Chapter 2

Page 99, Practice Problems, 2.2.1

S

- 1. 0.0082 mol/s (rate of its consumption = rate of its production at equilibrium)
- 2. <u>0.0041 mol O</u>2_

3. <u>0.13 q O₂</u>

5. <u>0.15 g O</u>2 S

Page 100, Quick Check

- 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
- 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

Page 101, Quick Check

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

Page 104, 2.1 Review Questions

- 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. 0.0040 <u>mol N₂O₄</u>

s b. <u>0.14 q NH</u>₃

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 prod-

ucts 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 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.
- 9.
- The Plot of Rate (forward and reverse) as a function of
 - Time for a Reaction Achieving Equilibrium 0 5 10 15 20 25 30 time (s)



- 10. a. the orange gas would become paler
 b. the concentration of reactants (NO₂)
 decreases while the concentration of products (N₂O₄) 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

Page 110, Practice Problems 2.2.1

 a. The system will restore equilibrium by removing some of the added Fe³⁺.
 b. right

equilibrium is re-established.

- 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.



Page 112, Practice Problems 2.2.2

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



Page 114, Quick Check

- 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.

Page 116, 2.2 Review Questions

- 1. a. Equilibrium will be restored by removing some of the added NO
 - b. right
 - c. decreased

2. 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^+).
- 6.

		add NH₃	remove some H ₂	$addN_2$
Equil. Conc.	N ₂	Increase	Increase	Increase
	H_2	Increase	Decrease	Decrease
	NH₃	Increase	Decrease	Increase

- 7. 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 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:



 Increase. Equilibrium 2 shifts towards products to remove some of the added H⁺. This decreases [NH₃] which in turn shifts equilibrium 1 left to replace some of the lost

Page 125, Practice Problems 2.3.2

- 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:



Page 126, Practice Problems 2.3.3

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

Page 129, Practice Problems 2.3.4

- 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).

NH₃. This increases [Cu²⁺].

- The AgCH₃COO(s) would slowly disappear. Equilibrium 2 shifts towards products to remove some of the added H⁺. This decreases [CH-3COO⁻] 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.

Page 121, Quick Check

- 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

Page 122, Practice Problems 2.3.1

- 1. Left. Increased number of NOCI; decreased numbers of NO and Cl₂. All concentrations increased due to compression.
- Right. Increased numbers of Ag⁺and S₂O_{3²}; decreased number of Ag(S₂O₃)_{2²}. All concentrations decreased.
- 3. No. The system cannot relieve any of the added pressure by shifting in either direction.



3. For example:



Page 130, Quick Check

- 1. Ammonia
- 2. adding a catalyst

Page 132, 2.3 Review Questions

- 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:



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.

17.

		Decrease Volume	Decrease Temperature
	N2	Increase	Decrease
Equil.	H ₂	Increase	Decrease
Conc.	NH₃	Increase	Increase
Equil. No.	N ₂	Decrease	Decrease
	H ₂	Decrease	Decrease
	NH₃	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.



- 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.)

21.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.4 \text{ kJ/mol}$					
.	Le Chatelier Predicts		Chemical Kinetics Explains		
Stress	Response	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 NH₃	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, more than r _f	net forward rx	

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

Page 139, Quick Check

- 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
- H₂O₂ because larger and more complex molecules have more possible configurations (ways of positioning their parts relative to each other).

Page 141, Practice Problems 2.4.1

- 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 $(s \rightarrow l)$

Page, 144 Practice Problems 2.4.2

- 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)
- entropy decreases (the drive towards decreasing enthalpy is towards products therefore the drive towards increasing entropy must be towards reactants)

Page 147, 2.4 Review Questions

- 1. a. Br₂(*g*) because gases have more entropy than liquids
 - b. $SO_3(g)$ because larger and more complex molecules have more possible configuratio 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.
- 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)
- 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
- 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.

