

4. The equation



is simply the sum of the two equations given.



Therefore, the equilibrium constant for the equation is the product of  $K_1$  and  $K_2$ .  $K = K_1 K_2 = (4.9 \times 10^4)(1.0 \times 10^{-14}) = 4.9 \times 10^{-10}$ .

5. In a homogeneous equilibrium, all the of the reactants and products are in the same phase. In a heterogeneous equilibrium, two or more different phases (solid, liquid, gas or solute) are present. Therefore, a and c are homogeneous equilibria and b and d are heterogeneous equilibria.
7. The magnitude of the equilibrium constant usually tells us whether products or reactant predominate in the equilibrium mixture or whether they are present in roughly equal concentrations. If  $K$  is very large ( $K \gg 1$ ), products predominate. However, if  $K$  is very small ( $K \ll 1$ ), reactants predominate. If  $K \approx 1$ , there will be comparable concentrations of reactants and products. Care must be taken in using this rule of thumb where coefficients of reactants and products are very different.
8. The reaction quotient,  $Q$ , is an expression which has a form identical to the equilibrium constant, but whose concentrations are not limited to equilibrium concentrations. It is useful in determining whether a reaction is at equilibrium ( $Q = K$ ), and if not the direction the reaction needs to go to reach equilibrium.
9. The equilibrium composition of a reaction can be altered by changing concentrations or partial pressures of reactants and/or products, changing the volume of the vessel (only if there are different numbers of moles of gaseous reactants and products), changing the temperature of the mixture.
10. The platinum is acting as a catalyst, a substance that increases the rate of a reaction without being consumed in the reaction. At room temperature, the rate of the reaction between  $\text{H}_2$  and  $\text{O}_2$  is very small, because the activation energy is large. The platinum provides a suitable surface on which the reaction can occur at a greater rate, via a different mechanism with a smaller activation energy. The reaction could also be sped by igniting the mixture with a spark, thereby providing the required activation energy. The catalyst does not influence the equilibrium composition of the reaction mixture, only the rate at which equilibrium is established.

$$13. \quad x \text{ mol H}_2 \times \frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2} = \frac{2}{3} x \text{ mol NH}_3$$

15.  $\text{CO (g)} + 2 \text{H}_2 \text{(g)} \rightleftharpoons \text{CH}_3\text{OH (g)}$  Starting with 2 mol CO and 2 mol  $\text{H}_2$ , the maximum yield of  $\text{CH}_3\text{OH}$  would be 1 mol. Since the reaction is at equilibrium, there must be some  $\text{H}_2$  remaining. Therefore, less than 1 mol of  $\text{CH}_3\text{OH}$  is produced.

16. The reaction may be written as:  $4 \text{H}_2 \text{(g)} + \text{Fe}_3\text{O}_4 \text{(s)} \rightleftharpoons 3 \text{Fe (s)} + 4 \text{H}_2\text{O (g)}$  where an equilibrium exists between all four substances. The reaction quotient for the reaction is given to the right:

$$Q_p = \frac{P_{\text{H}_2\text{O}}^4}{P_{\text{H}_2}^4}$$

When water vapor is passed over the hot iron,  $Q_p$  exceeds  $K_p$  and the reverse reaction predominates. When hydrogen gas is passed over the hot magnetic iron oxide,  $Q_p$  is smaller than  $K_p$  and the forward reaction must predominate.

24. Since equimolar amounts of NO and  $\text{NO}_2$  are produced in the reaction, 0.90 mol of NO is also formed. The formation of 0.90 mol of NO and  $\text{NO}_2$  requires that 0.90 mol of  $\text{N}_2\text{O}_3$  react, so the number of moles of  $\text{N}_2\text{O}_3$  remaining is  $3.00 - 0.90 = 2.10$  mol  $\text{N}_2\text{O}_3$ .

26.

