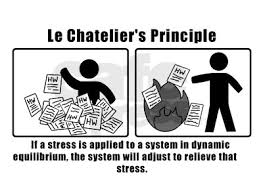
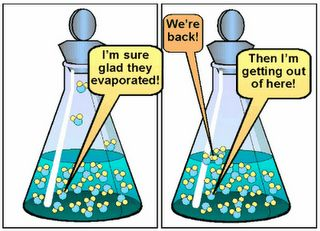
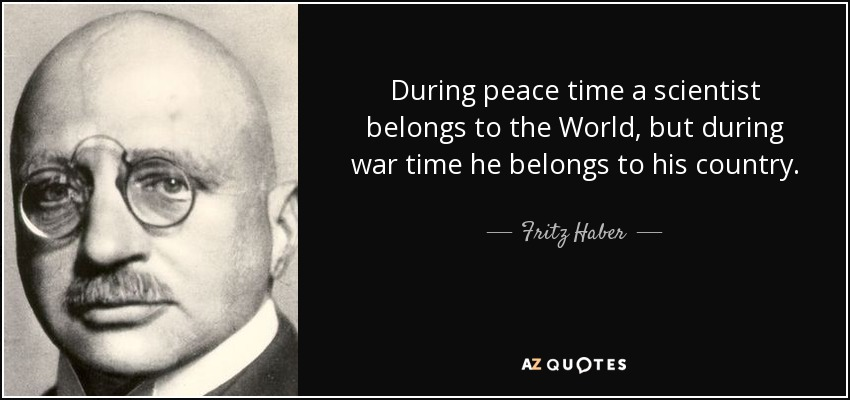
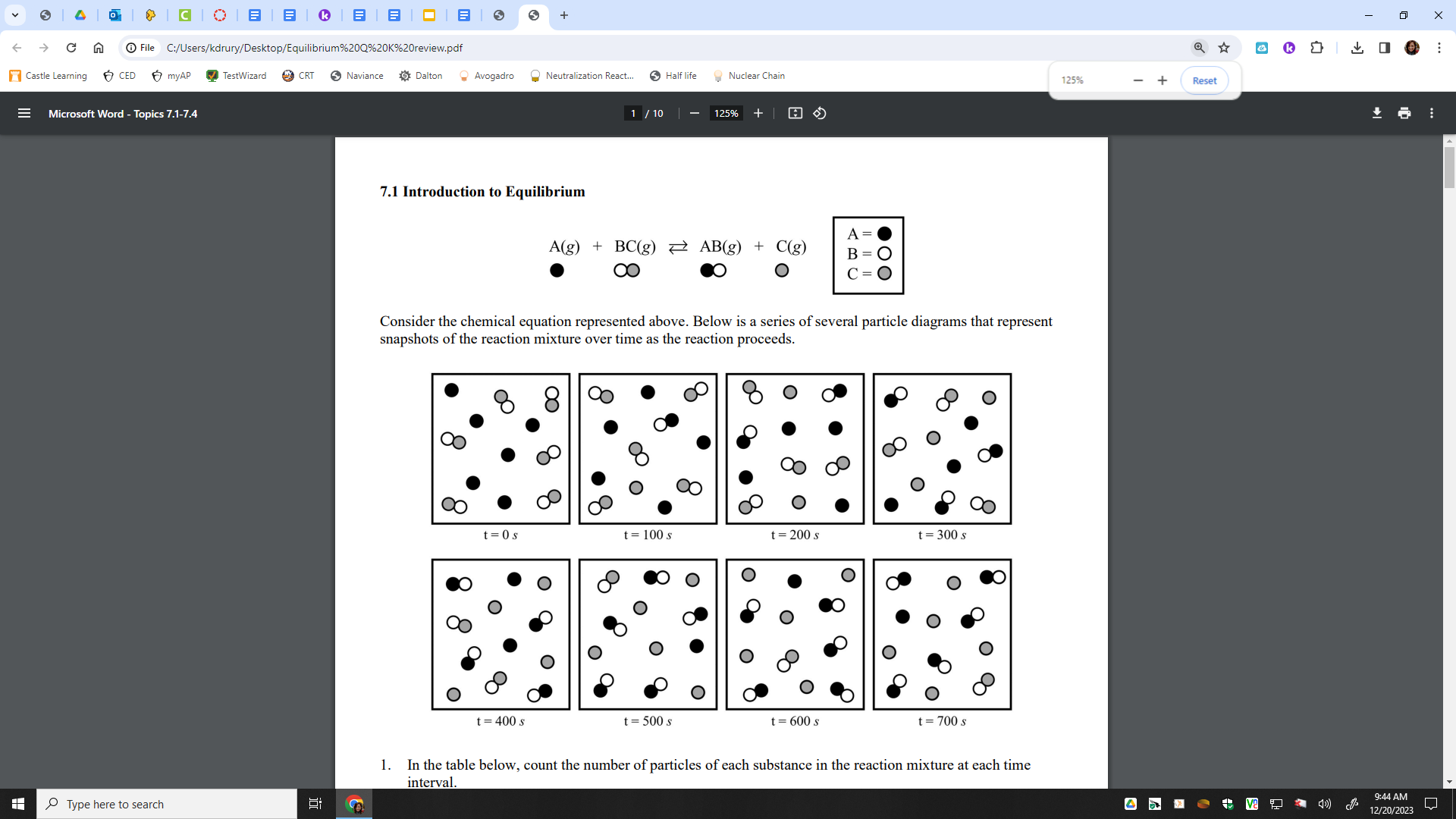
**AP Learning Objectives:**

