BC Science Chemistry 12 Chapter 2 – Chemical Equilibrium Answer Key

September 20, 2012

2.1 Introduction to Dynamic Equilibrium

Warm Up (page 72)

- 1. yes
- 2. cars are leaving the city at the same rate
- 3. cars are leaving the city at a greater rate than they are entering the city

Practice Problems – Determining Equivalent Reaction Rates at Equilibrium (page 73)

1. 0.0082 mol/s (rate of its consumption = rate of its production at equilibrium)

2.
$$0.0082 \text{ mol SO}_3 \text{ x } \frac{1 \text{ mol O}_2}{2 \text{ mol SO}_3} = \frac{0.0041 \text{ mol O}_2}{\text{s}}$$

3. $0.0041 \text{ mol } O_2 \ x \ \frac{32.0 \text{ g } O_2}{1 \text{ mol } O_2} = \frac{0.13 \text{ g } O_2}{\text{s}}$

Quick Check (page 75)

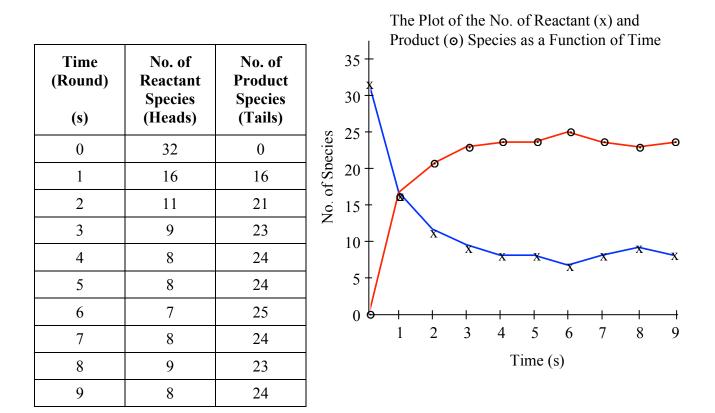
- 1. because the forward and reverse reactions continue to occur
- 2. i. constant macroscopic properties
- ii. closed system iii. a change in conditions causes an equilibrium shift
- 3. no chemicals are entering or leaving the defined system
- 4. a property that is large enough to be measured or observed with the unaided eye

Quick Check (page 76)

- 1. False
- 2. True
- 3. True
- 4. False

Activity2.1: A Mathematical Model of Dynamic Equilibrium That Makes Cents (page 77)

For example:



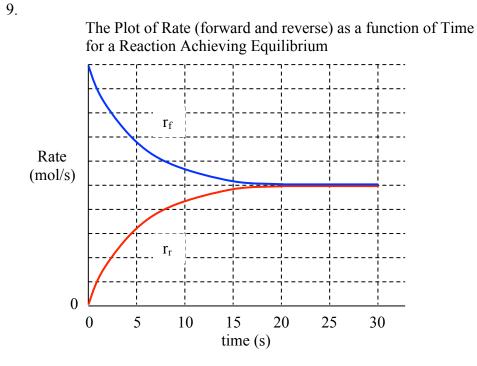
(Note: Recall that a 1 molar concentration represents 6.02×10^{23} particles per litre of solution as opposed to the 32 particles observed in this activity. With numbers this high, the actual number of particles of each chemical species wavers significantly at equilibrium but this represents a very small standard percent deviation and a difference in concentrations that is neither visible nor detectable by any instrumentation hence the macroscopic properties are constant.)

- 1. a reactant species becoming a product species or vice-versa
- 2. higher activation energy, more difficult collision geometry
- 3. higher concentration of products increases their probability of colliding with each other

2.1 Review Questions (page 79)

- 1. a. equilibrium
 - b. steady state
 - c. equilibrium
 - d. steady state
 - e. equilibrium
- 2. a. yes
 - b. yes
 - c. no
 - d. yes
 - e. no

- 3. a. $0.012 \frac{\text{mol } H_2}{\text{s}} \propto \frac{1 \text{ mol } N_2}{3 \text{ mol } H_2} = 0.0040 \frac{\text{mol } N_2 O_4}{\text{s}}$
 - b. $0.012 \text{ mol } \text{H}_2 \text{ x } \frac{2 \text{ mol } \text{NH}_3}{3 \text{ mol } \text{H}_2} \text{ x } \frac{17.0 \text{ g } \text{NH}_3}{1 \text{ mol } \text{NH}_3} = \frac{0.14 \text{ g } \text{NH}_3}{\text{s}}$
- 4. a. The rate of melting would become greater than the rate of freezing so net melting would occur and the ice cube would begin to decrease in size.
 - b. Water is still evaporating but the water level is not dropping because the rate of condensation has become equal to the rate of evaporation.
- 5. No. Not until you reinstate the original temperature and the system shifts back to restore its original concentrations. Increasing the temperature may just have provided the activation energy to initiate a reaction.
- 6. a. The concentrations of the reactants and products remain relatively constant within the flame.
 - b. The system isn't closed. The rate of the forward reaction does not equal the rate of the reverse reaction; in fact, there is no reverse reaction.
 (The concentrations of the reactants hold steady within the flame because reactants are continuously drawn into the flame to replace those being consumed; not because products are being converted back into reactants. The concentrations of the products hold steady within the flame because the products are leaving the flame at the same rate as new product particles are being formed; not because products are being converted back into reactants.)
- 7. Equilibria are closed whereas cyclic mechanisms such as this are open. The two steps in the cyclic mechanism are not the exact same reaction proceeding in opposite directions as is the case with an equilibrium. Each step in a two-step cyclic reaction consumes and produces chemicals not involved in the other step. As a result, equilibria are self-perpetuating since the forward and reverse reactions continuously supply each other with all their reactants whereas cyclic reactions stop as soon as one of their reactants runs out.
- 8. a. For example: otherwise the [NO] would not be constant.b. For example: otherwise the [H₂O] would not be constant.



- 10. a. the orange gas would become paler
 - b. the concentration of reactants (NO₂) decreases while the concentration of products (N_2O_4) increases
 - c. the forward rate decreases while the reverse rate increases
- 11. It would establish equilibrium in the same way as usual but from the opposite direction. The concentration of the products and the reverse rate decrease while the concentration of reactants and the forward rate increase until the forward rate equals the reverse rate and equilibrium is re-established.