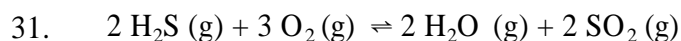
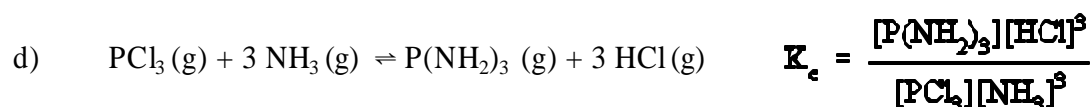
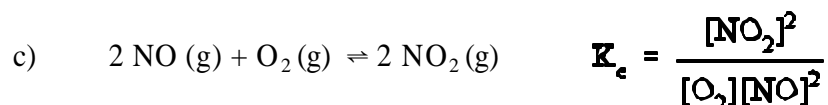
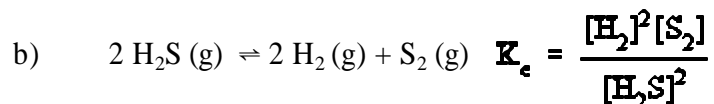
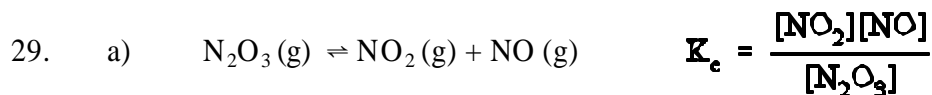
	2 NO (g) +	Br <sub>2</sub> (g)	$\rightleftharpoons$	2 NOBr (g)
initial mol	0.0524	0.0262		0
change in mol	-2x	-x		+2x
equilibrium mol	0.0655 - 2x	0.0328 - x		2x

2x is the number of moles of NOBr. Since this corresponds to 0.0311 mol,  $x = 0.01555$  mol. Therefore, at equilibrium we have 0.0311 mol NOBr,  $0.0524 - 2(0.01555) = 0.0213$  mol NO,  $0.0262 - 0.01555 = 0.0106$  mol  $\text{Br}_2$ .

28.

	CO (g) +	2 H <sub>2</sub> (g)	$\rightleftharpoons$	CH <sub>3</sub> OH (g)
initial mol	0.1500	0.3000		0
change in mol	-x	-2x		+x
equilibrium mol	0.1500 - x	0.3000 - 2x		x

The number of moles of CO at equilibrium is  $0.1187 \text{ mol} = 0.1500 - x$ . Therefore,  $x = 0.0313$  mol. the number of moles of  $\text{H}_2$  is  $0.3000 - 2(0.0313) = 0.2374$  mol and the number of moles of  $\text{CH}_3\text{OH}$  is  $x = 0.0313$  mol.



33. The equation for the original reaction is:  $2 \text{N}_2\text{O}_5(\text{g}) \rightleftharpoons 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ . If this equation is halved and reversed, it becomes:  $2 \text{NO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_5(\text{g})$  and its equilibrium constant expression is:

$$K_c = \frac{[\text{N}_2\text{O}_5]}{[\text{NO}_2]^2[\text{O}_2]^{1/2}}$$

Alternatively, if the reaction is halved, we simply halve all of the exponents in the equilibrium constant expression. When we reverse the reaction, we invert the equilibrium constant expression.

35. The second equation is simply the reverse of the first. Therefore, the value of its equilibrium constant at the same temperature is the reciprocal of the equilibrium constant of the original equation:

$$\frac{1}{1.84} = 0.543$$

37. The equilibrium concentrations are as follows:

$$[\text{H}_2] = \frac{0.488 \text{ mol}}{6.00 \text{ L}} = 0.08133 \text{ M} \quad [\text{I}_2] = \frac{0.206 \text{ mol}}{6.00 \text{ L}} = 0.03433 \text{ M}$$

$$[\text{HI}] = \frac{2.250 \text{ mol}}{6.00 \text{ L}} = 0.3750 \text{ M}$$

Since these are equilibrium concentrations, we simply plug them into the equilibrium constant expression to determine the equilibrium constant.

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.3750)^2}{(0.08133)(0.03433)} = 50.4$$

39.

	2 SO <sub>2</sub> (g)	+ O <sub>2</sub> (g)	⇌	2 SO <sub>3</sub> (g)
initial [ ]	0.0200	0.0100		0
change in [ ]	-2x	-x		+2x
equilibrium [ ]	0.0200 - 2x	0.0100 - x		2x

2x is the concentration of SO<sub>3</sub>. Since this corresponds to 0.0148 M, x = 0.0074 M.

Therefore, at equilibrium we have [SO<sub>3</sub>] = 0.0148 M, [SO<sub>2</sub>] = 0.0200 - 2(0.0074) = 0.0052 M and [O<sub>2</sub>] = 0.0100 - 0.0074 = 0.0026 M.

Since these are equilibrium concentrations, we simply plug them into the equilibrium constant expression to determine the equilibrium constant.

$$K_c = \frac{[\text{SO}_3]^2}{[\text{O}_2][\text{SO}_2]^2} = \frac{(0.0148)^2}{(0.0026)(0.0052)^2} = 3.1 \times 10^3$$

41.