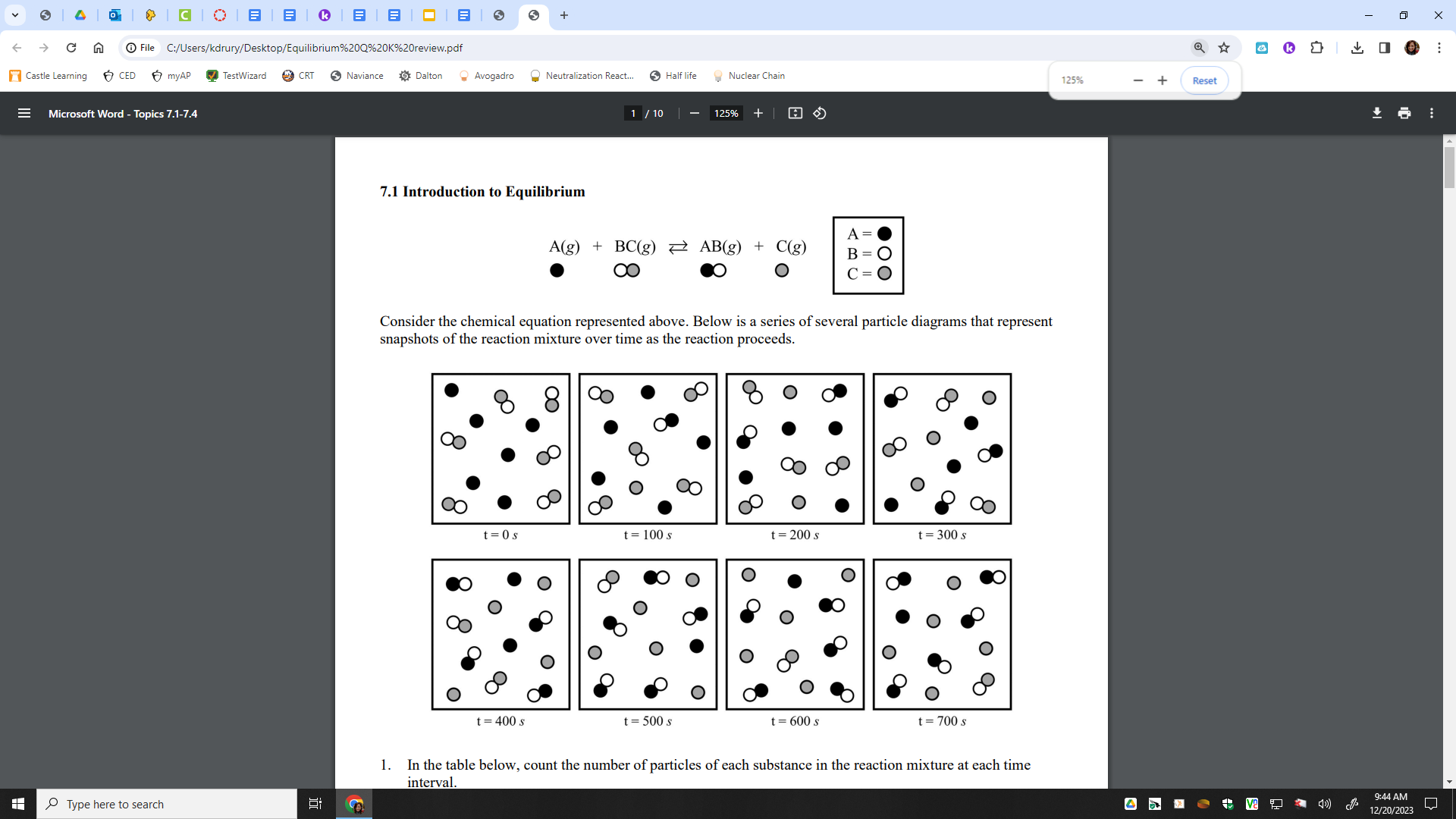
* Explain the relationship between the occurrence of a reversible chemical or physical process, and the establishment of equilibrium, to experimental observations (7.1)
* Explain the relationship between the direction in which a reversible reaction proceeds and the relative rates of the forward and reverse reactions.(7.2)
* Represent the reaction quotient Qc p or Q , for a reversible reaction, and the corresponding equilibrium expressions Kc = Qc or K p = Qp . (7.3)
* Calculate Kc or K p based on experimental observations of concentrations or pressures at equilibrium. (7.4)
* Explain the relationship between very large or very small values of K and the relative concentrations of chemical species at equilibrium (7.5)
* Represent a multistep process with an overall equilibrium expression, using the constituent K expressions for each individual reaction(7.6)
* Identify the concentrations or partial pressures of chemical species at equilibrium based on the initial conditions and the equilibrium constant.(7.7)
* Represent a system undergoing a reversible reaction with a particulate model. (7.8)
* Identify the response of a system at equilibrium to an external stress, using Le Châtelier's principle.(7.9)
* Explain the relationships between Q, K, and the direction in which a reversible reaction will proceed to reach equilibrium. (7.10)
* Calculate the solubility of a salt based on the value of K sp for the salt.(7.11)
* Identify the solubility of a salt, and/or the value of K sp for the salt, based on the concentration of a common ion already present in solution.(7.12)
* Identify the qualitative effect of changes in pH on the solubility of a salt.(7.13)
* Explain the relationship between the solubility of a salt and changes in the enthalpy and entropy that occur in the dissolution process. (7.14)