2.2 Le Châtelier's Principle

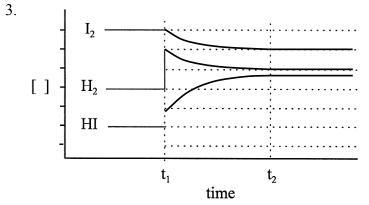
Warm Up (page 83)

- 1. the forward and reverse reaction rates
- 2. it would decrease
- 3. lower frequency of collisions between O_2 and SO_2
- 4. No

Practice Problems – Predicting How an Equilibrium System Will Respond to Having Some Reactant or Product, Added or Removed (page 85)

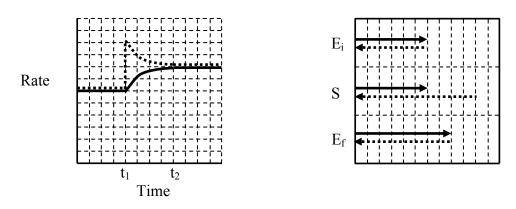
- 1. a. The system will restore equilibrium by removing some of the added Fe^{3+} .
 - b. right
 - c. $[Fe^{3+}]$ and $[FeSCN^{2+}]$ will be increased. $[SCN^{-}]$ will be decreased.
- a. The system will restore equilibrium by replacing some of the removed Fe³⁺.
 b. left
 - c. $[Fe^{3^+}]$ and $[FeSCN^{2^+}]$ will be decreased. $[SCN^-]$ will be increased.

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Practice Problems – Describing the Shift Mechanism (page 87)

- 1. a. increases the reverse rate resulting in a net reverse reaction (shift left)
 - b. decreases the reverse rate resulting in a net forward reaction (shift right)
 - c. decreases the forward rate resulting in a net reverse reaction (shift left)
- 2. For example:

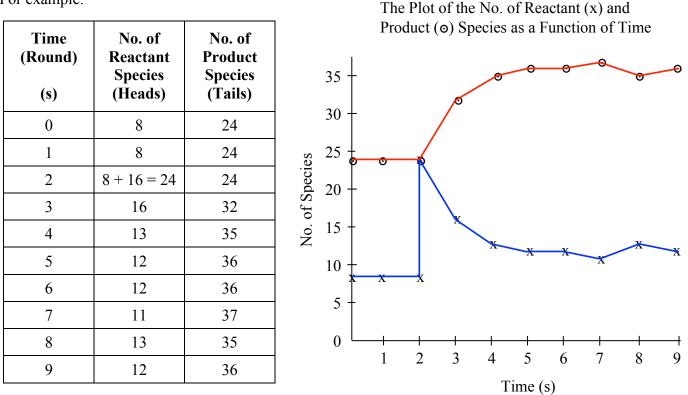


Quick Check (page 89)

- 1. For example: An equilibrium system subjected to a stress will restore equilibrium by partially alleviating the stress.
- 2. it will shift to replace some of the removed product
- 3. any action that has a different effect on the forward reaction rate than it does on the reverse reaction rate
- 4. it increases them both equally
- 5. True. This is a bit of a trick question. $[HNO_2]$ will be greater than $[H_2SO_3]$ regardless whether HNO_2 is the limiting reactant or it is the reactant in excess.

Activity 2.2: How an Equilibrium System 'Copes' With Stress (page 90)

For example:



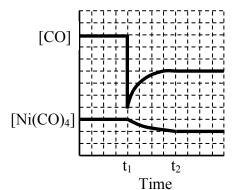
- 1. the number it rose to in Round 2 minus 15; the number it rose to in Round 2 minus 1
- 2. For example: 12

2.2 Review Questions (page 92)

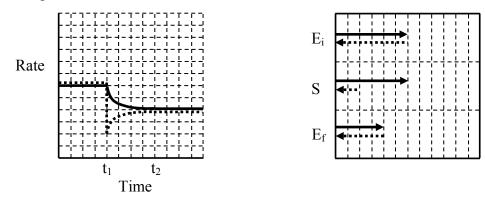
- 1. a. Equilibrium will be restored by removing some of the added NO
 - b. right
 - c. decreased
- a. the forward rate decreases resulting in a net reverse rate (shift left)
 b. decreased
- 3. $[Ag^+]$ and $[Ag(S_2O_3)_2^{3-}]$ will be increased. $[S_2O_3^{2-}]$ will be decreased. For example: Only some of the added Ag^+ is removed so its concentration increases. The system shifts left which decreases $[S_2O_3^{2-}]$ and increases $[Ag(S_2O_3)_2^{3-}]$.
- 4. a. The equilibrium would shift left thereby replacing some of the removed LDL and consuming some HDL in the process.
 - b. Either add some X or remove some Y
- 5. Decrease the wine's pH (by adding H^+).

		add NH ₃	remove some H ₂	add N ₂
	N_2	Increase	Increase	Increase
Equil. Conc.	H_2	Increase	Decrease	Decrease
cone.	NH ₃	Increase	Decrease	Increase

- a. Add H⁺ (the system would shift left if you add P⁻ or remove HP but you don't know whether the shift would undershoot the equilibrium's original position and leave the solution yellow, overshoot the equilibrium's original position and turn the solution red, or regain the equilibrium's original position and turn the solution orange.)
 - b. Add OH⁻ to remove (neutralize) some H⁺.
- 8. a. left
 - b. right
 - c. right
 - d. left
- 9. It increases the reverse rate by the same amount.
- 10. a. right
 - b. gradually turn green
- 11. For example:



12. For example:



13. Increase. Equilibrium 2 shifts towards products to remove some of the added H^+ . This \bigcirc Edvantage Interactive2012-09-207

decreases [NH₃] which in turn shifts equilibrium 1 left to replace some of the lost NH_3 . This increases [Cu²⁺].

- 14. The AgCH₃COO(*s*) would slowly disappear. Equilibrium 2 shifts towards products to remove some of the added H⁺. This decreases [CH₃COO⁻] which in turn shifts equilibrium 1 right to replace some of the lost CH₃COO⁻. This decreases the amount of AgCH₃COO(*s*).
- 15. if NO is in excess (O₂ is limiting)
- 16. For example: Continuously remove product as it is formed or continuously replace reactant as it is consumed.

2.3 How Equilibria Respond to Volume and Temperature Changes

Warm Up (page 96)

- 1. force per unit area
- 2. compress
- 3. average kinetic energy of the particles
- 4. frequently and more forcefully

Quick Check (page 97)

- 1. by shifting to relieve some of the added pressure
- 2. the gas's or solutes part of the total pressure or the pressure exerted by this gas or solute alone in a mixture of gases or solutes.
- 3. by shifting to replace some of the lost osmotic pressure

Practice Problems – Predicting How an Equilibrium Will Respond to a Volume Change (page 100)

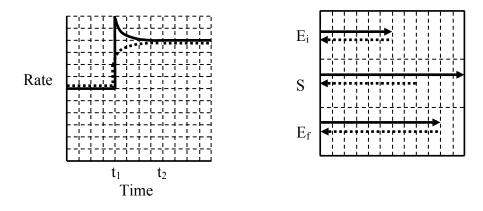
- 1. Left. Increased number of NOCl; decreased numbers of NO and Cl₂. All concentrations increased due to compression.
- 2. Right. Increased numbers of Ag^+ and $S_2O_3^{2-}$; decreased number of $Ag(S_2O_3)_2^{3-}$. All concentrations decreased.
- 3. No. The system cannot relieve any of the added pressure by shifting in either direction.