	2 NOBr (g)	⇌	Br <sub>2</sub> (g)	+ 2 NO (g)
initial [ ]	2.00		0	0
change in [ ]	-2x		+x	+2x
equilibrium [ ]	2.00 - 2x		x	2x

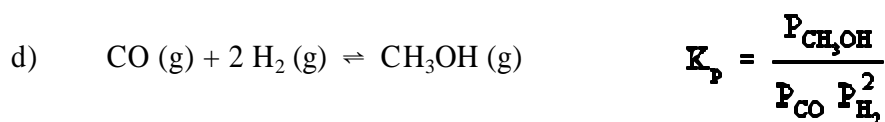
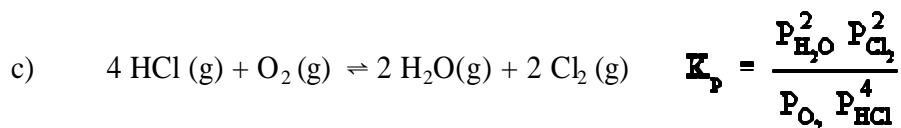
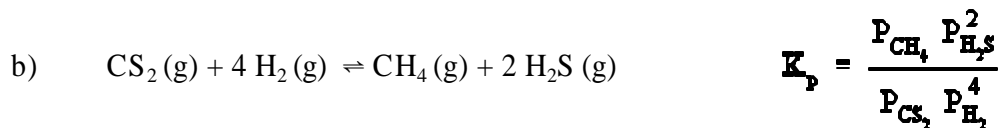
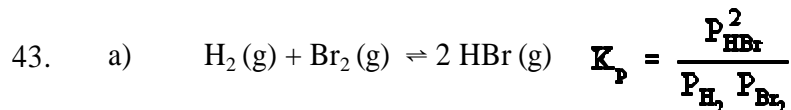
$$x = 0.094$$

$$[\text{NOBr}] = 2.00 - 2(0.094) \text{ M} = 1.81 \text{ M}$$

$$[\text{NO}] = 2(0.094) \text{ M} = 0.188 \text{ M}$$

$$[\text{Br}_2] = 0.094 \text{ M}$$

$$K_c = \frac{[\text{Br}_2][\text{NO}]^2}{[\text{NOBr}]^2} = \frac{(0.094)(0.188)^2}{(1.81)^2} = 1.0 \times 10^{-3}$$



45.  $K_p = K_c (RT)^{\Delta n}$  where  $R$  is the gas constant,  $0.082058 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$

$T$  is the absolute temperature

$n$  is the difference between the number of moles of gaseous products and reactants

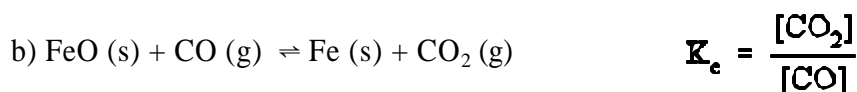
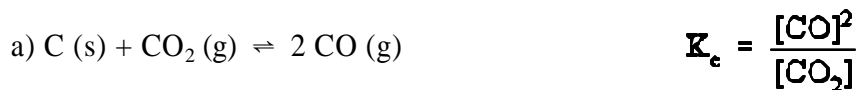
here  $\Delta n = 3 - 5 = -2$  and  $RT = 96.25$

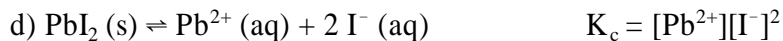
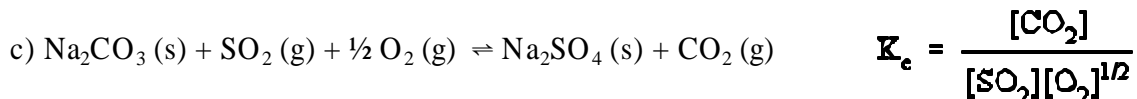
$$K_p = 0.28 (96.25)^{-2} = 3.0 \times 10^{-5}$$

47. Here,  $\Delta n = -1/2$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{6.55}{(73.85)^{-1/2}} = 56.3$$

49. The concentrations of pure solids and liquids do not appear in the equilibrium constant expression.





51. a) This reaction has an extremely small equilibrium constant, indicating that only an exceedingly small amount of product is formed. The reaction is nowhere near completion.
- b) This reaction has an extremely large equilibrium constant, indicating that proceeds very nearly to completion.

53. From the size of  $K_c$ , we expect that practically no decomposition occurs.

$$1.0 \times 10^{-95} = \frac{[\text{H}_2][\text{F}_2]}{[\text{HF}]^2} = \frac{[\text{H}_2][\text{F}_2]}{(1.00)^2}$$

Since the  $\text{H}_2$  and  $\text{F}_2$  come solely from the decomposition of  $\text{HF}$ ,  $[\text{H}_2] = [\text{F}_2]$

$$[\text{H}_2] = \sqrt{1.0 \times 10^{-95}} = 3.2 \times 10^{-48} \text{ M}$$

This is in agreement with our prediction that the reaction has practically no tendency to proceed.