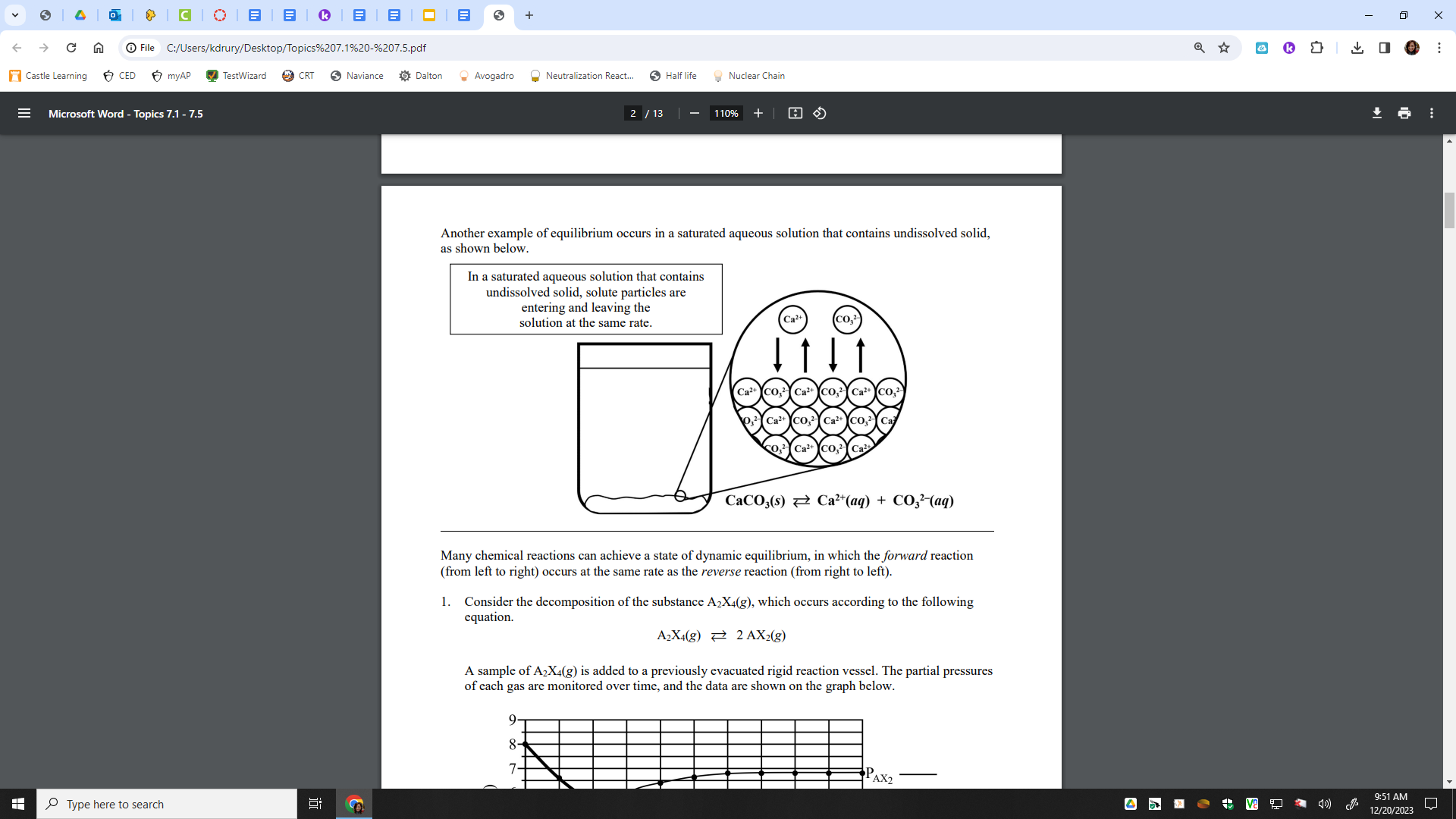
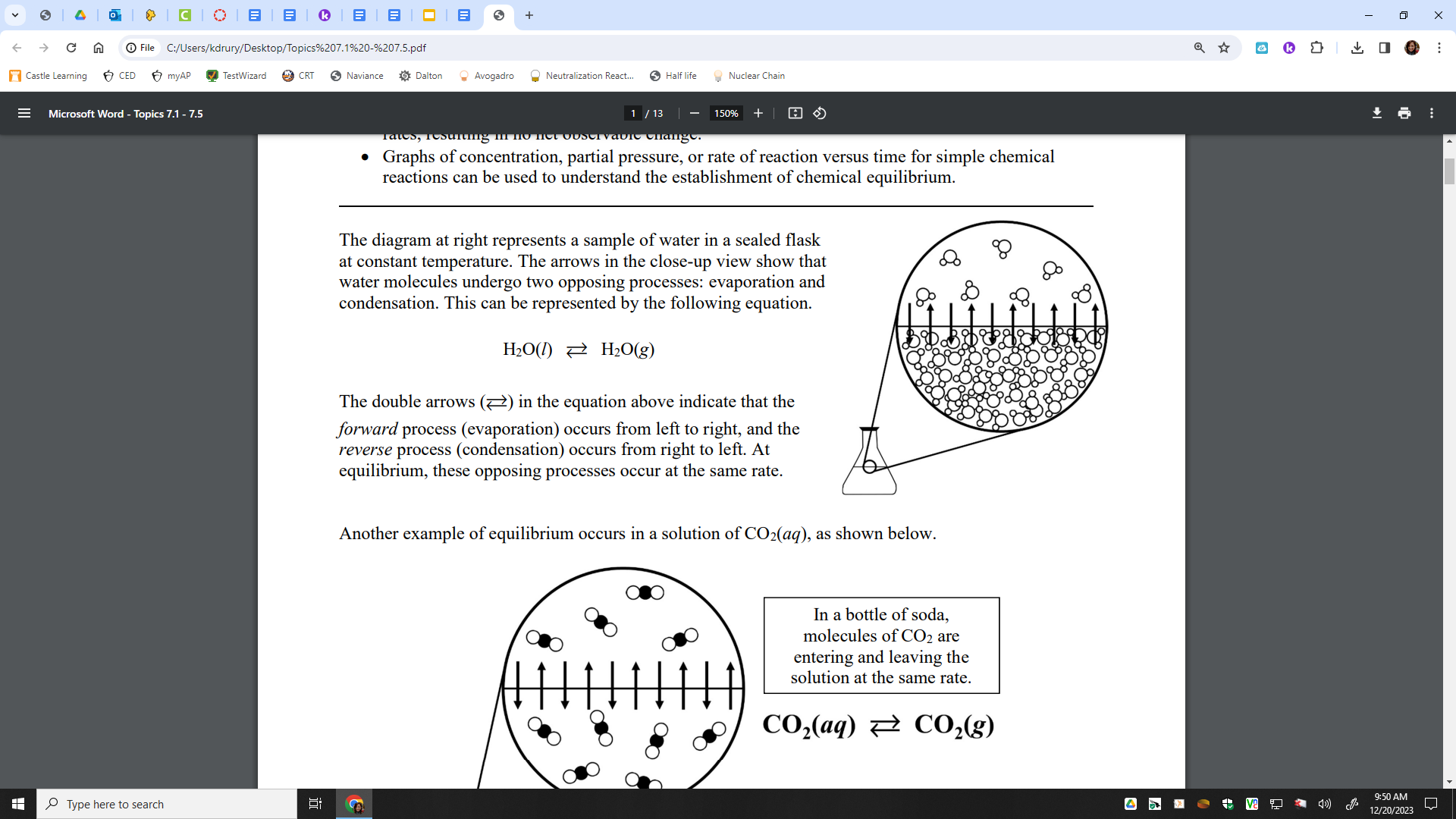
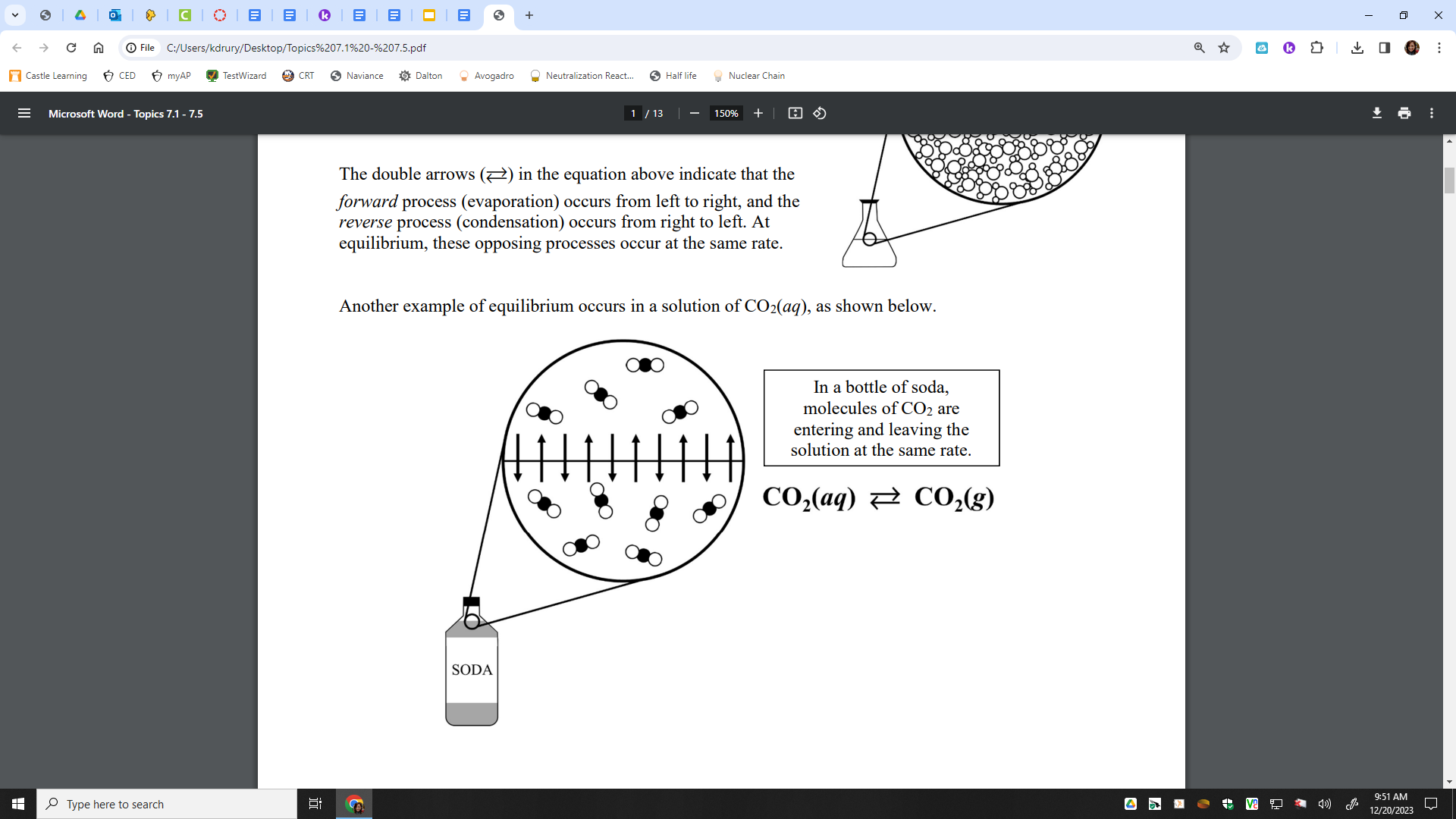


