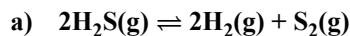


Chapter 5

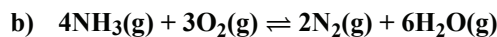
Chemical Equilibrium

1. What are the units of K_p and K_c for each of the following:



$$K_p = \frac{P_{\text{H}_2}^2 P_{\text{S}_2}}{P_{\text{H}_2\text{S}}^2} = \frac{\text{atm}^2 \times \text{atm}}{\text{atm}^2} = \text{atm}$$

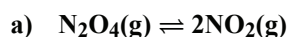
$$K_c = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{\text{M}^2 \times \text{M}}{\text{M}^2} = \text{M}$$



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

$$K_c = \frac{[\text{N}_2]^2 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^3} = \frac{\text{M}^2 \times \text{M}^6}{\text{M}^4 \times \text{M}^3} = \text{M}$$

3. Determine K_c values for the following at 298 K:



$$K_p = 0.15 \text{ atm}$$

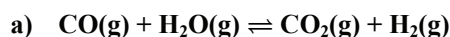
$$K_c = K_p \times (\text{RT})^{-\Delta n_g} \quad \& \quad \Delta n_g = 2 - 1 = 1, \text{ so } K_c = 0.15 \text{ atm} \times \frac{\text{K} \cdot \text{mol}}{0.0821 \text{ L} \cdot \text{atm}} \times \frac{1}{298 \text{ K}} = 0.0061 \text{ M}$$



$$K_p = 0.86 \text{ atm}^{-1}$$

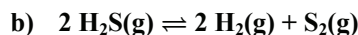
$$\Delta n_g = -1, \text{ so } K_c = 0.86 \text{ atm}^{-1} \times \frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K} = 21 \text{ M}^{-1}$$

5. Determine the value of K_p for each of the following: Use Eq. 5.2, $K_c = K_p(\text{RT})^{\Delta n_g}$



$$K_c = 23.2 \text{ at } 600 \text{ K}$$

$$\Delta n_g = 0 \text{ for the reaction, so } K_p = K_c = 23.2$$



$$K_c = 2.3 \times 10^{-4} \text{ M at } 1405 \text{ K}$$

$$\Delta n_g = 1, \text{ so } K_p = (2.3 \times 10^{-4} \frac{\text{mol}}{\text{L}}) (0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 1450 \text{ K})^1 = 2.7 \times 10^{-2} \text{ atm}$$

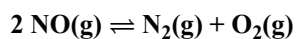
7. a) Determine K for: $\text{HI}(\text{g}) \rightleftharpoons \frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{I}_2(\text{s})$ given $\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightleftharpoons 2 \text{HI}(\text{g}) \quad K = 8.6$

We are asked to find the value of K for a reaction given the value for the reaction that is $\frac{1}{2}$ of the reverse of the original reaction. Consequently, $K_2 = (K_1)^{-0.5} = 8.6^{-0.5} = 0.34$

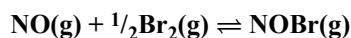
b) Determine K_c for: $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$ given $\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) \quad K_c = 3.61 \text{ M}^{-1/2}$

This reaction is simply twice the original reaction: $K_2 = (K_1)^2 = 3.61^2 = 13.0 \text{ M}$

9. Given the following:



$$K_1 = 2.4 \times 10^{30}$$



$$K_2 = 1.4$$

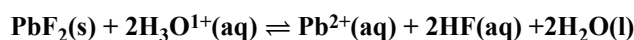
Determine K for $\frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) + \frac{1}{2} \text{Br}_2(\text{g}) \rightleftharpoons \text{NOBr}(\text{g})$

$$\frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{NO}(\text{g}) \quad K_1^{-1/2} = (2.4 \times 10^{30})^{-1/2} = 6.5 \times 10^{16}$$



NO(g) cancels, giving net equation. By rule 3, $K = (K_1^{-1/2}) \times K_2 = 9.0 \times 10^{-16}$

11. Lead fluoride dissolves in strong acid by the following reaction:

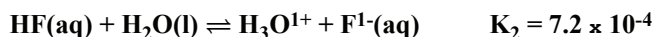
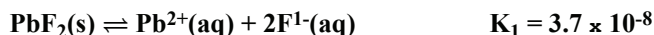


a) What is the equilibrium constant expression for the reaction?

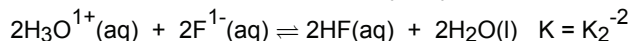
$$K = \frac{[\text{Pb}^{2+}][\text{HF}]^2}{[\text{PbF}_2][\text{H}_3\text{O}^{1+}]^2}$$

Chemical Equilibrium

- b) Use the following to determine the value of the equilibrium constant of the above reaction:



Reverse the second reaction and multiply it by two



Addition of the above equation and the first equation yields the reaction of interest.

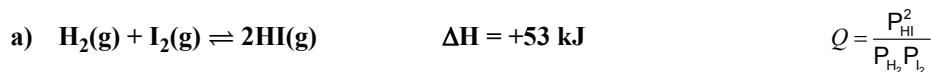
Therefore, the equilibrium constant is $K = \frac{K_1}{K_2^2} = \frac{3.7 \times 10^{-8}}{(7.2 \times 10^{-4})^2} = 7.1 \times 10^{-2}$

13. Equal numbers of moles of Cl_2 and NO are placed in a vessel at some temperature where they reach the following equilibrium: $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{ClNO}(\text{g})$. Indicate whether each of the following statements about the resulting equilibrium mixture is true, false, or depends upon the value of the equilibrium constant.

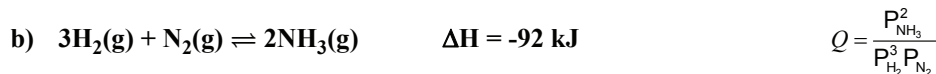
	$2\text{NO}(\text{g})$	+	$\text{Cl}_2(\text{g})$	\rightleftharpoons	$2\text{ClNO}(\text{g})$
Initial	a		a		0
Δ	- 2x		- x		+ 2x
Equilibrium	a - 2x		a - x		2x

- a) $[\text{NO}] > [\text{ClNO}]$ $(a - 2x) > (2x)$ is true only if x is small, so it depends upon K
- b) $[\text{Cl}_2] < [\text{NO}]$ $(a-x) < (a-2x)$ cannot be true. It is always false.
- c) $[\text{Cl}_2] > [\text{ClNO}]$ $(a-x) > 2x$ is true only if x is small Thus, this statement depends upon the value of K.

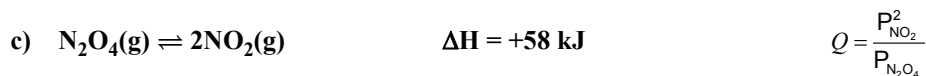
15. What effect (increase, decrease, or no effect) does increasing the volume of the following equilibrium mixtures at constant temperature have on Q ? What effect does each have on K ?