Practice Problems – Describing the Shift Mechanism Resulting From a Volume Change (page 102)

- 1. The reverse rate would increase more than the forward rate resulting in a net reverse reaction (shift left).
- 2. The reverse rate would decrease more than the forward rate resulting in a net forward reaction (shift right).

3. For example:

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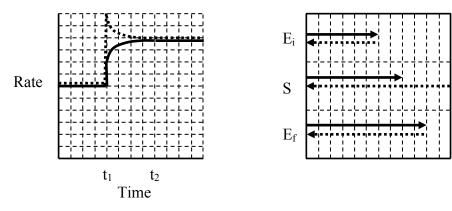


Practice Problems – Predicting How an Equilibrium Will Respond to a Temperature Change (page 104)

- 1. Left. Increased [SO₂] and [O₂]; decreased [SO₃].
- 2. Right. Increased [HI]; decreased [H₂] and [I₂].

Practice Problems – Describing the Shift Mechanism Resulting From a Temperature Change (page 107)

- 1. The reverse rate would increase more than the forward rate resulting in a net reverse reaction (shift left).
- 2. The forward rate would decrease more than the reverse rate resulting in a net reverse reaction (shift left).
- 3. For example:



Quick Check (page 109)

- 1. Ammonia
- 2. adding a catalyst

2.3 Activity: Dealing With Pressure (page 111)

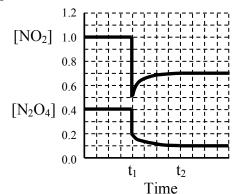
The equilibrium responds to the compression by shifting left to relieve some of the added pressure. Diagram 3 (Final Equilibrium) should thus have $(10 - 2x) \text{ NO}_2$ molecules and $(4 + x) \text{ N}_2\text{O}_4$ molecules where x = 1, 2, 3, or 4. For example, the final equilibrium mixture might

have 4 NO_2 molecules and $7 \text{ N}_2\text{O}_4$ molecules. After becoming a darker orange when compressed (Stress), the mixture lightens as the system shifts to the left to restore equilibrium (Final Equilibrium).

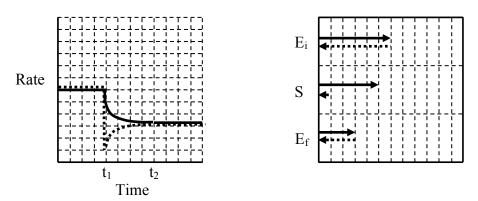
- 1. decreases; increases.
- 2. The molecules are bouncing around inside the syringe. NO_2 molecules are colliding together and forming N_2O_4 molecules at the same rate that individual N_2O_4 molecules are breaking apart to form NO_2 molecules.
- 3. The mixture would become paler. The equilibrium shifts left to replace some of its lost K.E. and warm itself.

2.3 Review Questions (page 111)

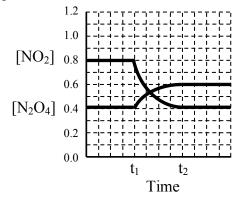
- a. The equilibrium will shift left to replace some of the lost osmotic pressure.
 b. increased number of SCN⁻ ions; decreased [SCN⁻]
- 2. The reverse reaction rate decreases more than the forward reaction rate (greater sum of reaction coefficients) resulting in a net forward reaction (shift right).
- 3. The equilibrium will shift left to relieve some of the added pressure. (Note that the carbon atoms are in the solid phase.) The reverse reaction rate increases more than the forward reaction rate resulting in a net reverse reaction (shift left).
- 4. When the system's volume changes but the sum of the gaseous or aqueous reactant coefficients equals the sum of the gaseous or aqueous product coefficients in the balanced equation.
- 5. For example:



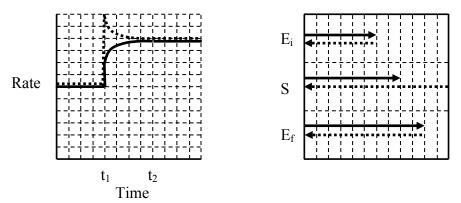
6. For example:



- 7. Less soluble. Increasing the temperature shifts the equilibrium to the left to remove some of the added kinetic energy and cool itself.
- 8. Right. Le Chatelier's Principle: Increasing the temperature shifts the equilibrium to the right to remove some of the added kinetic energy and cool itself. Chemical Kinetics: Increasing the temperature increases the forward reaction rate more than the reverse reaction rate resulting in a net forward reaction (shift right).
- 9. For example:



10. For example:

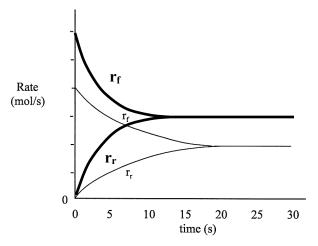


- 11. Endothermic. A decrease in temperature shifts an equilibrium in the exothermic direction to replace some of the lost kinetic energy and warm itself up. Cooling shifted this equilibrium to the left therefore the reverse reaction is exothermic and the forward reaction is endothermic.
- 12. a. left
 - b. it was heated
- 13. Decreasing the temperature decreases the reverse reaction rate more than the forward reaction rate resulting in a net forward reaction (shift right).
- 14. An equilibrium's endothermic direction has a higher activation energy than its exothermic direction.
- 15. high temperature; low pressure

16. Lower temperatures slowly generate a high percent yield whereas higher temperatures quickly generate a low percent yield.

		Decrease Volume	Decrease Temperature
	N_2	Increase	Decrease
Equil. Conc.	H_2	Increase	Decrease
cone.	NH ₃	Increase	Increase
	N_2	Decrease	Decrease
Equil. No.	H_2	Decrease	Decrease
1.0.	NH ₃	Increase	Increase

18. Note: the forward rate is greater at the start of the reaction and equilibrium is achieved sooner with greater forward and reverse rates.



19. a. left

- b. left
- c. right
- d. right
- 20. a. left
 - b. The shift would cause the piston to fall further. (In this situation, the shift would result in the volume decreasing at a constant pressure rather than decreasing the pressure in a constant volume.)

2	1	
_	_	-

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.4 \text{ kJ/mol}$				
Starses	Le Chatelier Predicts		Chemical Kinetics Explains	
Stress	Response	Shift	Effect	Net Rx
add H ₂	remove some of the added H ₂	right	increase r _f	net forward rx
add NH ₃	remove some of the added NH ₃	left	increase r _r	net reverse rx
remove N ₂	replace some of the removed N ₂	left	decrease r _f	net reverse rx
decrease volume (compress)	relieve some of the added pressure	right	increase r _f more than r _r	net forward rx
decrease temperature	replace some of the lost K.E.	right	decrease r _r more than r _f	net forward rx

- 22. a. left
 - b. right
 - c. left
 - d. right

2.4 Entropy Change verses Enthalpy Change

Warm Up (page 117)

- 1. Rubik's cube organized
- 2. Messy room disorganized
- 3. Leaf pile organized
- 4. Einstein's hair disorganized
- 5. Junk drawer disorganized
- 6. Library shelves organized
- 7. Crowded street disorganized
- 8. Checker board organized

Quick Check (page 119)

- 1. a substance's or system's state of disorganization or randomness
- 2. A perfect crystal at zero degrees Kelvin has 0 entropy.
- 3. Ag because more electrons provide more positional variability
- 4. H₂O₂ because larger and more complex molecules have more possible configurations (ways of positioning their parts relative to each other).