**Equilibrium Review**

****

****

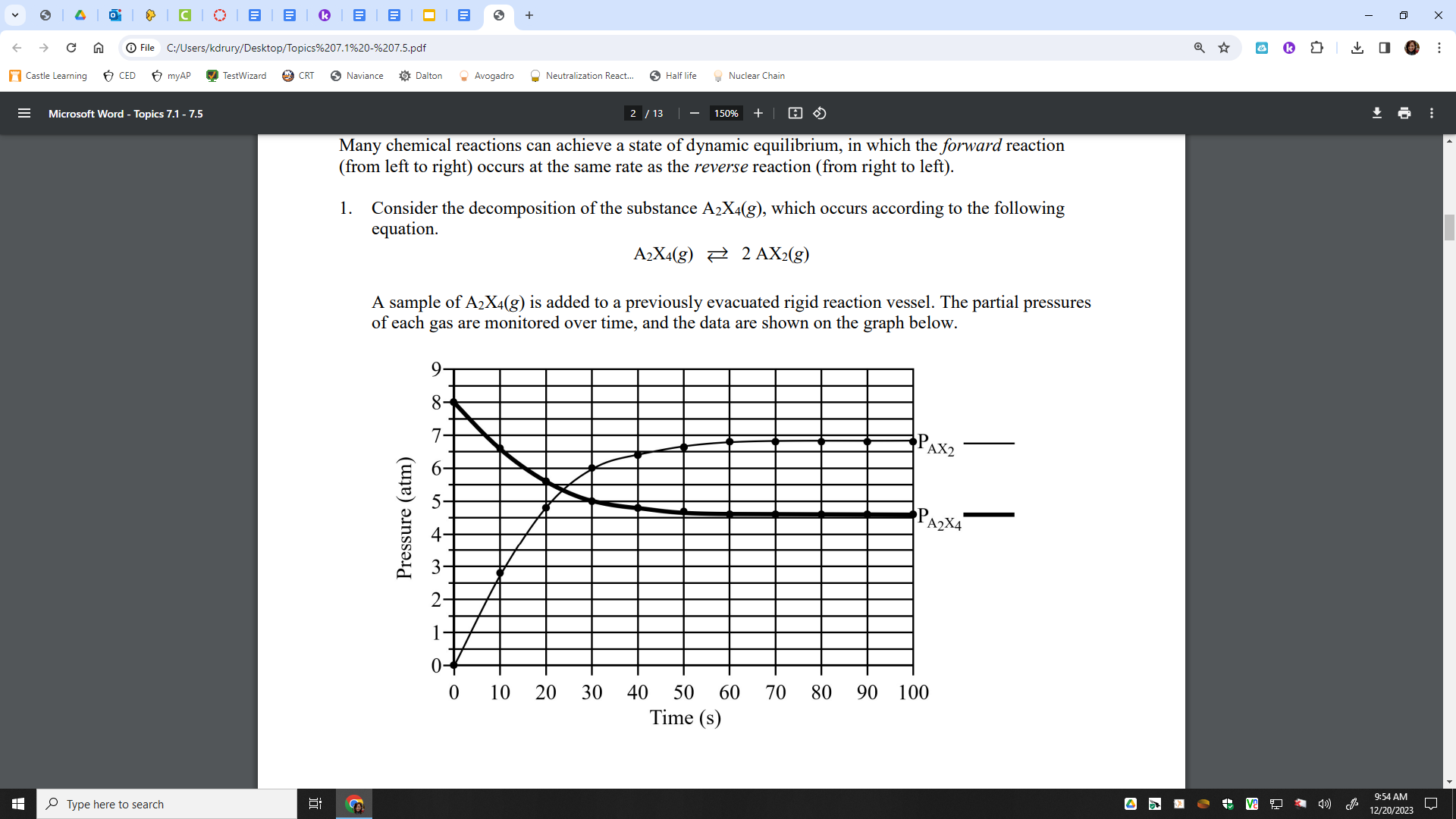
1. Consider the chemical equation represented above. Below it, a series of particle diagrams represent the reaction mixture over time as the reaction proceeds. Label the diagrams above by counting the number of each substance in the reaction mixture at each time interval.
2. At which point was equilibrium achieved? Justify your answer.
3. On each diagram below, identify why each represents an equilibrium system. The first is done for you.

1. On the same diagrams, explain observations you may see when these representations are at equilibrium.
2. Consider the decomposition reaction below. The partial pressures of each gas are monitored over time and the data is graphed below. A2X4(g) ↔ 2AX2(g)

*Use the words increasing, decreasing, or remaining the same:*

* 1. During the first 30 seconds of the reaction,
     1. the partial pressure of the reactant is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
     2. the partial pressure of the product is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
     3. the rate of the forward reaction is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
     4. the rate of the reverse reaction is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
  2. During the last 30 seconds of the reaction,
     1. the partial pressure of the reactant is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
     2. the partial pressure of the product is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
     3. the rate of the forward reaction is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
     4. the rate of the reverse reaction is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
  3. At what point did the reaction hit an equilibrium? Justify your answer.