55. For the reaction,  $K_c = 3.07 \times 10^{-4}$  at  $24^\circ\text{C}$  and  $Q = \frac{[\text{Br}_2][\text{NO}]^2}{[\text{NOBr}]^2}$

$$\text{a) } Q = \frac{(0.0123)(0.0162)^2}{(0.0720)^2} = 6.23 \times 10^{-4} \quad Q > K_c, \text{ reaction goes to the left}$$

$$\text{b) } Q = \frac{(0.0139)(0.0159)^2}{(0.121)^2} = 2.40 \times 10^{-4} \quad Q < K_c, \text{ reaction goes to the right}$$

$$\text{c) } Q = \frac{(0.0181)(0.0134)^2}{(0.103)^2} = 3.06 \times 10^{-4} \quad Q \approx K_c, \text{ reaction is } \sim \text{ at equilibrium}$$

$$\text{d) } Q = \frac{(0.0105)(0.0121)^2}{(0.0472)^2} = 6.90 \times 10^{-4} \quad Q > K_c, \text{ reaction goes to the left}$$

$$57. \quad Q = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{0.020}{(0.10)(0.10)^2} = 20.$$

$K_c = 10.5$        $Q > K_c$  so the reaction goes to the left.

$$59. \quad K_c = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = \frac{[\text{COCl}_2]}{(0.012)(0.025)} = 1.23 \times 10^3$$

$$[\text{COCl}_2] = 1.23 \times 10^3 (0.012)(0.025) = 0.37 \text{ M}$$

61.

	$\text{I}_2(\text{g})$ +	$\text{Br}_2(\text{g})$	$\rightleftharpoons$	$2 \text{IBr}(\text{g})$
initial [ ]	0.00030	0.00030		0
change in [ ]	-x	-x		+2x
equilibrium [ ]	$0.00030 - x$	$0.00030 - x$		2x

$$K_c = \frac{[\text{IBr}]^2}{[\text{I}_2][\text{Br}_2]} = \frac{(2x)^2}{(0.00030 - x)(0.00030 - x)} = 1.2 \times 10^2$$

Taking the square root of both sides of the equation:

$$\frac{2x}{0.00030 - x} = \sqrt{1.2 \times 10^2} = 10.95$$

$$2x = 10.95(0.00030 - x) = 0.00328 - 10.95x$$

$$12.95x = 0.00328$$

$$x = 2.54 \times 10^{-4}$$

$$[\text{I}_2] = [\text{Br}_2] = 0.00030 - 0.000254 = 4.6 \times 10^{-5} \text{ M}$$

$$[\text{IBr}] = 2(2.54 \times 10^{-4}) = 5.08 \times 10^{-4} \text{ M}$$

63.

	CO <sub>2</sub> (g) +	C (s)	⇌	2 CO (g)
initial [ ]	1.00	–		0
change in [ ]	–x	–		+2x
equilibrium [ ]	1.00 – x	–		2x

$$K_c = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{(2x)^2}{(1.00 - x)} = 14.0$$

$K_c$  is fairly large, so  $x$  is not likely to be negligible relative to 1.00 in the denominator. We will have to set up and solve the quadratic equation.

$$4x^2 = 14.0 - 14.0x$$

Rearranging,

$$4x^2 + 14.0x - 14.0 = 0$$

which is of the form  $ax^2 + bx + c = 0$ , where  $a = 4$  (exactly),  $b = 14.0$  and  $c = -14.0$

The quadratic formula gives the roots of such an equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-14.0 \pm \sqrt{14.0^2 - 4(4)(-14.0)}}{2(4)} \quad \text{so } x = 0.81 \text{ or } -4.31$$

The second root is physically meaningless because there cannot be any negative concentrations, so we reject it and take the first root.

$$[\text{CO}] = 2(0.81) \approx 1.6 \text{ M} \text{ and } [\text{CO}_2] = 1.00 - 0.81 = 0.19 \text{ M}$$

65.