Increasing the volume decreases the partial pressures, but, since $\Delta n_g = 0$, the effect is the same on the numerator and denominator, so Q is unchanged. Pressure changes have no effect on K.

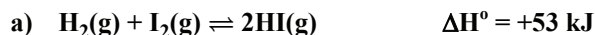


Increasing the volume of the reaction decreases all of the partial pressures. However, the denominator will decrease faster than the numerator because of the difference in exponents. Consequently, Q increases. Again, changing the pressure has no effect on K.



Q decreases because the numerator decreases faster than the denominator because of the exponent difference. Changes in volume do not affect K.

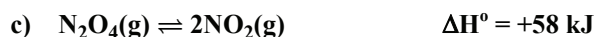
17. Does increasing the volume of each of the equilibria in Exercise 15 increase the number of moles of reactant, product, or neither?



$\Delta n_g = 0$, so increasing the volume has no effect on the number of moles of product or reactants.



$\Delta n_g < 0$, so increasing the volume increases Q (Exercise 15b), and $Q > K$. Consequently, the net reaction will shift to the left and the number of moles of reactant increases.



$\Delta n_g > 0$, so increasing the volume decreases Q (Exercise 15c), and $Q < K$. Consequently, the reaction shifts to the right, and the number of moles of product increases.

19. Consider the equilibrium, $\text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{NH}_4\text{HS}(\text{s})$, $\Delta\text{H}^\circ < 0$. Which of the following would increase the number of moles of ammonia in the equilibrium mixture?

a) **increasing the temperature:**

Reaction is exothermic ($\Delta\text{H}^\circ < 0$), so increasing temperature pushes reaction to right, increasing the number of moles of NH_3 .

b) **increasing the volume of the container:**

Increasing the volume decreases all concentrations, which increases Q . $Q > K$, so the equilibrium shifts to the left, which increases the number of moles of ammonia.

c) **adding H_2S gas:**

Adding more reactant forces the K_c equilibrium to the right decreasing the number of moles of ammonia.

d) **adding more NH_4HS solid:**

Adding a solid does not affect Q , so the equilibrium does not shift.

21. Consider the following: $\text{P}_4(\text{s}) + 6\text{Cl}_2(\text{g}) \rightleftharpoons 4\text{PCl}_3(\text{l})$ $\Delta\text{H} < 0$. What happens to the mass of phosphorus in each of the following:

a) **the volume is increased**

An increase in volume favors the side with the greater number of moles of gas, so the volume increase produces $\text{Cl}_2(\text{g})$. Thus, the mass of P_4 also increases.

b) **chlorine is removed**

The reaction makes Cl_2 to counteract its removal. The amount of P_4 also increases.

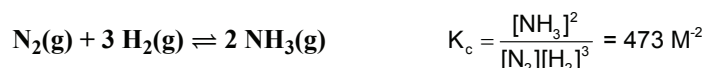
c) **phosphorus trichloride is added**

PCl_3 is a pure liquid, so it has no effect.

d) **the mixture is cooled**

The reaction is exothermic, so heat is a product. The mixture reacts so as to produce heat to counteract the cooling. Consequently, P_4 is consumed.

23. What is the concentration of ammonia in an equilibrium mixture that is 0.015 M H_2 and 0.250 M N_2 ?



Solve the equilibrium expression for $[\text{NH}_3]$: $K_c[\text{N}_2][\text{H}_2]^3 = [\text{NH}_3]^2$

Substitute given values $\sqrt{K_c[\text{N}_2][\text{H}_2]^3} = [\text{NH}_3] = \sqrt{(473)(0.250)(0.015)^3} = 0.020 \text{ M}$

25. What is the partial pressure of H_2 if the equilibrium partial pressures of I_2 and HI are 485 torr and 1293 torr, respectively? $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ $K = 12.0$

The equilibrium constant expression is $K = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})}$

Solve the expression for P_{H_2} : $(P_{\text{H}_2}) = \frac{(P_{\text{HI}})^2}{K(P_{\text{I}_2})} = \frac{(1293 \text{ torr})^2}{(12)(485 \text{ torr})} = 287 \text{ torr}$

Note, torr can be used instead of atmosphere because $\Delta n_g = 0$, so the 760 torr/atm factor cancels in the K_p expression.

Chemical Equilibrium

27. A mixture of 1.00 mol of NH_3 and 0.400 mol of N_2 produces 0.780 mol of NH_3 at equilibrium in a 5.00-L container. The reaction is $2 \text{NH}_3(\text{g}) \rightleftharpoons 3 \text{H}_2(\text{g}) + \text{N}_2(\text{g})$

a) What are the equilibrium concentrations of the gases?

	$2 \text{NH}_3(\text{g})$	\rightleftharpoons	$3 \text{H}_2(\text{g})$	$+$	$\text{N}_2(\text{g})$
Initial	0.200		0		0.080 M
Δ	-0.044		0.066		0.022 M
Final	0.156		0.066		0.102 M

The Δ line was determined as follows: $\Delta[\text{NH}_3] = \text{Final} - \text{initial} = 0.156 - 0.200 = -0.044 \text{ M}$

$$\Delta[\text{H}_2] = \frac{0.044 \text{ mol NH}_3(\text{g})}{\text{L}} \times \frac{3 \text{ mol H}_2(\text{g})}{2 \text{ mol NH}_3(\text{g})} = 0.066 \text{ M H}_2(\text{g})$$

$$\Delta[\text{N}_2] = \frac{0.044 \text{ mol NH}_3(\text{g})}{\text{L}} \times \frac{1 \text{ mol N}_2(\text{g})}{2 \text{ mol NH}_3(\text{g})} = 0.022 \text{ M N}_2(\text{g})$$

b) What is the value of K_c for the reaction shown above?

$$K_c = \frac{[\text{H}_2(\text{g})]^3 [\text{N}_2]}{[\text{NH}_3]^2} = \frac{(0.066)^3 (0.102)}{(0.156)^2} = 1.2 \times 10^{-3} \text{ M}^2$$

29. Phosgene, a toxic gas used in the synthesis of many organic compounds, decomposes according to the reaction: $\text{COCl}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$. Phosgene is heated in a flask. At a certain temperature, the equilibrium mixture is found to contain 0.050 M CO, 0.050 M Cl_2 , and 0.50 M COCl_2 . What is the value of K_c at this temperature?

$$K_c = \frac{[\text{CO}(\text{g})][\text{Cl}_2(\text{g})]}{[\text{COCl}_2(\text{g})]} = \frac{(0.050\text{M})(0.050\text{M})}{0.50\text{M}} = 5.0 \times 10^{-3} \text{ M}$$

31. A sealed container is filled with 1.40 atm of PCl_5 and heated until the PCl_5 decomposes. What is the equilibrium constant for the following reaction at the temperature of the experiment if the total pressure inside the container is 2.60 atm at equilibrium? $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

Initial condition are given, so create the reaction table.