****

LeChatelier Rules:

1. If a substance (or heat) is ADDED shift AWAY from that substance (or heat)

2. If a substance (or heat) is TAKEN shift TOWARDS that substance (or heat)

3. If pressure is added, there is less volume/room for moles. Shift towards the side with less moles.

4. If pressure is relieved, there is more room. Shift towards the side with more moles.

5. Catalysts speed up the forward AND reverse reaction. Therefore equilibrium is unchanged.

6. At equilibrium RATES are equal. Not amount!

1. Circle which **direction** the equilibrium will shift towards to relieve the stress and cite the rule used:

**2NH3(g)  N2(g) + 3H2(g) + heat**

Rule #

* 1. Ammonia is added **left right no effect \_\_\_\_\_**
  2. Nitrogen is added **left right no effect \_\_\_\_\_**
  3. Hydrogen is added **left right no effect \_\_\_\_\_**
  4. Heat is added **left right no effect \_\_\_\_\_**
  5. Ammonia is removed **left right no effect \_\_\_\_\_**
  6. Nitrogen is removed **left right no effect \_\_\_\_\_**
  7. Hydrogen is removed **left right no effect \_\_\_\_\_**
  8. Heat is removed **left right no effect \_\_\_\_\_**
  9. Pressure is increased **left right no effect \_\_\_\_\_**
  10. Pressure is decreased **left right no effect \_\_\_\_\_**
  11. A catalyst is added **left right no effect \_\_\_\_\_**

1. Circle what will happen to the **Nitrogen** to relieve the stress:

**N2(g) + 3H2(g) + heat 2NH3(g)** 

* 1. Ammonia is removed **increase decrease remain the same**
  2. Heat is added **increase decrease remain the same**
  3. Pressure is increased **increase decrease remain the same**
  4. Heat is removed **increase decrease remain the same**
  5. Ammonia is added **increase decrease remain the same**
  6. Hydrogen is removed **increase decrease remain the same**
  7. Hydrogen is added **increase decrease remain the same**

1. Indicate how each of the following changes affects the amount of each gas in the system below, for which ΔHreaction = +9.9 kcal. **H2(g) + CO2(g)  H2O(g) + CO(g)**

a) addition of CO2 \_\_\_ \_\_\_ \_\_\_

b) addition of H2O \_\_\_ \_\_\_ \_\_\_

c) increase in temperature \_\_\_ \_\_\_ \_\_\_ \_\_\_

d) decrease in the volume of the container \_\_\_ \_\_\_ \_\_\_ \_\_\_

**Equilibrium Expressions**

*For the following three reactions,*

*a) write the Keq expression in terms of concentration, Kc.*

*b) given the equilibrium concentrations, state whether each equilibrium is product-favored, reactant-*

*favored, or fairly even ([products] ≈ [reactants]).*

*c) calculate the value of Kc.*

1. N2(g) + 3 H2(g) ⮀ 2 NH3(g)

| At equilibrium: | [N2] = 1.50 M  [H2] = 2.00 M  [NH3]= 0.010M |
| --- | --- |
|  |  |

2. HF(aq) ⮀ H+(aq) + F-(aq)

| At equilibrium: | [HF] = 0.55 M  [H+] =0.0010 M  [F-]=0.0010 M |
| --- | --- |

3. Fe3+(aq) + SCN-(aq) ⮀ FeSCN2+(aq)

| At equilibrium: | [Fe3+] = 0.55 M  [SCN-] = 0.0010 M  [FeSCN2+]=0.0010M |
| --- | --- |

**Summarize:** Fill in the blanks with product-favored, reactant-favored, or approximately equal.

| **Kc** | **state of equilibrium** |
| --- | --- |
| Kc >> 1 |  |
| Kc << 1 |  |
| Kc ≈ 1 |  |

**Important Note:**

Since the concentrations of solids and liquids are constant, they are incorporated into the equilibrium constant, Keq. That means, just leave them out of the Kc or Kp expression. Only include (g) and (aq)!

5. Write equilibrium expressions for each of the following reactions:

a) CaCO3(s)  CaO(s) + CO2(g)

b) Ni(s) + 4CO(g)  Ni(CO)4(g)

c) 5CO(g) + I2O5(s)  I2(g) + 5CO2(g)

d) Ca(HCO3)2(aq)  CaCO3(s) + H2O(l) + CO2(g)

6. Rate the reactions in order of their increasing tendency to proceed toward completion:

(a) 4NH3(g) + 3O2(g)  2N2(g) + 6H2O(g) Kp = 1 x 10228 atm

(b) N2(g) + O2(g)  2NO(g) Kp = 5 x 10-31

(c) 2HF(g)  H2(g) + F2(g) Kp = 1 x 10-13

(d) 2NOCl(g)  2NO(g) + Cl2(g) Kp = 4.7 x 10-4 atm

7. a. Write the Kc expression for 2 SO2(g) + O2(g) ⮀ 2 SO3(g)

| At equilibrium: | [SO2] = 1.50 M | [O2] = 1.25 M | [SO3]= 3.50 M |
| --- | --- | --- | --- |

1. Calculate the value of Kc:
2. If we **reverse** the equation, it is: 2 SO3(g) ⮀ 2 SO2(g) + O2(g)

Write the Kc expression for this equation and calculate the new value of Kc:

1. How does the expression and the value of Kc in 7c compare with those in 7b?
2. If we now **multiply all of the coefficients by ½:** SO3(g) ⮀ SO2(g) + ½ O2(g)

Write the Kc expression for this equation and calculate the new value of Kc:

1. How does the expression and the value of Kc in 7e compare with those in 7b?

g. What would happen to the Kc expression and its value if we **doubled** the coefficients?

8. Summarize:

| **Equation** | **Kc expression & Value** |
| --- | --- |
| doubled |  |
| reversed |  |
| halved |  |

9. Consider an equilibrium that occurs in two steps:

H2S(aq) ⮀ H+(aq) + HS-(aq)

HS-(aq) ⮀ H+(aq) + S2-(aq)

(a) Write the overall reaction.

(b) How do the Kc’s for the two steps (Kc1 & Kc2) relate to the Kc of the overall reaction (Kc)?

