

$$P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = x$$

$$\text{Total pressure} = P_{\text{NH}_3} + P_{\text{H}_2\text{S}} = x + x = 2x$$

$$2x = 0.614 \text{ atm}$$

$$x = 0.307 \text{ atm}$$

$$K_p = P_{\text{NH}_3} \cdot P_{\text{H}_2\text{S}} = (0.307)(0.307) = 0.0942$$

$$K_p = 0.0942$$