Practice Problems – Predicting by Inspection Whether Entropy Increases or Decreases (page 121)

- 1. increases because the number of gas molecules increases $(0 \rightarrow 1)$
- 2. increases because the sulphur atoms go from being in a solid to being in a gas as well as splitting up to become part of 8 separate molecules.
- 3. increases because this is simply a solid melting $(s \rightarrow l)$

Practice Problems – Predicting an Equilibrium's Position from its Thermodynamics or Vice-Versa (page 125)

- 1. not occur (both drives towards reactants)
- 2. exothermic (the drive towards increasing entropy is towards reactants therefore the drive towards decreasing enthalpy must be towards products)
- 3. entropy decreases (the drive towards decreasing enthalpy is towards products therefore the drive towards increasing entropy must be towards reactants)

2.4 Review Questions (page 126)

- 1. a. $Br_2(g)$ because gases have more entropy than liquids
 - b. $SO_3(g)$ because larger and more complex molecules have more possible configuration
 - c. Pb(s) because more electrons provide more positional variability
- 2. a. increasing because the number of gas molecules increases $(2 \rightarrow 4)$
 - b. increasing because common items split up (Cl atoms go from being together in 1 molecule to being in 2 separate molecules. Unable to verify with standard entropies because NOCl₂ is an unstable reaction intermediate with no standard entropy value available.)
 - c. decreasing because the number of gas molecules decreases $(3 \rightarrow 0)$
 - d. increasing because common items split up
 - e. increasing because the oxygen atoms go from being in a solid to being in a gas.
- 3. a. completion (both drives towards products)
 - b. not occur (both drives towards reactants)
 - c. equilibrium (enthalpy decreases towards products & entropy increases towards reactants)
 - d. completion (both drives towards products)
- 4. endothermic; entropy increases towards products therefore enthalpy must decrease towards reactants
- 5. an endothermic reaction in which entropy decreases (entropy increases and enthalpy decreases towards reactants)
- 6. increasing; enthalpy decreases towards reactants therefore entropy must increase towards products
- 7. right; entropy increases towards reactants therefore enthalpy must decrease towards products. The equilibrium will shift in the exothermic direction to replace some of the lost kinetic energy and warm itself.
- 8. Maximum entropy is achieved just short of the completed reaction because even if the

entropy of the products is much greater than the entropy of the reactants, a mixture containing a very small proportion of reactants will have a greater entropy than products alone.

2.5 The Equilibrium Constant

Warm Up (page 130)

- 1. 3.1422. $e = mc^2$
- 3. Avogadro's number, N, 6.02×10^{23}
- 4. The accuracy of values derived from constants is limited by the accuracy of the constants.

Practice Problems – Determining Keq from the Equilibrium Concentrations (page 132)

1.
$$Keq = [H_2][I_2] = (4.56 \times 10^{-3}) (7.4 \times 10^{-4}) = 0.019$$

[HI]² (1.35 x 10⁻²)²

- 2. a. $Keq = [N_2O_4] = (1.73 \times 10^{-4}) = 11.5$ $[NO_2]^2 = (3.88 \times 10^{-3})^2 = 11.5$
 - b. exothermic; When cooled, equilibria shift in the exothermic direction to replace some of the lost kinetic energy and warm themselves. The higher Keq indicates this reaction shifted to the right at the lower temperature therefore the forward reaction is exothermic.

3.
$$Keq = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.14)^2}{(0.020)[H_2]^3} = 1.7 \times 10^2$$

$$[H_2]^3 = \frac{(0.14)^2}{(0.020)(1.7 \times 10^2)} = 5.76 \times 10^{-3}$$

 $[H_2] = 0.18 \text{ M}$

Quick Check (page 135)

- 1. a. right
- b. no change 2. left; decrease; decrease
- 3. false

Quick Check (page 136)

1.
$$Keq = [\underline{H_2O}]^3$$

 $[B_2H_6][O_2]^3$
2. $Keq = [\underline{Cl_2}]^2[\underline{H_2O}]^2$
 $[HCl]^4[O_2]$

3.
$$Keq = [HBr]^2$$

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[H₂]
4. *Keq* =
$$[Ca^{2+}][CO_3^{2-}]$$

Quick Check (page 137)

- 1. $\frac{1}{0.018} = 56$
- 2. $\sqrt{0.018} = 0.13$
- 3. $\sqrt{55.56} = 7.5$

Practice Problems – Determining the Direction a System Will Proceed to Achieve Equilibrium, Given its Reactant and Product Concentrations (page 138)

1. Trial $Keq = \frac{[CO] [H_2]^3}{[CH_4] [H_2O]} = \frac{(0.10) (0.30)^3}{(0.025) (0.045)} = 2.4$

2.4 < 4.7 therefore the reaction will proceed to the right to achieve equilibrium

- 2. Trial $Keq = [N_2O_4] = (4.0 \text{ mol} / 0.50 \text{ L}) = 0.89$ $[NO_2]^2 = (1.5 \text{ mol} / 0.50 \text{ L})^2 = 0.89$ 0.89 < 0.940 therefore the reaction will proceed to the right to achieve equilibrium
- 3. $Keq = [H^+][SO_4^{2-}] = (0.10)(0.10) = 0.012$ [HSO₄⁻] (0.83)

Trial Keq = (0.10)(0.20) = 0.022(0.93)

0.022 > 0.012 therefore the system will shift left to restore equilibrium, increasing the [HSO₄⁻].

Quick Check (page 139)

- 1. completely
- 2. partially
- 3. completely

2.5 Activity: What's My Constant? (page 140)

- * The 'Easy' matrix is messed up in the complimentary copy of the worktext (sorry!). The columns (A,B,C) should actually be the rows (Set 1,2,3). The 'Challenging' matrix also has one mistake in the complimentary copy. In the 'Challenging' matrix, A = 14 not 12, in Set 3.
- 1. (Easy) A + B + C = 30
- 2. (Challenging) $\underline{B+C} = 8$

(Really Hard) $(B - A)^2 - C = 16$

Results and Discussion

3. In this situation, it's not about getting the right answer; it's about getting the same answer. If your expression provides the same answer each time then it is correct.