	$\text{PCl}_5(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g})$	$+$	$\text{Cl}_2(\text{g})$
Initial	1.40		0		0 atm
Δ	-x		+x		+x atm
Final	(1.40-x)		x		x atm

Evaluate the total pressure in terms of x: $P_{\text{TOTAL}} = P_{\text{PCl}_5} + P_{\text{PCl}_3} + P_{\text{Cl}_2} = 2.60 \text{ atm} = (1.40 - x) + x + x \text{ atm}$

Solve for x: $2.60 = 1.40 + x \rightarrow x = 1.20 \text{ atm}$. Thus, $P_{\text{PCl}_5} = 1.40 - x = 0.20 \text{ atm}$; $P_{\text{PCl}_3} = P_{\text{Cl}_2} = x = 1.20 \text{ atm}$

Write the expression for K and substitute the partial pressures: $K = \frac{(P_{\text{PCl}_3})(P_{\text{Cl}_2})}{(P_{\text{PCl}_5})} = \frac{(1.20)(1.20)}{0.20} = 7.2$

33. At some temperature, 0.400 mol NO, 0.300 mol Cl_2 and 0.700 mol CINO are introduced into a 20.0-L flask and allowed to react. What is the value of K_c for the following reaction at this temperature if the equilibrium mixture contained 0.900 mol CINO? $2 \text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{CINO}(\text{g})$

First, convert all moles to molarity by dividing each by the 20.0 L volume. Next, determine $\Delta[\text{CINO}]$ as the final concentration minus the initial concentration: $\Delta[\text{CINO}] = \text{final} - \text{initial} = 0.0450 - 0.0350 = +0.0100 \text{ M}$

then determine the other Δ 's in the reaction table base on $\Delta[\text{CINO}]$.

$$\Delta[\text{NO}] = \frac{0.0100 \text{ M CINO}(\text{g})}{\text{L}} \times \frac{2 \text{ mol NO}(\text{g})}{2 \text{ mol CINO}(\text{g})} = 0.0100 \text{ M NO}(\text{g})$$

$$\Delta[\text{Cl}_2] = \frac{0.0100 \text{ M CINO}(\text{g})}{\text{L}} \times \frac{1 \text{ mol Cl}_2(\text{g})}{2 \text{ mol CINO}(\text{g})} = 0.0100 \text{ M Cl}_2(\text{g})$$

Construct the reaction table.

	2 NO(g)	+	Cl ₂ (g)	⇌	2 ClNO(g)
Initial	0.0200		0.0150		0.0350 M
Δ	-0.0100		-0.0050		+0.0100 M
Final	0.0100		0.0100		0.0450 M

Use the equilibrium concentrations to calculate K:
$$K_c = \frac{[\text{ClNO}]^2}{[\text{NO}]^2[\text{Cl}_2]} = \frac{(0.0450)^2}{(0.0100)^2(0.0100)} = 2.03 \times 10^3 \text{ M}^{-1}$$

35. What is the value of K_c for the reaction $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$ at a temperature where 0.600 mol/L of SO_3 is 24.0% decomposed?

24.0% of 0.600 mole is 0.144 mol SO_3 decomposes. Next determine how much SO_2 and O_2 form.

$$0.144 \text{ mol SO}_3 \times \frac{2 \text{ mol SO}_2}{2 \text{ mol SO}_3} = 0.144 \text{ mol SO}_2 \quad \& \quad 0.144 \text{ mol SO}_3 \times \frac{1 \text{ mol O}_2}{2 \text{ mol SO}_3} = 0.072 \text{ mol O}_2$$

The reaction table is

	2 SO ₃ (g)	⇌	2 SO ₂ (g)	+	O ₂ (g)
Initial	0.60		0		0
Δ	-0.144		+0.144		+0.072
Equilibrium	0.456		0.144		0.072

$$K_c = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = \frac{[0.144]^2[0.072]}{[0.456]^2} = 7.18 \times 10^{-3} \text{ M}$$

37. At 2000 °C, water decomposes into hydrogen and oxygen. When 3.00 mol H_2O is heated in a sealed, 5.00-L container to 2000 °C, 2.00% of the water decomposes.

a) What is value of K_c for $2\text{H}_2\text{O}(g) \rightleftharpoons 2\text{H}_2(g) + \text{O}_2(g)$ at 2000 °C?

$(0.0200)(3.00) = 0.0600$ mol H_2O decomposes. Use stoichiometry to determine other Δ line entries

$$0.0600 \text{ mol H}_2\text{O} \times \frac{2 \text{ mol H}_2}{2 \text{ mol H}_2\text{O}} = 0.0600 \text{ mol H}_2 \quad \& \quad 0.0600 \text{ mol H}_2\text{O} \times \frac{1 \text{ mol O}_2}{2 \text{ mol H}_2\text{O}} = 0.0300 \text{ mol O}_2$$

	2H ₂ O(g)	⇌	2H ₂ (g)	+	O ₂ (g)	
Initial	3.00		0		0	mol
Δ	-0.06		+0.0600		+0.0300	mol
Equilibrium	2.94		0.0600		0.0300	mol

Divide the equilibrium moles by 5.00 L to obtain concentrations and place into K_c expression

$$K_c = \frac{[\text{H}_2]^2[\text{O}_2]}{[\text{H}_2\text{O}]^2} = \frac{[0.0120]^2[0.00600]}{[0.588]^2} = 2.50 \times 10^{-6} \text{ M}$$

b) What is the value of K_p at this temperature?

$$K_p = K_c(RT)^{\Delta n_g} = 2.50 \times 10^{-6} \left[(0.0821) \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} (2273\text{K}) \right]^1 = 4.66 \times 10^{-4} \text{ atm}$$

c) What is the standard free energy of formation of $\text{H}_2\text{O}(g)$ at 2000 °C?

K is numerically equal to K_p but is unitless, so

$$\Delta G^\circ = -RT \ln K = -(0.008314 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(2273)(\ln 4.66 \times 10^{-4}) = 1.45 \times 10^2 \text{ kJ}$$

for the above reaction. However, the formation reaction is $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(g)$, which is obtained by reversing the above reaction and multiplying through by $\frac{1}{2}$. Therefore, $\Delta G_f^\circ = -\frac{1}{2}\Delta G^\circ = -\frac{1}{2}(1.45 \times 10^2 \text{ kJ}) = -72.5 \text{ kJ}$.

Chemical Equilibrium

39. For the reaction: $2 \text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$, $K_c = 0.0160$ at 520°C . Calculate the concentration of all of the gases at equilibrium in a 6.00-L container starting with the following:

a) **0.400 mol HI**

Setup the reaction table in moles to avoid rounding errors and leading zeros.