	CO (g)	+	3 H <sub>2</sub> (g)	⇌	CH <sub>4</sub> (g)	+	H <sub>2</sub> O (g)
initial [ ]	0.1000		0.3000		0		0
change in [ ]	-x		-3x		+x		+x
equilibrium [ ]	0.1000 - x		0.3000 - 3x		x		x

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} = \frac{(x)(x)}{(0.1000 - x)(0.3000 - 3x)^3} = 3.92$$

$$\frac{(x)(x)}{(0.1000 - x)[3(0.1000 - x)]^3} = \frac{x^2}{27(0.1000 - x)^4} = 3.92$$

Multiplying each side by 27 and taking the square root we get:

$$\frac{x}{(0.1000 - x)^2} = \sqrt{(27)(3.92)} = 10.29$$

$$x = 10.29 (0.01000 - 0.2000 x + x^2)$$

$$10.29 x^2 - 3.058 x + 0.1029 = 0$$

The roots are:  $x = 0.258$  or  $x = 0.0387$ .

The first gives negative concentrations for CO and H<sub>2</sub> and is rejected.

$$[\text{CH}_4] = [\text{H}_2\text{O}] = 0.0387 \text{ M}$$

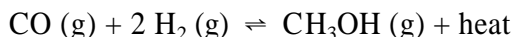
$$[\text{CO}] = 0.1000 - 0.0387 = 0.0613 \text{ M}$$

$$[\text{H}_2] = 0.3000 - 3(0.0387) = 0.184 \text{ M}$$

67. Since we are removing a component of the equilibrium which is on the product side, the forward reaction will predominate until equilibrium is reestablished.
69. Assuming the pressure is increased by decreasing the volume of the vessel, the side with fewer moles of gases will be favored.
- No effect since  $\Delta n = 0$
  - No effect since  $\Delta n = 0$
  - $\Delta n = +1$ , so the reactant side is favored. Equilibrium shifts to the left.

$$71. \quad \frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2}$$

This implies that if  $\Delta H^\circ > 0$ , an increase in temperature will lead to an increase in the value of  $\ln K$  and therefore in  $K$  itself. Since  $\Delta H^\circ < 0$ , an increase in temperature decreases  $K$  and raising the temperature decreases the fraction of methanol at equilibrium. Another more simple minded approach involves writing the equation as:



LeChatelier's Principle would tell us that increasing the temperature (adding heat, in effect) shifts the equilibrium to favor the production of more dihydrogen and carbon monoxide at the expense of methanol.

$$73. \quad \Delta H^\circ = [4 \text{ mol } (\Delta H_f^\circ(\text{H}_2\text{O (g)})) + 2 \text{ mol } (\Delta H_f^\circ(\text{NH}_3 \text{(g)}))] \\ - [7 \text{ mol } (\Delta H_f^\circ(\text{H}_2 \text{(g)})) + 2 \text{ mol } (\Delta H_f^\circ(\text{NO}_2 \text{(g)}))]$$

$$\Delta H^\circ = [4 \text{ mol } (-241.826 \frac{\text{kJ}}{\text{mol}}) + 2 \text{ mol } (-45.9 \frac{\text{kJ}}{\text{mol}})] \\ - [7 \text{ mol } (0) + 2 \text{ mol } (33.2 \frac{\text{kJ}}{\text{mol}})] = -1125.5 \frac{\text{kJ}}{\text{mol}}$$

Since  $\Delta H^\circ < 0$ , an increase in temperature leads to a decrease in the equilibrium constant.

75. Since  $\Delta n > 0$ , a decrease in pressure will increase the yield of products. Since  $\Delta H^\circ < 0$ , the equilibrium constant will increase with decreasing temperature. The optimum conditions for maximum yield of products are low temperature and low pressure. However, we must realize that the rate of reaction will also decrease with decreasing temperature, so there will be a trade-off in temperature between the rate of the reaction and the equilibrium constant.

$$77. \quad K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{0.015}{(0.096)(0.191)^2} = 4.3$$

$$79. \quad \frac{90.55 \text{ g CO}}{100 \text{ g mixture}} \times \frac{1 \text{ mol CO}}{28.01 \text{ g}} = \frac{0.03233 \text{ mol CO}}{100 \text{ g mixture}}$$

$$\frac{9.45 \text{ g CO}_2}{100 \text{ g mixture}} \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g}} = \frac{0.00215 \text{ mol CO}_2}{100 \text{ g mixture}}$$

The total number of moles is 0.03448 mol.