2.5 Review Questions (page 142)

- 1. At equilibrium $r_f = r_r$ therefore: 2.7 x 10⁻³ [N₂O₅] = 4.3 x 10⁻² [NO₂] [NO₃] $Keq = [NO_2][NO_3] = 2.7 \times 10^{-3} = 0.063$ [N₂O₅] = 4.3 x 10⁻²
- 2. No. The coefficients in a balanced chemical equation provide the ratio in which the reactants are consumed and the products are formed. The chemical equation in this question tells us that for each Cl₂ that reacts, 2 NO are consumed and 2 NOCl are produced but it provides no information about the ratio of the reactants and products present at equilibrium.
- 3. a. $Keq = [\underline{H}^+] [\underline{NO_2}^-]$ [HNO₂]

b.
$$Keq = [SO_2]^2 [O_2] [SO_3]^2$$

c.
$$Keq = [NO]^4 [H_2O]^6 [NH_3]^4 [O_2]^5$$

- 4. $Keq = \underline{[C_2H_2][H_2]^3} = \underline{(0.59 \text{ mol} / 2.0 \text{ L})(1.4 \text{ mol} / 2.0 \text{ L})^3}_{(0.38 \text{ mol} / 2.0 \text{ L})^2} = 2.8$
- 5. a. $[COBr_2] = 0.060 \text{ M}; [CO] = 0.030 \text{ M}; [Br_2] = 0.040 \text{ M}$ b. to replace some of the lost pressure c. $Keq = [CO] [Br_2] = (0.060) (0.080) = 0.040$ at equilibrium initially $[COBr_2] = (0.040) (0.050) = 0.040$ when equilibrium is restored (0.050)
- 6. $Keq = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[NH_3]^2}{(0.65)(0.85)^3} = 0.017$
 - $[NH_3]^2 = (0.017) (0.65) (0.85)^3 = 6.79 \times 10^{-3}$ $[NH_3] = \sqrt{6.79 \times 10^{-3}} = 0.082 \text{ M}$
- 7. Trial $Keq = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(8.0)^2}{(4.0)(3.0)^3} = 0.59$

 $0.59 \le 1.0$ therefore the reaction must proceed to the right to achieve equilibrium

8. a.
$$Keq = \frac{[H_2] [Fe^{2^+}]}{[H^+]^2}$$

b. $Keq = \frac{[CI^-]^2}{[\Gamma^-]^2 [Cl_2]}$
c. $Keq = \frac{1}{[CO_2]}$
d. $Keq = \frac{[CO_2(aq)]}{[CO_2(g)]}$
e. $Keq = [O_2]$
9. a. $Cl_2(g) \rightleftharpoons Cl_2(aq)$
b. $NH_4NO_2(s) \rightleftharpoons N_2(g) + 2H_2O(g)$
c. $CCl_4(g) \rightleftharpoons C(s) + 2Cl_2(g)$
d. $Keq = \frac{[Cl_2](aq)}{[Cl_2(g)]}$
c. $CCl_4(g) \rightleftharpoons C(s) + 2Cl_2(g)$
c. $CCl_4(g) \rightleftharpoons C(s) + 2Cl_2(g) \Leftrightarrow 2MgSO_4(s)$
c. $CCl_4(g) \doteq 125$

b.
$$\frac{1}{8.0 \times 10^{-2}} = 12.5$$

c. $\sqrt{12.5} = 3.5$

- 11. a. no effect
 - b. no effect
 - c. decrease
 - d. no effect
- 12. No. An equilibrium's position depends upon the initial reactant concentrations as well as the equilibrium constant. The lower the initial $[H_2O(g)]$, the greater the percent yield at equilibrium. Calculations reveal that if the initial $[H_2O(g)]$ is 1.0 M then there will be a 33% yield at equilibrium so the reactants are favoured but if the initial $[H_2O(g)]$ is only 0.10 M then there will be a 70% yield at equilibrium so the products are favoured. From Le Chatelier's perspective, lowering the concentrations causes a shift to the right to replace some of the lost pressure.
- 13. No. It is difficult to make meaningful comparisons between the equilibrium constants of different equilibria unless their expressions have identical forms. Calculations reveal that if each reaction's initial reactant concentration is 1.0 M then both of these equilibria will have a 50% yield at equilbrium.

- 14. a. same (It increases forward and reverse rates equally.)
 - b. same (There is only one chemical in the equilibrium expression so all of the lost O_2 is replaced.)
 - c. decreased (The equilibrium shifts to the left to replace some of the lost K.E.)

2.6 Equilibrium Problems

Warm Up (page 146)

Keq = 0.128	$N_2(g) +$	$3Cl_2(g) =$	$= 2NCl_3(g)$
Ι	3.0	11.0	0
С	- 2.0	- 6.0	+ 4.0
Е	1.0	5.0	4.0

$$Keq = \frac{[NCl_3]^2}{[N_2] [Cl_2]^3} = \frac{(4.0)^2}{(1.0) [Cl_2]^3} = 0.128$$
$$[Cl_2]^3 = 125 \qquad [Cl_2] = 5.0$$

Practice Problems – Determining Keq from the Initial Concentrations and One Equilibrium **Concentration** (page 148)

1.					
		$N_2(g)$ +	$+$ 3H ₂ (g) \rightleftharpoons	= 2NH ₃ (g	g)
	Ι	2.00	2.50	0	
	С	- 0.60	- 1.80	+ 1.20)
	Е	1.40	0.70	1.20	
	Keq = _	$\frac{[\rm NH_{3}]^{2}}{[\rm N_{2}] [\rm H_{2}]^{3}} =$	$= \frac{(1.20)}{(1.40)(0.7)}$	$\frac{2}{70)^3} = 3$.0
2.		$Ag^{+}(aq)$	$+ 2S_2O_3^2$	(aq) =	$= Ag(S_2O_3)_2^{3-}$
	Ι	0.80	1.3	30	0
	С	- 0.35	- 0.	.70	+ 0.35
	Е	0.45	0.6	50	0.35
$Keq = \frac{[Ag(S_2O_3)_2^{3-}]}{[Ag^+] [S_2O_3^{2-}]^2} = \frac{(0.35)}{(0.45) [0.60]^2} = 2.2$					
		2C(s) +	$-O_2(g) =$	≐ 2CO(g	g)
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3.	Ι	 1.4	0
	С	- 0.20	+0.40
	Е	1.2	0.40

6.0 g C - 1.2 g C = 4.8 g C consumed 4.8 g C x $\frac{1 \mod C}{12.0 \text{ g C}}$ = 0.40 mol C consumed 0.40 mol C x $\frac{1 \mod O_2}{2 \mod C}$ = 0.20 mol O₂ consumed $Keq = \frac{[CO]^2}{[O_2]} = \frac{(0.40)^2}{1.2}$ = 0.13

Practice Problems – Determining the Equilibrium Concentrations from *Keq* and the Initial Concentrations (page 152)

1.