	$2 \text{HI}(\text{g})$	\rightleftharpoons	$\text{H}_2(\text{g})$	$+$	$\text{I}_2(\text{g})$
Initial	0.400		0		0
Δ	$-2x$		$+x$		$+x$
Equilibrium	$0.400 - 2x$		x		x

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{\left(\frac{x}{6.00}\right)^2}{\left(\frac{0.400-2x}{6.00}\right)^2} = \frac{x^2(6.00)^{-2}}{(0.400-2x)^2(6.00)^{-2}} = \frac{x^2}{(0.400-2x)^2} = 0.0160$$

The volumes cancel, so we can do the problem in moles. This is always the case in reactions in which $\Delta n_g = 0$.

Take the square root of both sides: $\frac{x}{0.400 - 2x} = \sqrt{0.0160} = 0.1265$

Multiply both sides by the denominator and solve for x: $x = 0.0506 - 0.253x$ or $x = \frac{0.0506}{1.253} = 0.0404 \text{ mol}$

The question asks for concentrations, so we now convert.

$$[\text{H}_2] = [\text{I}_2] = \frac{0.0404 \text{ mol}}{6.00 \text{ L}} = 6.73 \times 10^{-3} \text{ M}; [\text{HI}] = \frac{(0.400 - 0.0808) \text{ mol}}{6.00 \text{ L}} = 0.0532 \text{ M}$$

b) **0.200 mol H₂ and 0.200 mol I₂**

As in Part A, we do the problem in moles to avoid rounding errors and preceding zeros.

	$2\text{HI}(\text{g})$	\rightleftharpoons	$\text{H}_2(\text{g})$	$+$	$\text{I}_2(\text{g})$
Initial	0		0.200		0.200 M
Δ	$+2x$		$-x$		$-x$
Equilibrium	$+2x$		$0.200 - x$		$0.200 - x$

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = 0.0160 = \frac{(0.200-x)^2}{(2x)^2} \rightarrow \sqrt{0.0160} = \sqrt{\frac{(0.200-x)^2}{(2x)^2}} = 0.126 = \frac{0.200-x}{2x}; \quad x = 0.160 \text{ mol}$$

$$[\text{H}_2] = [\text{I}_2] = \frac{(0.200-0.160) \text{ mol}}{6.00 \text{ L}} = 6.7 \times 10^{-3} \text{ M}; [\text{HI}] = \frac{2(0.160) \text{ mol}}{6.00 \text{ L}} = 0.0532 \text{ M}$$

Note that the answers to Parts A and B are identical, which shows that the same equilibrium is obtained regardless of the direction from which it was reached.

c) **0.200 mol H₂, 0.200 mol I₂, and 0.400 mol HI**

	$2\text{HI}(\text{g})$	\rightleftharpoons	$\text{H}_2(\text{g})$	$+$	$\text{I}_2(\text{g})$
Initial	0.400		0.200		0.200
Δ	$+2x$		$-x$		$-x$
Equilibrium	$0.400 + 2x$		$0.200 - x$		$0.200 - x$

$Q = 0.250 > K$, so rxn goes to the left.

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = 0.0160 = \frac{(0.200-x)^2}{(0.400+2x)^2} \quad \sqrt{0.0160} = \sqrt{\frac{(0.200-x)^2}{(0.400+2x)^2}} = 0.126 = \frac{0.200-x}{0.400+2x}$$

$$0.0506 + 0.253x = 0.200 - x \quad x = \frac{0.149}{1.253} = 0.119 \text{ M}$$

$$[\text{H}_2] = [\text{I}_2] = \frac{(0.200-0.119) \text{ mol}}{6.00 \text{ L}} = 0.0135 \text{ M}; [\text{HI}] = \frac{(0.400 + 0.238) \text{ mol}}{6.00 \text{ L}} = 0.106 \text{ M}$$

d) 0.200 mol H₂ and 0.300 mol I₂

	2HI(g)	⇌	H ₂ (g)	+	I ₂ (g)
Initial	0		0.200		0.300
Δ	+2x		- x		- x
Equilibrium	2x		0.200 - x		0.300 - x

$$\frac{(0.200-x)(0.300-x)}{(2x)^2} = \frac{0.0600 - 0.500x + x^2}{4x^2} = 0.0160$$

Both sides are not perfect squares, so we must use the quadratic formula. Multiply both sides by the denominator.

$$0.0600 - 0.500x + x^2 = 0.0640x^2 \quad \text{or in quadratic form: } 0.936x^2 - 0.500x + 0.0600 = 0$$

$$\text{use quadratic formula: } x = \frac{0.500 \pm \sqrt{0.500^2 - 4(0.936)(0.0600)}}{2(0.936)} = 0.352 \text{ or } 0.182$$

x cannot exceed the initial amount of H₂, so the higher number is discarded. x = 0.182 mol

$$[\text{H}_2] = \frac{(0.200-0.182) \text{ mol}}{6.00 \text{ L}} = 0.00300 \text{ M}; [\text{I}_2] = \frac{(0.300-0.182) \text{ mol}}{6.00 \text{ L}} = 0.0197 \text{ M}; [\text{HI}] = \frac{2(0.182) \text{ mol}}{6.00 \text{ L}} = 0.0607 \text{ M}$$

e)* 0.100 mol H₂, 0.200 mol I₂, and 0.300 mol HI

Q = (0.100)(0.200)/0.300² = 0.222 > K, so H₂ and I₂ react to produce HI.

	2HI(g)	⇌	H ₂ (g)	+	I ₂ (g)
Initial	0.300		0.100		0.200
Δ	+2x		- x		- x
Equilibrium	0.300 + 2x		0.100 - x		0.200 - x

$$\frac{(0.100-x)(0.200-x)}{(0.300 + 2x)^2} = \frac{0.0200 - 0.300x + x^2}{0.0900 + 1.200x + 4x^2} = 0.0160$$

$$0.0200 - 0.300x + x^2 = 0.00144 + 0.0192x + 0.0640x^2 \quad \text{rearrange to quadratic form: } 0.936x^2 - 0.3192x + 0.01856 = 0$$

$$\text{use quadratic formula: } x = \frac{0.3192 \pm \sqrt{0.3192^2 - 4(0.936)(0.01856)}}{2(0.936)} = 0.267 \text{ or } 0.0744$$

x cannot exceed the initial amount of H₂, so the higher number is discarded. x = 0.074 mol

$$[\text{H}_2] = \frac{(0.100-0.074) \text{ mol}}{6.00 \text{ L}} = 0.0043 \text{ M}; [\text{I}_2] = \frac{(0.200-0.074) \text{ mol}}{6.00 \text{ L}} = 0.0210 \text{ M}; [\text{HI}] = \frac{(0.300+2(0.074)) \text{ mol}}{6.00 \text{ L}} = 0.0747 \text{ M}$$

41. An equilibrium mixture is found to contain 1.200 mol each CO₂ and H₂ and 0.155 mol each CO and H₂O.

Δ_g = 0 for this reaction, so the volume cancels in the equilibrium constant expression. Consequently, the problem can be worked in moles rather than molarity. If Δ_g was not zero, this problem could not be worked without a volume.

a) What is the equilibrium constant for the reaction CO₂(g) + H₂(g) ⇌ CO(g) + H₂O(g)?

$$K = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} = \frac{(0.155)(0.155)}{(1.200)(1.200)} = 0.0167$$

b) What is the value of the reaction quotient immediately after the addition of 0.800 mol of each gas to this equilibrium mixture? How many moles of each gas would be present when equilibrium is reestablished?