Page 151, Practice Problems 2.5.1

- 1. *Keq* = 0.019
- 2. a. Keg = 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. $Keq = 1.7 \times 10^2$ [H₂] = 0.18 M

Page 153, Quick Check

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

Page 154, Quick Check

- 1. Keq = $[H_2O]^3$. [B₂H₆] [O₂]³
- 2. $Keq = \frac{[Cl_2]^2 [H_2O]^2}{[HCl]^4 [O_2]}$
- 3. Keq = $[HBr]^2$ [H₂]
- 4. $Keq = [Ca^{2+}][CO_3^{2-}]$

Page 154, Quick Check

- 1. 56
- 2. 0.13
- 3. 7.5

Page 156, Practice Problems 2.5.2

- 1. Trial $Keq = [CO] [H_2]^3 = (0.10) (0.30)^3 = 2.4$ [CH₄] [H₂O] (0.025) (0.045) 2.4 < 4.7 therefore the reaction will proceed to the right to achieve equilibrium
- 2. Trial $Keq = [N_2O_4] = (4.0 \text{ mol} / 0.50 \text{ L}) = 0.89$

 $[NO_2]^2 (1.5 \text{ mol} / 0.50 \text{ L})^2 \\ 0.89 < 0.940 \text{ therefore the reaction will} \\ \text{proceed to the right to achieve equilibrium}$

3.
$$Keq = [H^+] [SO_4^{2^-}] = (0.10) (0.10) = 0.012$$

 $[HSO_4^-] (0.83)$
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 [HSO_4^-].

Page 157, Quick Check

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

Page 159, 2.5 Review Questions

1. At equilibrium $r_f = r_r$ therefore: 2.7 x 10⁻³ [N₂O₅] = 4.3 x 10⁻² [NO₂] [NO₃]

$$Keq = [NO_2][NO_3] = 2.7 \times 10^{-3} = 0.063$$
$$[N_2O_5] \qquad 4.3 \times 10^{-2}$$

- 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 NOCI are produced but it provides no information about the ratio of the reactants and products present at equilibrium.
- 3. a. $Keq = [\underline{H^+}] [\underline{NO_2^-}]$ $[\underline{HNO_2}]$ b. $Keq = \underline{[SO_2]^2 [O_2]}$ $[SO_3]^2$ c. $Keq = \underline{[NO]^4 [\underline{H_2O}]^6}$ $[NH_3]^4 [O_2]^5$
- 4. Keq = 2.8
- 5. a. [COBr₂] = 0.060 M; [CO] = 0.030 M; [Br₂] = 0.040 M
 - b. to replace some of the lost pressure
 - c. Keq = 0.040 at equilibrium initially
 - = 0.040 when equilibrium is restored
- 6. 0.082 M
- 7. Trial Keq = 0.59
 0.59 < 1.0 therefore the reaction must proceed to the right to achieve equilibrium

8. a.
$$Keq = [\underline{H}_2] [\underline{F}e^{2+}] [\underline{H}^+]^2$$

b. $Keq = \underline{[Cl^-]^2} [\underline{I}^-]^2 [Cl_2]$
c. $Keq = \underline{1} [CO_2]$
d. $Keq = [\underline{CO}_2(aq)] [CO_2(g)]$

e. *Keq* =
$$[O_2]$$

9. a. $Cl_2(g) \rightleftharpoons Cl_2(aq)$ $Keq = [Cl_2(aq)]$ $[Cl_2(g)]$ b. $CCl_4(g) \rightleftharpoons C(s) + 2Cl_2(g)$ $Keq = [Cl_2]^2$ $[CCl_4]$

> c. $2MgO(s) + 2SO_2(g) + O_2(g) \rightleftharpoons 2MgSO_4(s)$ Keq = 1 $[SO_2]^2 [O_2]$

b 125

- 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.)

Page 164, Practice Problems 2.6.1

- 1. *Keq* = 3.0
- 2. *Keq* = 2.2
- 3. *Keq* = <u>0.13</u>

Page 168, Practice Problems 2.6.2

- 1. 1.2 mol Cl₂
- 2. $[C_2N_2]_{eq} = 1.89 \text{ M}$

3. $[HCI]_{eq} = 8.5 \text{ M}$

Page 169, Practice Problems 2.6.3

1. 0.75 M 2. 1.2 M

3. 0.26 M

Page 172, Practice Problems 2.6.4

1. a) $K_p = 0.133$

- b) K_p = 1.04
- 2. a) $x = \sqrt{0.3042} = 0.55$ atm
- b) x = 349 atm
- 3. 0.060
- 4. In (a), $\Delta n = 0$, so $K_p = K_c$. In (b), $\Delta n = -1$, so K_p does not equal K_c .