Use the ideal gas law to calculate the volume of the mixture:

$$V = \frac{nRT}{P} = \frac{(0.03448 \text{ mol})(0.082058 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(1123 \text{ K})}{1.000 \text{ atm}} = 3.18 \text{ L}$$

$$[\text{CO}] = \frac{0.03233 \text{ mol}}{3.18 \text{ L}} = 0.0102 \text{ M} \quad [\text{CO}_2] = \frac{0.00215 \text{ mol}}{3.18 \text{ L}} = 6.76 \times 10^{-4} \text{ M}$$

$$K_c = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{(0.0102)^2}{6.76 \times 10^{-4}} = 0.154$$

81. The concentrations are:

$$[\text{N}_2] = \frac{1.00 \text{ mol}}{2.00 \text{ L}} = 0.500 \text{ M} \quad [\text{H}_2] = \frac{1.00 \text{ mol}}{2.00 \text{ L}} = 0.500 \text{ M}$$

$$[\text{NH}_3] = \frac{2.00 \text{ mol}}{2.00 \text{ L}} = 1.00 \text{ M}$$

$$Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(1.00)^2}{(0.500)(0.500)^3} = 16.0$$

$Q > K_c$ , so the reverse reaction must predominate for equilibrium to be established.

83. Ordinarily, we would need to know the volume in order to determine the concentrations to plug into the reaction quotient. However, since there are equal numbers of moles on the product and reactant sides, the volumes in the numerator and denominator of the reaction quotient will cancel.

$$Q = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2]} = \frac{(\frac{1.00}{V})(\frac{1.00}{V})}{(\frac{1.00}{V})(\frac{1.00}{V})} = 1.00$$

$Q > K_c$  so the reverse reaction must predominate for equilibrium to be established.

85.

	2 HBr (g)	$\rightleftharpoons$	H <sub>2</sub> (g) +	Br <sub>2</sub> (g)
initial [ ]	0.010		0	0
change in [ ]	-2x		+x	+x
equilibrium [ ]	0.010 - 2x		x	x

$$K_c = 1.6 \times 10^{-2} = \frac{[\text{H}_2][\text{Br}_2]}{[\text{HBr}]^2} = \frac{x^2}{(0.010 - 2x)^2}$$

$$\sqrt{1.6 \times 10^{-2}} = \frac{x}{0.010 - 2x} = 0.126$$

$$x = 0.00126 - 0.252x$$

$$1.252x = 0.00126$$

$$x = 0.0010$$

[H<sub>2</sub>] = 0.0010 M or 0.0010 mol in 1.0 L

[Br<sub>2</sub>] = 0.0010 M or 0.0010 mol in 1.0 L

[HBr] = 0.010 - 2(0.0010) = 0.008 M or 0.008 mol in 1.0 L

87.

	COCl <sub>2</sub> (g)	$\rightleftharpoons$	CO (g) +	Cl <sub>2</sub> (g)
initial [ ]	0.0400		0	0
change in [ ]	-x		+x	+x
equilibrium [ ]	0.0400 - x		x	x

$$K_c = 8.05 \times 10^{-4} = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = \frac{x^2}{0.0400 - x}$$

$$x^2 + 8.05 \times 10^{-4}x - 3.22 \times 10^{-5} = 0$$

Solving the quadratic equation yields:  $x = 5.29 \times 10^{-3}$  and  $x = -6.09 \times 10^{-3}$

The second root is impossible, so  $5.29 \times 10^{-3}$  mol/L dissociates.

$$\% \text{ dissociated} = \frac{5.29 \times 10^{-3}}{0.0400} \times 100 = 13.2 \%$$

89.

	CO (g)	+	3 H <sub>2</sub> (g)	⇌	CH <sub>4</sub> (g)	+	H <sub>2</sub> O (g)
initial [ ]	0.100		0.400		0		0
change in [ ]	-x		-3x		+x		+x
equilibrium [ ]	0.100 - x		0.400 - 3x		x		x

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} = \frac{(x)(x)}{(0.100 - x)(0.400 - 3x)^3} = 3.92$$

Since  $K_c$  is close to 1, we can assume that there are comparable amounts of reactants and products at equilibrium. Start by assuming  $x \approx 0.050$ .

$$f(x) = = \frac{(0.050)(0.050)}{(0.100 - 0.050)(0.400 - 3(0.050))^3} = 3.2$$

This is very close to 3.92, but a little low, so we will increase our estimate of  $x$  to 0.055.

$$f(x) = = \frac{(0.055)(0.055)}{(0.100 - 0.055)(0.400 - 3(0.055))^3} = 5.2$$

This is greater than 3.92 and a little farther away than our initial value of 3.2, so our next iteration will involve a guess between 0.050 and 0.055, but a little close to 0.050.