	CO ₂ (g)	+	H ₂ (g)	⇌	CO(g)	+	H ₂ O(g)
Equilibrium	1.200		1.200		0.155		0.155
Add	0.800		0.800		0.800		0.800
Initial	2.000		2.000		0.955		0.955

$$Q = \frac{[\text{CO}(g)] \times [\text{H}_2\text{O}(g)]}{[\text{CO}_2(g)] \times [\text{H}_2(g)]} = \frac{(0.955)(0.955)}{(2.000)(2.000)} = 0.228$$

Q > K, so the reaction proceeds to the left, so the reaction table is:

Chemical Equilibrium

	CO ₂ (g)	+	H ₂ (g)	⇌	CO(g)	+	H ₂ O(g)
Initial	2.000		2.000		0.955		0.955
Δ	+x		+x		-x		-x
Initial	2.000 + x		2.000 + x		0.955 - x		0.955 - x

$\Delta n_g = 0$, so we can use moles in the equilibrium expression: $K = 0.0167 = \frac{(0.955-x)^2}{(2.000+x)^2}$

Take the square root: $\sqrt{0.0167} = \sqrt{\frac{(0.955-x)^2}{(2.000+x)^2}} = 0.129 = \frac{0.955-x}{2.000+x}$, or $0.258 + 0.129x = 0.955 - x$, so $x = 0.627$ mol

At equilibrium: $n(\text{CO}_2) = n(\text{H}_2) = 2.000 + x = 2.617$ moles, and $n(\text{CO}) = n(\text{H}_2\text{O}) = 0.955 - x = 0.338$ moles

43. What is the equilibrium concentration of F⁻ ion after mixing the following solutions? Hint: Mixing the solutions dilutes the reactants.

a) mixing 75.0 mL of 0.100 M HF with 75.0 mL of 0.100 M NH₃?

	NH ₃ (aq)	+	HF(aq)	⇌	NH ₄ ¹⁺ (aq)	+	F ⁻	K = 1.3 × 10 ⁷
Initial	0.0500		0.0500		0		0	
Δ	-x		-x		+x		+x	
Final	0.05 - x		0.05 - x		x		x	

$$K = 1.3 \times 10^7 = \frac{[\text{NH}_4^{1+}][\text{F}^{-}]}{[\text{NH}_3][\text{HF}]} = \frac{x^2}{(0.0500 - x)^2};$$

Take the square root of both sides: $\sqrt{1.3 \times 10^7} = \sqrt{\frac{x^2}{(0.05 - x)^2}} \Rightarrow 3.6 \times 10^3 = \frac{x}{(0.05 - x)}$

Then, solve for x: $1.8 \times 10^2 - 3.6 \times 10^3 x = x$ so $x = \frac{1.8 \times 10^2}{3.6 \times 10^3} = 0.050 = [\text{F}^{-}]$

When $K \gg 1$, the amount of product can be determined from stoichiometric considerations only because the reaction proceeds almost to completion.

b) mixing 75.0 ml of 0.100 M HF with 75.0 ml of 0.100 M KNO₂?

	NO ₂ ¹⁻ (aq)	+	HF(aq)	⇌	F ⁻	+	HNO ₂ (aq)	K = 1.8
Initial	0.0500 M		0.0500 M		0		0	
Δ	-x		-x		x		x	
Final	0.0500-x		0.0500-x		x		x	

$$K = 1.8 = \frac{[\text{F}^{-}][\text{HNO}_2]}{[\text{NO}_2^{-}][\text{HF}]} = \frac{x^2}{(0.0500 - x)^2}$$

Take the square root of both sides: $\sqrt{1.8} = \sqrt{\frac{x^2}{(0.0500 - x)^2}} \Rightarrow 1.34 = \frac{x}{(0.0500 - x)}$

Solve for x: $1.34(0.0500 - x) = x \rightarrow 0.067 - 1.34x = x \rightarrow 0.067 = 2.34x$

$x = 0.029 \text{ M} = [\text{F}^{-}]$. When $K \sim 1$, the concentrations of substances on both sides of the equilibrium are similar.

c) mixing 50.0 ml of 0.100 M HF with 50.0 ml of 0.100 M K₂SO₄?

	HF(aq)	+	SO ₄ ²⁻ (aq)	⇌	F ⁻ (aq)	+	HSO ₄ ¹⁻ (aq)	K=0.060
Initial	0.0500 M		0.0500 M		0		0	
Δ	-x		-x		x		x	
Final	0.0500-x		0.0500 - x		x		x	

Again, following the procedure in part (a) $\sqrt{0.060} = \sqrt{\frac{x^2}{(0.0500 - x)^2}} \Rightarrow 0.245 = \frac{x}{(0.0500 - x)}$

$0.245(0.0500 - x) = x \rightarrow 0.012 - 0.245x = x \rightarrow 0.012 = 1.245x$

$[\text{F}^{-}] = x = 0.0098 \text{ M}$. When $K \ll 1$, the amount of product is small.

45. Consider the following equilibrium at a temperature near 500 K: $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ $K = 0.650$. How many moles of PCl_3 would be in an equilibrium mixture produced by

a) placing 3.36 mol PCl_5 into an empty 4.82-L flask;

Setup the reaction table in concentrations.

	$\text{PCl}_5(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
Initial	0.697		0		0
Δ	-x		+x		+x
equilibrium	$0.697 - x$		x		x

$$K = \frac{x^2}{0.697 - x} = 0.650; \quad \text{Eliminate denominator: } x^2 = 0.453 - 0.650x; \quad \text{Rearrange: } x^2 + 0.650x - 0.453 = 0$$

$$x = \frac{-0.650 + \sqrt{0.650^2 - 4(1)(-0.453)}}{2(1)} = 0.422 \text{ M}$$

$$[\text{PCl}_5] = 0.697 - 0.422 = 0.275 \text{ M}; \quad [\text{PCl}_3] = [\text{Cl}_2] = 0.422 \text{ M}$$

$$\text{The question asks for moles. } \text{PCl}_5: (0.275 \text{ M})(4.82 \text{ L}) = 1.33 \text{ mol} \quad \text{PCl}_3 = \text{Cl}_2 = (0.422 \text{ M})(4.82 \text{ L}) = 2.03 \text{ mol}$$

b)* placing 2.68 mol PCl_3 and 3.65 mol Cl_2 into an empty 6.15-L flask.