Page 174, 2.6 Review Questions

1.

a.	$2CH_4(g) \rightleftharpoons C_2H_2(g) + 3H_2(g)$		
Ι	6.0	0	0
С	- 3.0	+ 1.5	+ 4.5
E	3.0	1.5	4.5

- 2. a. [NO₂]_{eq} = 0.6 M b. *Keq* = 3
- 3. a. $[A^{2+}]_{eq} = 0.80 \text{ M}$ b. Keq = 20.
- 4. a. Keq = 1.20[HCN] = 3.0 b.Keq = 1.20[C₂N₂] = 3.0
- [G3P] = 0.002 M [DHAP] = 0.038 M
 [H₂] = 0.522 M
- [CO] = 0.678 M
- 7. [HCN] = 1.02 M
- 8. $[H_2] = 0.62 \text{ mol } H_2$
- 9. a. [BCl₃] = 2 (0.1126) = 0.23 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
- 10. *Keq* = 2.8
- 11. a. $[H_2] = [CI_2] = 3.00 0.778 = 2.22 \text{ M}$

[HCI] = 4.00 + 2(0.778) = 5.56 Mb. The system shifted to the right and replaced some of the removed HCI. 12. Keq = <u>[FeSCN²⁺]</u> = <u>1.8</u> = 180 [Fe³⁺] [SCN⁻] (0.10)² *Keq = <u>0.72 - x</u> = 180 (*This equation is sufficient for the answer) (0.040 + x)² 0.72 - x = 180 (0.040 + x)² = 180 (0.0016 +

 $0.08x + x^2) = 0.288 + 14.4x + 180x^2$

$$180x^2 + 15.4x - 0.432 = 0$$



$$[H_2] = 4.0 M$$

 $[Br_2] = 9.0 M$
 $[HBr] = 12 M$

b.	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$			
Ι	2.5	5.0	0	
С	- 0.5	- 1.5	+ 1.0	
Е	2.0	3.5	1.0	

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

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

15. $[H_2]_i = 1.0 M$

16.
$$[PCI_5]_i = 2.55 \text{ M}$$

18. a)
$$K_p = \frac{(P P C l_3)(P C l_2)}{P P C l_5}$$

b) $K_p = \frac{P^2 P_2 O_5}{P^5 O_2}$
c) $K_p = \frac{1}{P C O_2}$
19. $K_p = K_c (RT)^{\Delta n}$

Review Question 4: $K_p = 1.7 \times 10^3$ Review Question 6: $K_p = 2.8 \times 10^{-5}$ Review Question 7: $K_p = 1.7 \times 10^{-3}$ 20. $Q = \frac{P^2 SO_3}{(P^2 SO_2)(P O_2)} = \frac{(0.10 \text{ atm})^2}{(0.20 \text{ atm})^2(0.20 \text{ atm})}$ $= 1.25 > 0.14 = K_p$ As $Q > K_p$, the equilibrium shifts left to reach equilibrium. 21. a) $\Delta P_A = -1.5$ atm, $\Delta P_B = -1.5$ atm and $\Delta P_C = +1.5$ atm so $A + B \rightleftharpoons C$ b) $K_p = \frac{P_C}{(P_A)(P_B)}$ c) $K_p = 0.60$ d) 15 22. $P N_2 = 3.0$ atm $P H_2 = 8.9 \text{ atm}$ $P NH_3 = 5.9 \text{ atm}$ $K_p = 0.017$ 23. $K_p = 1.78$ 24. a) $PCI_5(g) \neq PCI_3(g) + CI_2(g)$. For every mole of PCI_5 decomposed, a total of 2 moles of PCl₃ and Cl₂ combined are produced. Therefore, as the reaction reaches equilibrium (shifts right), the total number of moles of gas increase and the pressure increases. b) When the system reaches equilibrium, $P PCI_5 =$ 1.00 - 0.40 = 0.60 atm, P PCl₃ = 0.40 atm, P Cl₂ = 0.40 atm c) $K_p = 0.27$ d) If the decomposition were to go to completion, $P PCI_5 = 0.00 atm, P PCI_3 = 1.00 atm, P CI_2 = 1.00$ atm. Therefore, P_{total} 2.00 atm