$$f(x) = = \frac{(0.052)(0.052)}{(0.100 - 0.052)(0.400 - 3(0.052))^3} = 3.9$$

This is  $K_c$  to within two significant digits, so:

$$[\text{CH}_4] = [\text{H}_2\text{O}] = 0.052 \text{ M or } 0.52 \text{ mol in } 10.0 \text{ L}$$

$$[\text{CO}] = 0.100 - 0.052 = 0.048 \text{ M or } 0.48 \text{ mol in } 10.0 \text{ L}$$

$$[\text{H}_2] = 0.400 - 3(0.052) = 0.244 \text{ M or } 2.44 \text{ mol in } 10.0 \text{ L}$$

91. The fact that the amount of product increases as the temperature increases implies that the equilibrium constant increases with increasing temperature. This is consistent with an endothermic reaction.

$$93. \quad K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \quad \text{and} \quad K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$$

$$P_{\text{NH}_3} = [\text{NH}_3]RT \quad P_{\text{H}_2} = [\text{H}_2]RT \quad P_{\text{N}_2} = [\text{N}_2]RT$$

$$K_p = \frac{([\text{NH}_3]RT)^2}{([\text{N}_2]RT)([\text{H}_2]RT)^3} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \times \frac{(RT)^2}{(RT)^4} = K_c \times (RT)^{-2} = \frac{K_c}{(RT)^2}$$

Therefore,  $K_c = K_p (RT)^2$

$$95. \quad \text{a) } K_p = K_c \times (RT)^{\Delta n} = 0.153 \times [(0.082058)(1123)]^1 = 14.1$$

b)

	C (s) +	CO <sub>2</sub> (g)	⇌	2 CO (g)
initial P		1.50 atm		0
change in P		-x		+2x
equilibrium P		1.50 - x		2x

$$K_p = 14.1 = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = \frac{(2x)^2}{1.50 - x} = \frac{4x^2}{1.50 - x}$$

$$4x^2 + 14.1x - 21.15 = 0$$

The roots are 1.13 and -4.66. We reject the negative root.

$$P_{\text{CO}} = 2(1.13) = 2.26 \text{ atm} \quad P_{\text{CO}_2} = 1.50 - 1.13 = 0.37 \text{ atm}$$

$$97. \quad 35.8 \text{ g PCl}_5 \times \frac{1 \text{ mol PCl}_5}{208.24 \text{ g}} = 0.172 \text{ mol PCl}_5$$

$$\text{Initial concentration of PCl}_5 = \frac{0.172 \text{ mol PCl}_5}{5.0 \text{ L}} = 0.0344 \text{ M}$$

	PCl <sub>3</sub> (g) +	Cl <sub>2</sub> (g)	⇌	PCl <sub>5</sub> (g)
initial [ ]	0	0		0.0344
change in [ ]	+x	+x		-x
equilibrium [ ]	x	x		0.0344 - x

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{0.0344 - x}{(x)(x)} = 4.1$$

$$4.1x^2 + x - 0.0344 = 0$$

The roots are: 0.0306 and -0.274. We reject the second root.

$$[\text{PCl}_3] = [\text{Cl}_2] = 0.0306 \text{ M}$$

$$[\text{PCl}_5] = 0.0344 - 0.0306 = 0.0038 \text{ M}$$

b. The fraction of PCl<sub>5</sub> decomposed is:  $\frac{0.0306}{0.0344} = 0.89$

c. A smaller volume would favor the side of the equilibrium with fewer moles of gas. The PCl<sub>5</sub> would decompose to a lesser extent.

99.  $65.4 \text{ g SbCl}_5 \times \frac{1 \text{ mol SbCl}_5}{299.02 \text{ g}} = 0.219 \text{ mol SbCl}_5$

$$\text{Initial concentration of SbCl}_5 = \frac{0.219 \text{ mol SbCl}_5}{5.0 \text{ L}} = 0.0438 \text{ M}$$

If the SbCl<sub>5</sub> is 35.8% decomposed, then its equilibrium concentration is

$$[\text{SbCl}_5]_{\text{eq}} = (0.642)(0.0438 \text{ M}) = 0.0281 \text{ M}$$

$$[\text{SbCl}_3]_{\text{eq}} = [\text{Cl}_2]_{\text{eq}} = (0.358)(0.0438 \text{ M}) = 0.0157 \text{ M}$$

$$K_c = \frac{[\text{SbCl}_3][\text{Cl}_2]}{[\text{SbCl}_5]} = \frac{(0.0157)^2}{0.0281} = 0.00877$$

$$K_p = K_c \times (RT)^1 = 0.00877[(0.082058)(468)]^1 = 0.337$$

$$101. \quad 8.25 \text{ g SO}_2\text{Cl}_2 \times \frac{1 \text{ mol SO}_2\text{Cl}_2}{134.97 \text{ g}} = 0.0611 \text{ mol SO}_2\text{Cl}_2$$

$$\text{Initial concentration of SO}_2\text{Cl}_2 = \frac{0.0611 \text{ mol SO}_2\text{Cl}_2}{1.00 \text{ L}} = 0.0611 \text{ M}$$