**Mass Action Expression Practice**

1. Consider the following equilibrium, for which K=0.112 at 700C,

SO2(g) + ½ O2(g) ↔ SO3(g)

What is the value of K for the following reactions:

1. SO3(g) ↔ SO2(g) + ½ O2(g)
2. 2SO2(g) + O2(g) ↔ 2SO3(g)
3. 2SO3(g) ↔ 2SO2(g) + O2(g)
4. Consider the following equilibrium, for which K=1.1x10-2 at 25C,

HClO2(aq) ↔ H+  + ClO2-

What is the value of K for the following reactions:

1. 2HClO2(aq) ↔ 2H+ + 2ClO2-
2. ½ HClO2(aq) ↔ ½ H+ + ½ ClO2-
3. 3H+ + 3ClO2- ↔3HClO2(aq)
4. Consider the following equilibria at STP,

HF(aq) ↔ H+ + F- K1 = 2.0x10-3

H2C2O4(aq) ↔ 2H+ + C2O4-2 K2 = 1.0x10-4

What is the value of K for the following reaction:

2HF(aq) + C2O4-2 ↔ 2F- + H2C2O4(aq)

1. Consider the following equilibria at STP,

H2(g) + I2(g) ↔ 2HI(g) K1 = 2.5x10-8

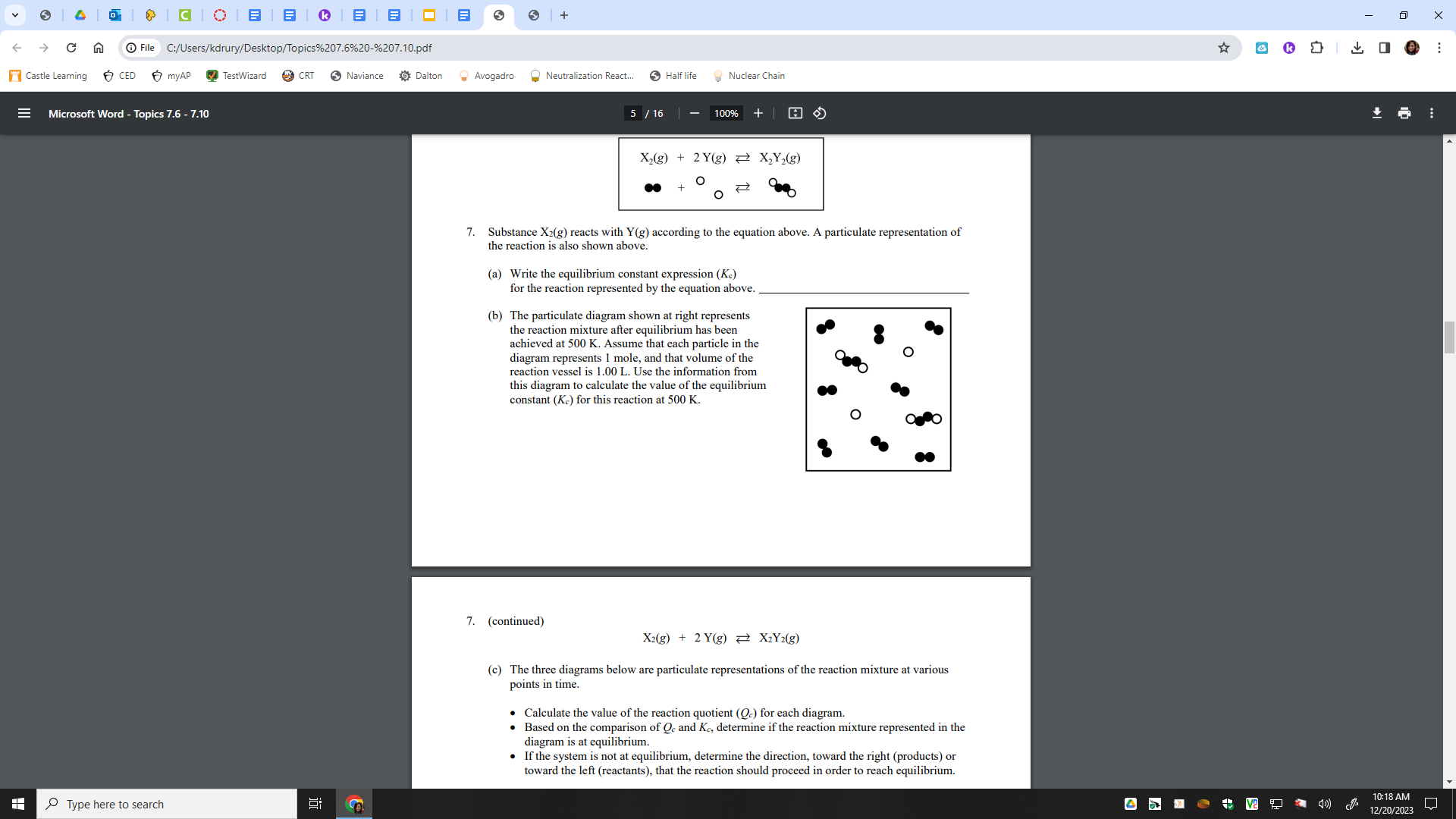
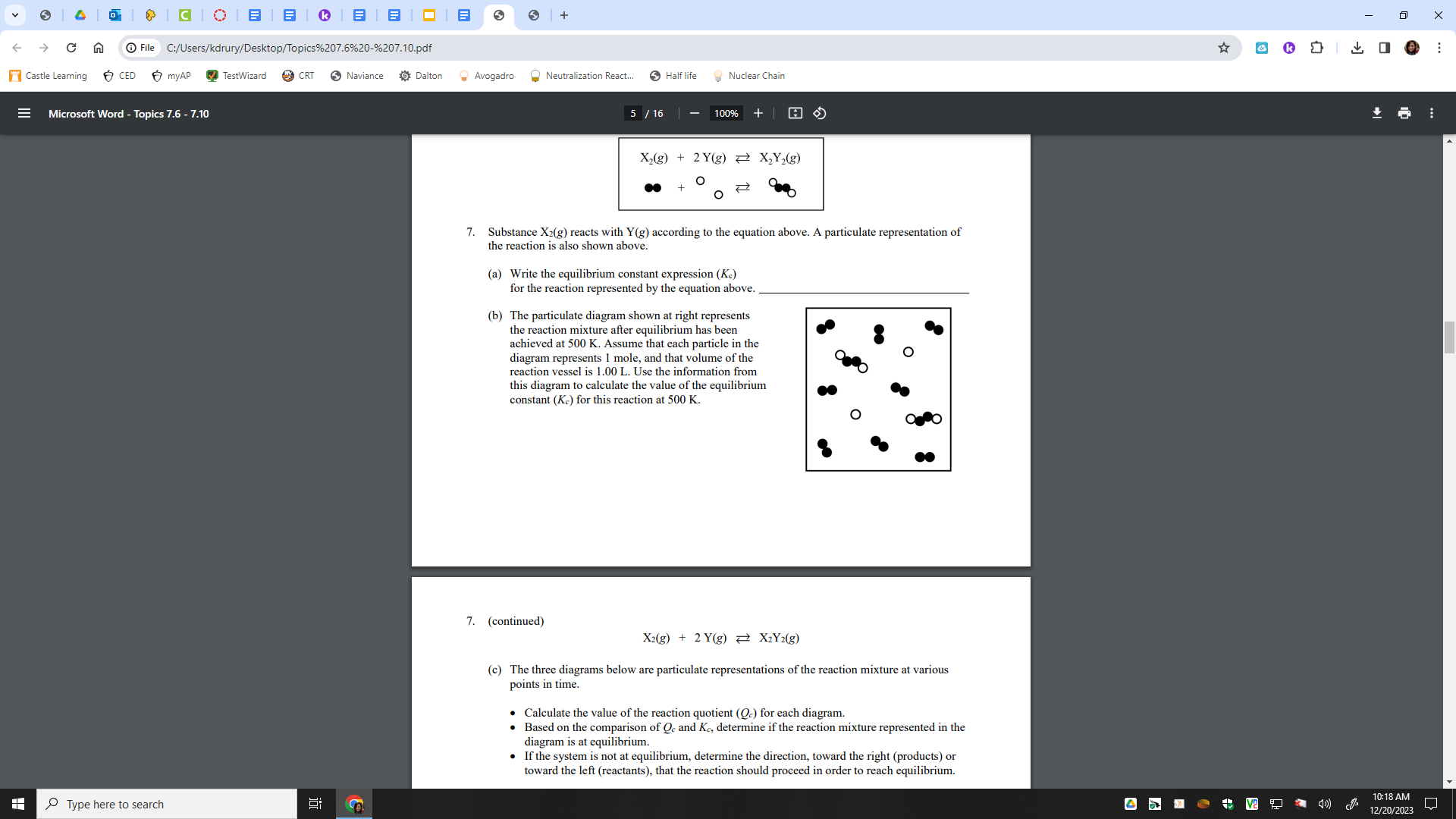
N2(g) + 3H2(g) ↔ 2NH3(g) K2 = 4.1x102