	2HCl(g) =	\doteq H ₂ (g) +	$- \operatorname{Cl}_2(g)$	
Ι	1.5	0	0	
С	- 2x	+ x	+ x	
Е	1.5 – 2x	Х	Х	
$Keq = [H_2][Cl_2] = \frac{x^2}{(1.5 - 2x)^2} = 0.36$				

$$\frac{x}{1.5 - 2x} = \sqrt{0.36} = 0.60$$

x = 0.60 (1.5 - 2x) = 0.90 - 1.2x

0.41

2.2x = 0.90

$$\mathbf{x} = \frac{0.90}{2.2} =$$

 $0.41 \frac{\text{mol } \text{Cl}_2}{\text{L}} \ge 3.00 \text{ L} = 1.2 \text{ mol } \text{Cl}_2$

	$H_2(g) + C_2N_2(g) \rightleftharpoons 2HCN(g)$				
Ι	2.00	2.00	4.00		
С	- x	- x	+2x		
Е	2.00 - x	2.00 - x	4.00 + 2x		

Trial
$$Keq = \frac{[\text{HCN}]^2}{[\text{H}_2] [\text{C}_2\text{N}_2]} = \frac{(4.00)^2}{(2.00)^2} = 4.00$$

4.00 < Keq = 5.00 therefore this reaction must proceed to the right to achieve equilibrium. * For the record, this trial *Keq* calculation isn't actually necessary because if you shift the system in the wrong direction then you'll get a negative value for 'x' that will still provide the correct equilibrium concentrations. The algebra is "idiot proof".

$$Keq = \frac{(4.00 + 2x)^2}{(2.00 - x)^2} = 5.00$$

$$\frac{4.00 + 2x}{2.00 - x} = \sqrt{5.00} = 2.24$$

$$4.00 + 2x = 2.24 (2.00 - x) = 4.48 - 2.24x$$

$$4.24x = 0.48$$

$$x = \frac{0.48}{4.24} = 0.11$$

$$[C_2N_2]_{eq} = 2.00 - 0.11 = 1.89 \text{ M}$$

	$H_2(g) =$	+ $\operatorname{Cl}_2(g) =$	= 2HCl(g)
Eo	6.00	6.00	12.0
Ι	6.00	6.00	5.00
С	- x	- x	+ 2x
E_{f}	6.00 - x	6.00 - x	5.00 + 2x

$$Keq = \frac{[\text{HCl}]^2}{[\text{H}_2] [\text{Cl}_2]} = \frac{(12.0)^2}{(6.0)^2} = 4.0$$

The system will shift to the right to replace some of the lost HCl.

$$Keq = \frac{(5.00 + 2x)^2}{(6.00 - x)^2} = 4.00$$

$$\frac{5.00 + 2x}{6.00 - x} = \sqrt{4.00} = 2.00$$

$$5.00 + 2x = 2.00 (6.00 - x) = 12.0 - 2.00x$$

$$4.00x = 7.0$$

$$x = \frac{7.0}{4.00} = 1.75$$

$$[HCl]_{eq} = 5.00 + 2(1.75) = 8.5 \text{ M}$$

Practice Problems – Determining the Initial Concentrations from *Keq* **and the Equilibrium Concentrations** (page 154)

	$2NiS(s) + 3O_2(g) \Rightarrow 2SO_2(g) + 2NiO(s)$				
Ι	$\left \right $	Х	0	$\Big $	
С	\langle	- 0.27	+ 0.18	\langle	
Е		x - 0.27	0.18		

$$Keq = \underline{[SO_2]^2}_{[O_2]^3} = \underline{(0.18)^2}_{(x-0.27)^3} = 0.30$$

$$\frac{(0.18)^2}{0.30} = (x - 0.27)^3 = 0.108$$

x - 0.27 = (0.108)^{1/3} = 0.476
x = 0.476 + 0.27 = 0.75
[O₂]_i = 0.75 M

2.

	2HI(g) =	$H_2(g)$	- I ₂ (g)
Ι	0.60 + 2x	0	0
С	- 2x	+ x	+ x
Е	0.60	Х	Х

$$Keq = \underline{[H_2][I_2]}_{[HI]^2} = \frac{x^2}{(0.60)^2} = 0.25$$
$$x^2 = (0.60)^2 (0.25) = 0.090$$
$$x = \sqrt{0.090} = 0.30$$
$$[HI]_i = 0.60 + 2(0.30) = 1.2 \text{ M}$$

$$2SO_{2}(g) + O_{2}(g) \rightleftharpoons 2SO_{3}(g)$$

$$\boxed{I \quad 0.050 + 2x \quad 0.040 + x \quad 0}$$

$$\boxed{C \quad -2x \quad -x \quad +2x}$$

$$\boxed{E \quad 0.050 \quad 0.040 \quad 2x}$$

$$Keq = \frac{[SO_{3}]^{2}}{[SO_{2}]^{2}[O_{2}]} = \frac{(2x)^{2}}{(0.050)(0.040)} = 100$$

$$4x^{2} = 100(0.050)(0.040) = 0.20$$

$$x^{2} = \frac{0.20}{4} = 0.050$$

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 $x = \sqrt{0.050} = 0.22$ $[O_2]_i = 0.040 + 0.22 = 0.26 M$

2.6 Activity: Visualizing Equilibria (page 155)

- 1. The equilibrium concentrations are independent of the direction from which equilibrium is achieved.
- 2. <u>6</u> = 1.5
 - 4
- 3. 28; Easily solved by trial and error or the following algebraic solution: Let the no. of 'A' molecules = xThe total no. of molecules = 20 + 50 = 70Therefore the no. of 'B' molecules = 70 - x

$$\frac{70 - x}{x} = 1.5$$

1.5 x = 70 - x
2.5 x = 70
x = $\frac{70}{2.5} = 28$

4. endothermic; Decreasing the temperature shifts an equilibrium in the exothermic direction (to replace some of the lost kinetic energy) which in this case was to the left therefore the forward reaction is endothermic.

2.6 Review Questions (page 157)

1	
I	•

a.	$2\mathrm{CH}_4(g) \rightleftharpoons \mathrm{C}_2\mathrm{H}_2(g) + 3\mathrm{H}_2(g)$		
Ι	6.0	0	0
С	- 3.0	+ 1.5	+ 4.5
Е	3.0	1.5	4.5

b.	N ₂ (g) +	\Rightarrow 3H ₂ (g) \Rightarrow	$= 2NH_3(g)$
Ι	2.5	5.0	0
С	- 0.5	- 1.5	+ 1.0
Е	2.0	3.5	1.0

		$2NO_2(g) \rightleftharpoons N_2O_4(g)$	
I	_	3.0	0
0	2	-2.4	+ 1.2
E	Ξ	0.6	1.2

a.
$$[NO_2]_{eq} = 0.6 \text{ M}$$

b. $Keq = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1.2}{(0.6)^2} = 3$

3.