	SO <sub>2</sub> Cl <sub>2</sub> (g)	⇌	SO <sub>2</sub> (g) +	Cl <sub>2</sub> (g)
initial [ ]	0.0611		0	0
change in [ ]	-x		+x	+x
equilibrium [ ]	0.0611 - x		x	x

$$K_e = 0.045 = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]} = \frac{x^2}{0.0611 - x}$$

$$x^2 + 0.045x - 2.75 \times 10^{-3} = 0$$

Solving the quadratic equation yields:  $x = 0.0346$  and  $x = -0.0796$  and we reject the negative root.

$$[\text{SO}_2] = [\text{Cl}_2] = 0.035 \text{ M}$$

$$[\text{SO}_2\text{Cl}_2] = 0.0611 - 0.0346 \text{ M} = 0.026 \text{ M}$$

b) The fraction of SO<sub>2</sub>Cl<sub>2</sub> decomposed is:  $\frac{0.035}{0.0611} = 0.57$

c) Addition of Cl<sub>2</sub> would shift the equilibrium to the left, decreasing the fraction of SO<sub>2</sub>Cl<sub>2</sub> decomposed.

103. This problem involves the technique of achieving equilibrium from the product side. We assume that the reaction goes to completion as written and that the products then react to a certain extent to reach equilibrium. Our familiar table has one additional line which accounts for complete reaction, and the changes in concentration are relative to these.

	$2 \text{ CH}_3\text{COOH (g)}$	$\rightleftharpoons$	$(\text{CH}_3\text{COOH})_2 \text{ (g)}$
initial [ ]	$4.0 \times 10^{-4}$		0
complete dimerization	0		$2.0 \times 10^{-4}$
change in [ ]	$+2x$		$-x$
equilibrium [ ]	$2x$		$2.0 \times 10^{-4} - x$

$$\text{a) } K_c = 3.2 \times 10^4 = \frac{[(\text{CH}_3\text{COOH})_2]}{[\text{CH}_3\text{COOH}]^2} = \frac{2.0 \times 10^{-4} - x}{(2x)^2}$$

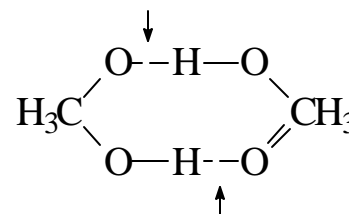
$$1.28 \times 10^5 x^2 + x - 2.0 \times 10^{-4} = 0$$

The roots are:  $3.6 \times 10^{-5}$  and  $-4.4 \times 10^{-5}$ . We reject the negative root.

$$[\text{CH}_3\text{COOH}] = 2(3.6 \times 10^{-5}) = 7.2 \times 10^{-5} \text{ M}$$

$$[(\text{CH}_3\text{COOH})_2] = 2.0 \times 10^{-4} - 3.6 \times 10^{-5} = 1.6 \times 10^{-4} \text{ M}$$

- b) These molecules are capable of intermolecular hydrogen bonding which results in a lower overall energy. A possible structure is shown with the hydrogen bonds indicated with arrows.



- c) The formation of the hydrogen bonds is an exothermic process, lowering the overall energy. As the temperature increases, the percentage of dimer will decrease because the equilibrium constant for this exothermic reaction will decrease.

$$105. \quad [\text{NO}] = 0.112 \text{ M} \quad [\text{Br}_2] = \frac{18.22 \text{ g}}{159.81 \frac{\text{g}}{\text{mol}}} = 0.114 \text{ M}$$

	2 NO (g) +	Br <sub>2</sub> (g)	⇌	2 NOBr (g)
initial mol	0.112	0.114		0
change in mol	-2x	-x		+2x
equilibrium mol	0.112 - 2x	0.114 - x		2x

However, we know that  $[\text{NOBr}] = 0.0824 \text{ M} = 2x$

So,  $[\text{NO}] = 0.112 - 0.0824 = 0.0296 \text{ M}$

$[\text{Br}_2] = 0.114 - 0.0412 = 0.0728 \text{ M}$

$$K_c = \frac{[\text{NOBr}]^2}{[\text{NO}]^2 [\text{Br}_2]} = \frac{(0.0824)^2}{(0.0296)^2 (0.0728)} = 1.1 \times 10^2$$