Setup the reaction table in concentrations. Note one extra significant figure is included.

	$\text{PCl}_5(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
Initial	0		0.4358		0.5935
Δ	+x		-x		-x
equilibrium	x		0.4358-x		0.5935-x

$$K = \frac{(0.4358-x)(0.5935-x)}{x} = 0.650; \quad \text{Expand numerator and eliminate denominator: } 0.2587 - 1.0293x + x^2 = 0.650x;$$

$$\text{Rearrange: } x^2 - 1.6793x + 0.2587 = 0; \quad \text{so } x = \frac{1.6793 \pm \sqrt{1.6793^2 - 4(1)(0.2587)}}{2(1)} = 1.51 \text{ or } 0.172$$

The answer cannot exceed 0.44 M, so $x = 0.172 \text{ M}$

$$[\text{PCl}_5] = 0.172 \text{ M}; \quad [\text{PCl}_3] = 0.436 - 0.172 = 0.264 \text{ M} \quad [\text{Cl}_2] = 0.594 - 0.172 = 0.422 \text{ M}$$

$$\text{moles: } \text{PCl}_5: (0.172 \text{ M})(4.82 \text{ L}) = 0.829 \text{ mol}; \quad \text{PCl}_3 = (0.264 \text{ M})(4.82 \text{ L}) = 1.27 \text{ mol}; \quad \text{Cl}_2 = (0.422 \text{ M})(4.82 \text{ L}) = 2.03 \text{ mol}$$

47. What is the concentration of H_2 in an equilibrium mixture formed by the decomposition of 0.100 M HI?

	$2\text{HI}(\text{g})$	\rightleftharpoons	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$
initial	0.100		0		0
Δ	-2x		+x		+x
equilibrium	$0.100-2x$		+x		+x

$$\Delta n_g = 0, \text{ so } K_p = K_c, \quad K = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = 0.64 = \frac{x^2}{(0.100 - 2x)^2}$$

Taking the square root of each side, we obtain $0.80 = \frac{x}{0.100-2x}$ and solving for x

$$x = \frac{0.08}{2.60} = 0.031 \text{ M}; \quad [\text{H}_2] = x = 0.031 \text{ M}$$

49. How many moles of I_2 are in an equilibrium mixture resulting when 0.20 mol H_2 and 0.40 mol HI are added to a 2.0-L flask and allowed to equilibrate?

We are given moles and asked for moles, and because $\Delta n_g = 0$, we can do the problem in moles. The reaction table in moles.

	$2\text{HI}(\text{g})$	\rightleftharpoons	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$
initial	0.40		0.20		0
Δ	-2x		+x		+x
equilibrium	$0.40-2x$		$0.20+x$		+x

Chemical Equilibrium

$$K = \frac{(0.20+x)(x)}{(0.40-2x)^2} = \frac{0.20x + x^2}{0.16 - 1.60x + 4x^2} = 0.64$$

Eliminate the denominator to obtain: $0.20x + x^2 = 0.1024 - 1.024x + 2.56x^2$.

Rearrange to quadratic form: $1.56x^2 - 1.224x + 0.1024 = 0$

$$x = \frac{1.224 \pm \sqrt{1.224^2 - 4(1.56)(0.1024)}}{2(1.56)} = 0.69 \text{ or } 0.095, \text{ but } x \text{ cannot exceed } 0.20, \text{ so } x = 0.095 \text{ mol.}$$

moles: $\text{HI} = 0.40 - 2(0.095) = 0.21 \text{ mol}$; $\text{H}_2 = 0.20 + 0.095 = 0.30 \text{ mol}$; $\text{I}_2 = 0.095 \text{ mol}$

50. The initial partial pressures of H_2 and CO_2 in a reaction flask are each 1.64 atm. What is the equilibrium pressure

51. If a reaction mixture is 0.200 M H_2 , 0.200 M CO_2 , 0.400 M CO and 0.400 M H_2O , what will the equilibrium concentrations be?

	$\text{H}_2(\text{g})$	+	$\text{CO}_2(\text{g})$	\rightleftharpoons	$\text{H}_2\text{O}(\text{g})$	+	$\text{CO}(\text{g})$
Initial	0.200		0.200		0.400		0.400
Δ	-x		-x		+x		+x
equilibrium	0.200-x		0.200-x		0.400+x		0.400+x

$$K = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]} = 16 = \frac{(0.400+x)^2}{(0.200-x)^2}. \text{ Take the square root of each side } 4 = \frac{0.400+x}{0.200-x}$$

Solve for x: $x = \frac{0.400}{5} = 0.08 \text{ M}$; $[\text{H}_2] = [\text{CO}_2] = 0.200 - 0.08 = 0.12 \text{ M}$, $[\text{H}_2\text{O}] = [\text{CO}] = 0.400 + 0.08 = 0.48 \text{ M}$

53. What are the equilibrium concentrations resulting from the equilibration of 0.300 M H_2 , 0.500 M CO_2 , 0.100 M CO and 0.600 M H_2O ?

	$\text{H}_2(\text{g})$	+	$\text{CO}_2(\text{g})$	\rightleftharpoons	$\text{H}_2\text{O}(\text{g})$	+	$\text{CO}(\text{g})$	
Initial	0.300		0.500		0.600		0.100	$Q = 40 > K$
Δ	-x		-x		+x		+x	
equilibrium	0.300-x		0.500-x		0.600+x		0.100+x	

$$K = \frac{(0.600+x)(0.100+x)}{(0.300-x)(0.500-x)} = \frac{0.0600 + 0.700x + x^2}{0.150 - 0.800x + x^2} = 16.0$$

eliminate denominator: $0.0600 + 0.700x + x^2 = 2.40 - 12.8x + 16.0x^2$

$$\text{Rearrange to quadratic form: } 15.0x^2 - 13.5x + 2.34 = 0, \text{ so } x = \frac{13.5 \pm \sqrt{13.5^2 - 4(15.0)(2.34)}}{2(15.0)} = 0.666 \text{ or } 0.234$$

x cannot exceed 0.300, so $x = 0.234 \text{ M}$

$[\text{H}_2] = 0.300 - 0.234 = 0.066 \text{ M}$; $[\text{CO}_2] = 0.500 - 0.234 = 0.266 \text{ M}$;

$[\text{H}_2\text{O}] = 0.600 + 0.234 = 0.834 \text{ M}$; $[\text{CO}] = 0.100 + 0.234 = 0.334 \text{ M}$

55. An equilibrium mixture contains 0.800 mol HI , 0.200 mol I_2 , and 0.200 mol H_2 in a 1.00-L container. How many moles of I_2 must be removed in order to double the number of moles of H_2 at equilibrium?