	$A^{2+}(aq) + 3B^{-}(aq) \Rightarrow AB_{3}^{-}(aq)$		
Ι	1.80	3.40	0
С	- 1.00	- 3.00	+ 1.00
Е	0.80	0.40	1.00

a.
$$[A^{2^+}]_{eq} = 0.80 \text{ M}$$

b. $Keq = \frac{[AB_3^-]}{[A^{2^+}][B^-]^3} = \frac{1.00}{(0.80)(0.40)^3} = 20.$

4. a.

Keq = 1.20	$H_2(g) +$	$C_2N_2(g) =$	\Rightarrow 2HCN(g)
Ι	6.5	3.0	0
С	- 1.5	- 1.5	+ 3.0
Е	5.0	1.5	3.0

$$Keq = \frac{[\text{HCN}]^2}{[\text{H}_2] [\text{C}_2\text{N}_2]} = \frac{[\text{HCN}]^2}{(5.0) (1.5)} = 1.20$$
$$[\text{HCN}]^2 = (1.20) (5.0) (1.5) = 9.0$$
$$[\text{HCN}] = \sqrt{9.0} = 3.0$$

b.

Keq = 1.20	$H_2(g) +$	$C_2N_2(g) =$	\Rightarrow 2HCN(g)
Ι	5.4	4.8	0
С	- 1.8	- 1.8	+ 3.6
Е	3.6	3.0	3.6

$$Keq = \frac{[\text{HCN}]^2}{[\text{H}_2] [\text{C}_2\text{N}_2]} = \frac{(3.6)^2}{(3.6) [\text{C}_2\text{N}_2]} = 1.20$$
$$[\text{C}_2\text{N}_2] = \frac{3.6}{1.2} = 3.0$$

5.

	$G3P(aq) \rightleftharpoons DHAP(aq)$	
Ι	0.020	0.020
С	- x	+ x
Е	0.020 - x	0.020 + x

Trial Keq = [DHAP] = 0.020 = 1.0 (obvious by inspection)

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1.0 < 19 therefore the system must proceed to the right to achieve equilibrium

$$\frac{0.020 + x}{0.020 - x} = 19$$

$$0.020 + x = 19 (0.020 - x) = 0.38 - 19x$$

$$20x = 0.36$$

$$x = \frac{0.36}{20} = 0.018$$

$$[G3P] = 0.020 - 0.018 = 0.002 M$$

$$[DHAP] = 0.020 + 0.018 = 0.038 M$$

6.

	$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$			
Ι	0.600	0.600	0.600	
С	- X	- x	+ x	+ x
Е	0.600 - x	0.600 - x	0.600 + x	0.600 + x

Trial $Keq = [H_2O][CO] = (0.600)^2 = 1.00$ (obvious by inspection) [H₂][CO₂] = (0.600)²

1.00 < 1.69 therefore this system must proceed to the right to achieve equilibrium

$$\frac{(0.600 + x)^2}{(0.600 - x)^2} = 1.69$$

$$\frac{0.600 + x}{0.600 - x} = \sqrt{1.69} = 1.30$$

$$0.600 + x = 1.30 (0.600 - x) = 0.780 - 1.3x$$

$$2.3x = 0.180$$

$$x = \frac{0.180}{2.3} = 0.078$$

$$[H_2] = 0.600 - 0.078 = 0.522 M$$

$$[CO] = 0.600 + 0.078 = 0.678 M$$

1	
1	•

Keq = 1.20	$H_2(g) + C_2N_2(g) \approx 2HCN(g)$		
Ι	1.44	1.44	0
С	- x	- x	+2x
Е	1.44 – x	1.44 – x	2x

$$Keq = \frac{[\text{HCN}]^2}{[\text{H}_2] [\text{C}_2\text{N}_2]} = \frac{(2x)^2}{(1.44 - x)^2} = 1.20$$

$$\underline{2x} = \sqrt{1.20} = 1.10$$

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25

$$1.44 - x$$

$$2x = 1.10 (1.44 - x) = 1.58 - 1.10x$$

$$3.1x = 1.58$$

$$x = \frac{1.58}{3.10} = 0.510$$

[HCN] = 1.02 M

8.

		$H_2(g)$ -	$+$ F ₂ (g) \rightleftharpoons	$= 2 \mathrm{HF}(g)$	
	Ι	2.0	2.0	0	
	С	- x	- x	+2x	
	Е	2.0 - x	2.0 - x	2x	
_	$Keq = \frac{[\text{HF}]^2}{[\text{H}_2] [\text{F}_2]} = \frac{(2x)^2}{(2.0 - x)^2} = 121$ $\frac{2x}{2.0 - x} = \sqrt{121} = 11.0$				
		1.0(2.0-x)	= 22.0 - 11	1.0x	
	13.0x =	= 22.0			
$x = \frac{22.0}{13.0} = 1.69$					
$[H_2] = 2.0 - 1.69 = 0.31 \text{ M}$					
($0.31 \text{ mol}_{L} \ge 0.62 \text{ mol}_{H_2}$				

		$2BN(s) + 3Cl_2(g) \rightleftharpoons 2BCl_3(g) + N_2(g)$							
	Ι	$\left \right $	0.84	0	0				
	С		- 3x	+2x	+ x				
	Е	/	0.84 - 3x	2x	х				
	$Keq = \underline{[BCl_3]^2 [N_2]}_{[Cl_2]^2} = \underline{(2x)^2 (x)}_{(0.84 - 3x)^3} = 0.045$								
$\frac{4x^3}{(0.84-3x)^3} = 0.045$									
_	$\underline{1.587x}_{=} = (0.045)^{1/3} = 0.3557$								

$$0.84 - 3x$$

1.587x = 0.3557 (0.84 - 3x) = 0.299 - 1.067x2.654x = 0.299 $x = \frac{0.299}{2.654} = 0.1126$

- a. $[BCl_3] = 2(0.1126) = 0.23 \text{ M}$ (rounded off to the appropriate number of sig.figs.)
- b. No, the reaction would run out of BN(s) and thus go to completion before reaching equilibrium. The flask only contains 1.0 g BN(s) but 1.40 g are required to achieve equilibrium as shown in the following calculations:

 $3x = 3 (0.1126) = 0.3378 \text{ M Cl}_2$ is consumed achieving equilibrium

 $\begin{array}{r} 0.3378 \ \underline{\text{mol } Cl_2} \ x \ 0.250 \ \text{L} = \ 0.08445 \ \text{mol } Cl_2 \ \text{reacted} \\ 1.008445 \ \text{mol } Cl_2 \ x \ \underline{2 \ \text{mol } BN} \ 3 \ \underline{3 \ \text{mol } Cl_2} \ x \ \underline{24.8 \ \text{g } BN} \ = \ 1.40 \ \text{g } BN \\ 1 \ \text{mol } BN \end{array}$

10. For example:

	$2CH_4(g) \rightleftharpoons C_2H_2(g) + 3H_2(g)$			Trial Keq
Ι	0	0.60	0.60	-
С	+ 2x	- x	- 3x	-
E?	0.10	0.55	0.45	5.0 🗵
E?	0.16	0.52	0.36	0.95 🗵
E?	0.12	0.54	0.42	2.8 🗹

$$Keq = [\underline{C_2H_2}][\underline{H_2}]^3 = (0.54)(0.42)^3 = 2.8$$
$$(0.12)^2$$

11.