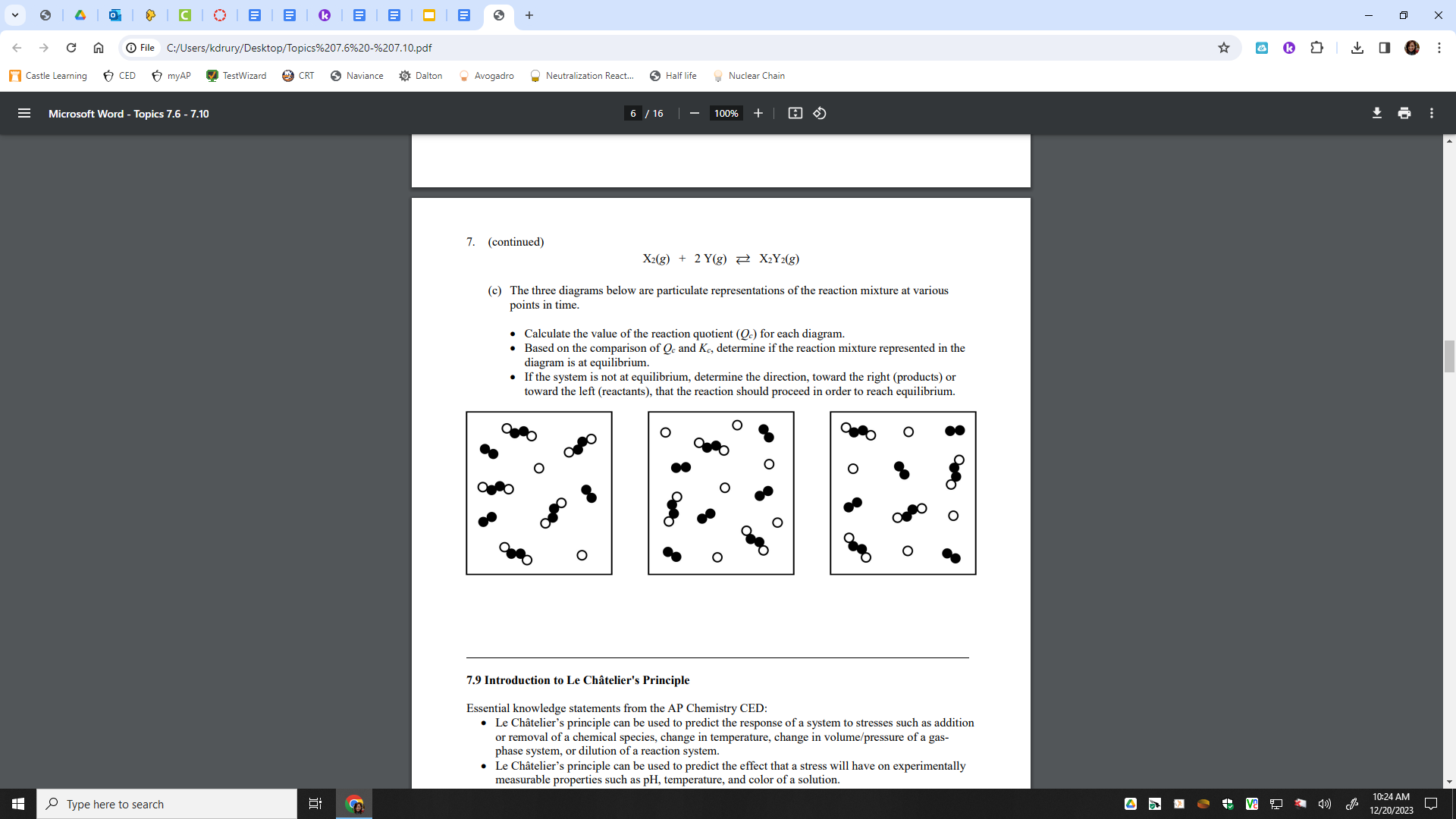
What is the value of K for the following reaction:

2NH3(g) + 3I2(g) ↔ 6HI(g) + N2(g)

1. In each question above, identify the reaction that most drives towards completion.

**Equilibrium Practice**

1. The reaction PCl3(g) + Cl2(g) ↔ PCl5(g) comes to equilibrium at 498K and the concentrations are 10.0M, 9.0M and 12.0M respectively. Calculate the equilibrium constant.
2. For the Haber process, an equilibrium mixture at 600K contained 0.31M N2, 0.50M H2, and 0.14M NH3. Calculate Kc. N2(g) + 3H2(g) ↔ 2NH3(g)
3. For the gaseous reaction: 2NO + Cl2 ↔ 2NOCl, the pressures at equilibrium are 1.2 atm, 0.30 atm, and 0.05 atm respectively. Calculate Kp at 100K.
4. The equilibrium constant for the reaction CO + H2O(l) ↔ CO2 + H2 is K=4.0 at a given T. At equilibrium, the mixture contains 0.80mol CO, 0.35mol water and 2.2mol CO2. How many moles of H2 are present in 1.00L?
5. Use the key and images provided:
   1. Write the Kc for the reaction shown.
   2. The diagram shows a reaction mixture after equilibrium is achieved at 500K. Assume each particle represents one mole of the substance and the reaction vessel is 1.00L. Calculate the value of the Kc.
   3. The three diagrams below represent the mixture at various times during the reaction. calculate the Q (similar to K but may not be equilibrium yet) of each diagram and determine if the reaction is at equilibrium.