The initial equilibrium tells us that $K = 0.0625$. The change is calculated from the given final concentration of H_2 .

	2HI	\rightleftharpoons	I_2	+	H_2
Eq.	0.800		0.200		0.200
Initial	0.800		0.200-x		0.200
Δ	-0.400		0.200		0.200
Equilibrium	0.400		0.400-x		0.400

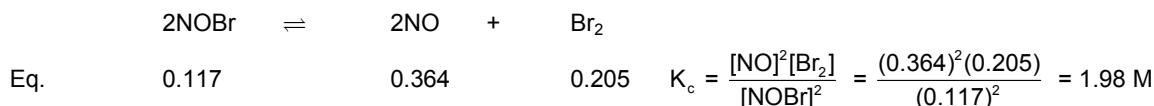
$$\text{Get the value of } K \text{ from the initial equilibrium: } K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{(0.200)(0.200)}{(0.800)^2} = 0.0625$$

$$0.0625 = \frac{0.400(0.400-x)}{0.400^2} \Rightarrow 0.400 - x = \frac{(0.0625)(0.400)^2}{0.400} = 0.0250$$

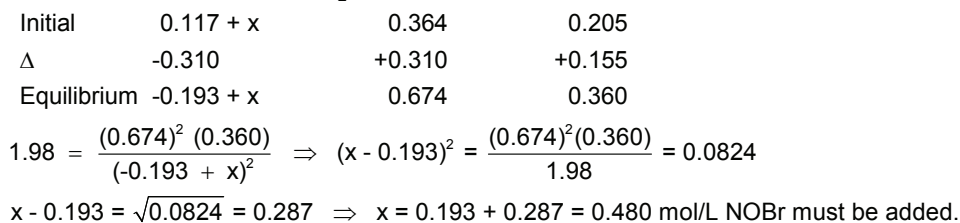
$x = 0.400 - 0.025 = 0.375 \text{ mol/L}$ I_2 must be removed

57. An equilibrium mixture is 0.117 M NOBr, 0.364 M NO, and 0.205 M Br₂.

a) What is the value of K_c for the reaction 2NOBr ⇌ 2NO + Br₂?



b) How many moles per liter of NOBr must be added to the equilibrium mixture to produce an equilibrium mixture that is 0.360 M in Br₂?



c) The equilibrium temperature is 373 K. What is K_p?

$$K_p = K_c \times RT^{\Delta n_g} \quad \& \quad \Delta n_g = 1 + 2 - 2 = 1 \text{ mol, so } K_p = 1.98 \text{ M} \times (0.0821 \times 373)^1 = 60.6 \text{ atm}$$

d) What is ΔG° at 373 K?

$$\Delta G^\circ = -RT \ln K = -(8.314)(373) \ln(60.6) = -12.7 \text{ kJ}$$

59. At 25 °C, the solubility of I₂ is 3.0×10⁻⁴ g/mL in water and 2.9×10⁻² g/mL in CCl₄. Iodine is readily extracted from water with CCl₄. The amount of I₂ remaining in each solvent after an extraction is dictated by the equilibrium constant for the extraction process: I₂(H₂O) ⇌ I₂(CCl₄).

a) Use the solubility of I₂ in each solvent to determine the equilibrium constant for the extraction at 25 °C. Substitute the equilibrium concentrations into the equilibrium constant expression.

$$K = \frac{[\text{products}]}{[\text{reactants}]} = \frac{2.9 \times 10^{-2} \text{ g/mL}}{3.0 \times 10^{-4} \text{ g/mL}} = 97$$

b) What mass of I₂ remains in the water when 200. mL of an aqueous solution containing 55.0 mg of I₂ is extracted with 20. mL of CCl₄?

The mass of iodine present in both phases after equilibration will be the same as the mass before equilibration.

Let x = mass of I₂ in H₂O (mg), then 55 - x = mass of I₂ in CCl₄ (mg)

$$97 = \frac{(55 - x)/20.}{x/200.} \Rightarrow 97x = 10(55 - x) = 550 - 10x$$

$$107x = 550 \Rightarrow x = 5.1 \text{ mg I}_2 \text{ in water}$$

A mass of 5.1 mg I₂ remains in the aqueous solution.

c) What mass of I₂ remains in the water when 200. mL of an aqueous solution containing 55.0 mg of I₂ is extracted twice with 10. mL of CCl₄?

Set up the problem the same as Part b). This time two mass balance calculations are needed to solve the problem.

Let x = mass of I₂ in H₂O after first extraction (mg), then 55 - x = mass of I₂ in CCl₄ after first extraction (mg)

$$97 = \frac{(55 - x)/10.}{x/200.} \Rightarrow 97x = 20(55 - x) = 1100 - 20x \Rightarrow x = 9.402 \text{ mg I}_2 \text{ in water}$$

After the first extraction 9.402 mg I₂ remains in the aqueous solution.

y = mass of I₂ in H₂O after second extraction, then 9.402 - y = mass of I₂ in CCl₄ after second extraction (mg)

$$97 = \frac{(9.402 - y)/10.}{y/200.} \Rightarrow 97y = 20(9.402 - y) = 188.0 - 20y$$

$$117y = 188.0 \Rightarrow y = 1.6 \text{ mg I}_2 \text{ in water}$$

After the second extraction 1.6 mg I₂ remains in the aqueous solution. Note that this is less than the amount left in the aqueous solution after a single 20. mL extraction.

Chemical Equilibrium

- d) What volume of CCl_4 would have to be used to extract 50.0 mg of the I_2 from the original aqueous solution in one extraction?

If 50.0 mg I_2 is extracted, then 5.0 mg I_2 remains in the aqueous solution. Its concentration will be 5.0 mg/200. mL = 0.025 mg/mL. The equilibrium constant tells us that the concentration of the organic layer will be 97 times as large: $97(0.025 \text{ mg/mL}) = 2.425 \text{ mg/mL}$. The minimal volume of CCl_4 can be calculated now: $50.0 \text{ mg}/(2.425 \text{ mg/mL}) = 20.6 \text{ mL}$.

61. Consider the following equilibrium at 400 K: $\text{Br}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{BrCl}(\text{g})$ $K = 7.0$

- a) A mixture contains 1.80 mol BrCl and 0.60 mol of Br_2 and 1.40 mol Cl_2 in a 4.26-L container. How many moles of Cl_2 must be removed to obtain an equilibrium mixture that contains 1.00 mol Br_2 ?

Show the removal of x mol Cl_2 in the initial line. The final amount of Br_2 is given as 1.00 mol, so $\Delta = +0.40$ for Br_2 . Δ is the same for Cl_2 , but it is twice as great for BrCl . Once the other D's are entered, the other equilibrium amounts can be determined. Thus, the reaction table has the following form.