	$H_2(g)$ +	$ Cl_2(g) =$	= 2HCl(g)
Eo	3.00	3.00	7.50
Ι	3.00	3.00	4.00
С	- X	- X	+ 2x
E_{f}	3.00 - x	3.00 - x	4.00 + 2x

$$Keq = \frac{[\text{HCl}]^2}{[\text{H}_2] [\text{Cl}_2]} = \frac{(7.50)^2}{(3.00)^2} = 6.25$$

$$Keq = \frac{(4.00 + 2x)^2}{(3.00 - x)^2} = 6.25$$

$$\frac{4.00 + 2x}{(3.00 - x)^2} = \sqrt{6.25} = 2.50$$

$$4.00 + 2x = 2.50 (3.00 - x) = 7.50 - 2.50x$$

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$$4.50x = 3.50$$
$$x = \frac{3.50}{4.50} = 0.778$$

- a. $[H_2] = [Cl_2] = 3.00 0.778 = 2.22 \text{ M}$ [HCl] = 4.00 + 2(0.778) = 5.56 M
- b. The system shifted to the right and replaced some of the removed HCl.

12.

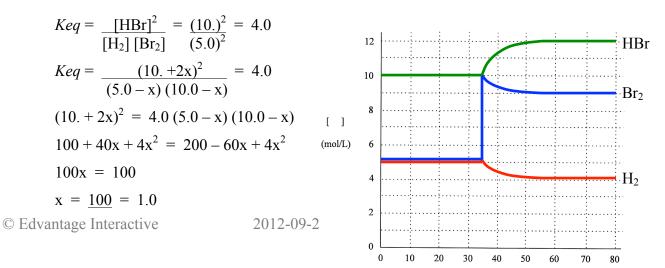
	$\operatorname{Fe}^{3+}(aq) + \operatorname{SCN}^{-}(aq) \rightleftharpoons \operatorname{FeSCN}^{2+}(aq)$			
Eo	0.10	0.10	1.8	
Ι	0.040	0.040	0.72	
С	+ x	+ x	- X	
E_{f}	0.040 + x	0.040 + x	0.72 - x	

$$Keq = \underline{[FeSCN^{2+}]}_{[Fe^{3+}]} [SCN^{-}] = \underline{1.8}_{(0.10)^2} = 180$$

* $Keq = \frac{0.72 - x}{(0.040 + x)^2} = 180$ (*This equation is sufficient for the answer) 0.72 - x = 180 (0.040 + x)^2 = 180 (0.0016 + 0.08x + x^2) = 0.288 + 14.4x

 $0.72 - x = 180 (0.040 + x)^2 = 180 (0.0016 + 0.08x + x^2) = 0.288 + 14.4x + 180x^2$ $180x^2 + 15.4x - 0.432 = 0$

	$H_2(g)$	+ Br ₂ (g) =	\doteq 2HBr(g)
Eo	5.0	5.0	10.
Ι	5.0	10.0	10.
C	- X	- x	+ 2x
Ef	5.0 - x	10.0 - x	10. + 2x



 $\begin{array}{l} 100 \\ [H_2] = 5.0 - 1.0 = 4.0 \mbox{ M} \\ [Br_2] = 10.0 - 1.0 = 9.0 \mbox{ M} \\ [HBr] = 10. + 2(1.0) = 12 \mbox{ M} \end{array}$

14.

	$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$		
Ι	Х	0	0
С	- 3.60	+ 3.60	+ 1.80
Е	x - 3.60	3.60	1.80

$$[SO_3]^2 (x - 3.60)^2$$

$$\frac{(3.60)^2 (1.80)}{3.83 \times 10^{-2}} = (x - 3.60)^2$$

$$609 = (x - 3.60)^2$$

$$\sqrt{609} = 24.7 = x - 3.60$$

$$x = 28.3$$

a.
$$[SO_3]_{eq} = 28.3 - 3.60 = 24.7 \text{ M}$$

b.
$$28.3 \mod_L x \ 0.500 \text{ L} = 14.2 \text{ mol}$$

15.

		$H_2(g)$ -	+ $I_2(g) \rightleftharpoons$	= 2HI(g)	
	Ι	Х	Х	0	
	С	- 0.50	- 0.50	+ 1.0	
	Е	x - 0.50	x - 0.50	1.0	
$Keq = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.0)^2}{(x - 0.50)^2} = 4.0$					
	$\frac{1.0}{x - 0.50} = \sqrt{4.0} = 2.0$				

$$1.0 = 2.0 (x - 0.50)$$
$$1.0 = 2.0x - 1.0$$

$$2.0x = 2.0$$

$$x = \frac{2.0}{2.0} = 1.0$$

$$[H_2]_i = 1.0 M$$

16. © Edvantage Interactive $Keq = [SO_2]^2 [O_2] = (3.60)^2 (1.80) =$

$$PCl_{5}(g) \rightleftharpoons PCl_{3}(g) + Cl_{2}(g)$$

$$I \qquad x \qquad 0 \qquad 0$$

$$C \qquad -1.50 \qquad +1.50 \qquad +1.50$$

$$E \qquad x - 1.50 \qquad 1.50 \qquad 1.50$$

$$Keq = \underline{[PCl_{3}][Cl_{2}]}_{[PCl_{5}]} = \underline{(1.50)^{2}}_{(x - 1.50)} = 2.14$$

2.25 = 2.14 (x - 1.50) = 2.14x - 3.212.14x = 5.46

$$x = \frac{5.46}{2.14} = 2.55$$

 $[PCl_5]_i = 2.55 \text{ M}$

	$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$		
Eo	0.24	0.10	1.20
Ι	0.24	0.10 + x	1.20
С	- 0.10	- 0.05	+ 0.10
E_{f}	0.14	0.05 + x	1.30

$$Keq = \frac{[NO_2]^2}{[NO]^2 [O_2]} = \frac{(1.20)^2}{(0.24)^2 (0.10)} = 250$$
$$\frac{(1.30)^2}{(0.14)^2 (0.05 + x)} = 250$$
$$\frac{(1.30)^2}{(0.14)^2 (250)} = 0.345 = 0.05 + x$$
$$x = 0.29$$
$$0.29 \text{ mol} x \ 1.0 \text{ L} = 0.29 \text{ mol} \text{ O}_2$$