	$\text{Br}_2(\text{g})$	+	$\text{Cl}_2(\text{g})$	\rightleftharpoons	$2\text{BrCl}(\text{g})$	
initial	0.60		1.40 - x		1.80	moles
change	+0.40		+0.40		-0.80	moles
equilibrium	1.00		1.80 - x		1.00	moles

Substitute the above equilibrium amounts into the equilibrium constant expression to obtain the following:

$$K = 7.0 = \frac{\left(\frac{1.00}{4.26}\right)^2}{\frac{1.00}{4.26} \times \frac{1.80 - x}{4.26}} = \frac{1.00}{1.80 - x} \quad \text{Note that the volumes cancel } (\Delta n_g = 0).$$

Next solve for x : $7.0(1.80) - 7.0x = 1.00$, which produces $x = 11.6/7.0 = 1.6 \text{ mol Cl}_2$.

Note that more Cl_2 must be withdrawn than is present in the initial mixture, but that is ok because more Cl_2 is produced as it is removed.

- b) How many moles of chlorine should be added to 0.424 moles of bromine at 400 K to produce 0.500 mol of BrCl at equilibrium?

The reaction table:

	$\text{Br}_2(\text{g})$	+	$\text{Cl}_2(\text{g})$	\rightleftharpoons	$2\text{BrCl}(\text{g})$	
initial	0.424		x		0	moles
Δ	-0.250		-0.250		+0.500	moles
equilibrium	0.174		x - 0.250		0.500	moles

The problem states that 0.500 mol BrCl will be present at the new equilibrium. This means that the change of BrCl will be +0.500 mol. The stoichiometry of the equilibrium can be used to determine the other values in the Δ line. This allows other entries in the table to be calculated. The only variable is the quantity of Cl_2 added. Substitution of the equilibrium values into the equilibrium expression leads to the following equation. Note that volumes cancel, so the problem can be solved in moles.

$$K = 7.0 = \frac{(0.500/4.26)^2}{(0.174/4.26)[(x - 0.250)/4.26]} = \frac{0.500^2}{0.174(x - 0.250)}$$

$$1.218x - 0.3045 = 0.500^2 \Rightarrow 1.218x = 0.5545 \Rightarrow x = 0.455 \text{ mol Cl}_2 \text{ must be removed.}$$

- c) What are the partial pressures of the gases in an equilibrium mixture formed from the partial decomposition of BrCl if the initial pressure of BrCl was 1.84 atm?

The following table can be used to solve the problem.

	$\text{Br}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{BrCl}(\text{g})$			$K = 7.0$
initial	0	0	1.84	atm
change	+ x	+ x	- 2x	atm
equilibrium	x	x	1.84 - 2x	atm

Partial pressures are proportional to activities, so the partial pressures can be used in to the equilibrium expression.

$$K = 7.0 = \frac{(1.84 - 2x)^2}{(x)(x)} \Rightarrow \sqrt{7} = \frac{1.84 - 2x}{x} \Rightarrow 2.6x = 1.84 - 2x \Rightarrow x = \frac{1.84}{4.6} = 0.40 \text{ atm}$$

$$P_{\text{Br}_2} = P_{\text{Cl}_2} = x = 0.40 \text{ atm. } P_{\text{BrCl}} = 1.84 - 2x = 1.04 \text{ atm.}$$

63. PCl_5 is added to a container at some temperature to a total pressure of 1.000 atm where it begins to decompose. At equilibrium, the total pressure of the container is 1.544 atm. What is the value of the equilibrium constant at this temperature?

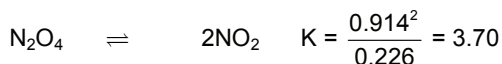
Setup the reaction table with x to determine pressure changes.

	PCl_5	\rightarrow	PCl_3	+	Cl_2
Initial	1.000		0		0
Δ	-x		+x		+x
Equilibrium	1.000-x		x		x

The total pressure is the sum of partial pressures: $1.544 = 1.000 - x + x + x = 1.000 + x$, so $x = 0.544$ atm.

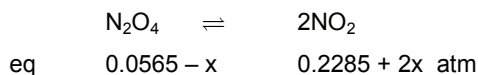
$$P_{\text{PCl}_5} = 1.000 - 0.544 = 0.456 \text{ atm}; \quad P_{\text{PCl}_3} = P_{\text{Cl}_2} = 0.544 \text{ atm}; \quad K = \frac{0.544^2}{0.456} = 0.649$$

65. The following equilibrium pressures were measured in a 5.00 L container near 350 K: $P_{\text{N}_2\text{O}_4} = 0.226$ atm and $P_{\text{NO}_2} = 0.914$ atm. What would the equilibrium pressures be if the volume were changed to 20.0 L? ... to 1.00 L?



We use Boyle's law ($PV = k$) to determine that the pressures at 20.0 L.

$$(0.226 \text{ atm})(5.00 \text{ L}) = P_{\text{N}_2\text{O}_4}(20.0 \text{ L}), \text{ so } P_{\text{N}_2\text{O}_4} = 0.0565 \text{ atm. Similarly, } P_{\text{NO}_2} = 0.2285 \text{ atm. } Q = \frac{0.2285^2}{0.0565} = 0.924 < K$$

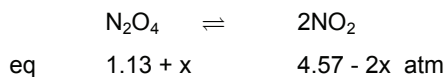


$$\text{Setup the equilibrium constant expression: } 3.70 = \frac{(0.2285 + 2x)^2}{0.0565 - x} = \frac{0.0522 + 0.914x + 4x^2}{0.0565 - x}$$

Express quadratic equation: $3.70(0.0565 - x) = 0.209 - 3.70x = 0.0522 + 0.914x + 4x^2$ or

$$4x^2 + 4.614x - 0.157 = 0, \text{ so } \frac{-4.614 + \sqrt{4.614^2 - 4(4)(-0.157)}}{2(4)} = 0.0331 \text{ atm. } P_{\text{N}_2\text{O}_4} = 0.0234 \text{ atm \& } P_{\text{NO}_2} = 0.295 \text{ atm}$$

The initial pressures in a 1.00 L flask would be $P_{\text{N}_2\text{O}_4} = 1.13$ atm & $P_{\text{NO}_2} = 4.57$ atm. $Q = \frac{4.57^2}{1.13} = 18.5 > K$



$$\text{Setup the equilibrium constant expression and solve: } 3.70 = \frac{(4.57 - 2x)^2}{1.13 + x} = \frac{20.885 - 18.28x + 4x^2}{1.13 + x} \Rightarrow x = 0.911 \text{ atm}$$

$$P_{\text{N}_2\text{O}_4} = 2.75 \text{ atm \& } P_{\text{NO}_2} = 2.04 \text{ atm.}$$