**Equilibrium Quotient**

1. What is the equilibrium quotient of a mixture which contains 0.41atm SO2, 0.16atm O2, and 0.57atm SO3? Which way will the reaction 2SO2 + O2 ↔ 2SO3 shift to reach an equilibrium where K=3.40?
2. The Kc for the reaction: 2NO ↔ N2 + O2, all species in the gas phase, is 0.0024. In a 1L flask, 0.024mol NO, 2.0mol N2 and 2.6mol O2 exist. Is the system at equilibrium? If not, how would the reaction shift?
3. Consider the equilibrium: 2 SO2(g) + O2(g) ↔ 2 SO3(g) Kc = 4.36 M-1
4. Calculate the Q in which concentrations are [SO2]=2.00M, [O2]=1.50M and [SO3]= 1.25M.
5. Does this mixture shift toward the reactants or products to reach equilibrium?
6. PbCl2 (s) 🡨🡪 Pb2+ (aq) + 2Cl- (aq)

Experimentally, the amount of Pb2+ and Cl- does not depend on the amount of PbCl2. Why?

H2(g) + I2(g) ↔ 2 HI(g) Kc = 51 at 448°C

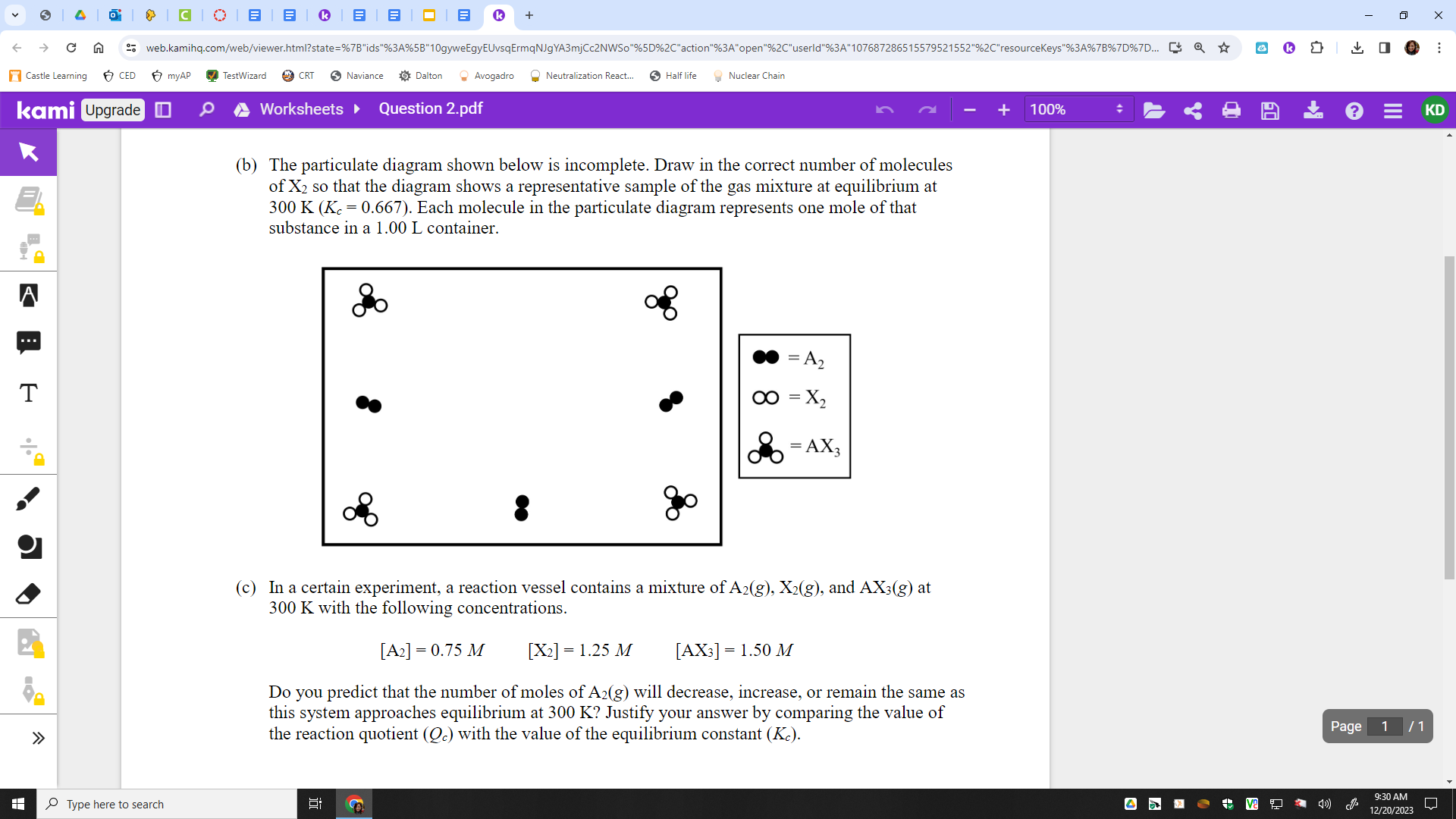
1. For each set of experimental conditions listed in the table below, use the data to calculate the value of the reaction quotient (Qc). Compare Kc with Qc and choose one of the following consequences.

* The system is already at equilibrium.
* The system should proceed toward the products (from left to right) until equilibrium is achieved.
* The system should proceed toward the reactants (from right to left) until equilibrium is achieved

| [H2] | [I2] | [HI] | Q | K vs Q | Consequence |
| --- | --- | --- | --- | --- | --- |
| 0.35M | 0.45M | 3.0M |  |  |  |
| 4.6M | 1.4M | 4.2M |  |  |  |
| 0.90M | 0.81M | 6.1M |  |  |  |

A2(g) + 3 X2(g) ← → 2 AX3(g) Kc = 0.667 at 300 K

1. Substance A2(g) reacts with substance X2(g) according to the equation shown above.
   1. Write the expression for the equilibrium constant (Kc) for the reaction.
   2. The particulate diagram shown below is incomplete. Draw in the correct number of molecules of X2 so that the diagram shows a representative sample of the gas mixture at equilibrium at 300 K (Kc = 0.667). Each molecule in the particulate diagram represents one mole of that substance in a 1.00 L container.



* 1. In a certain experiment, a reaction vessel contains a mixture of A2(g), X2(g), and AX3(g) at 300 K with the following concentrations.

[A2] = 0.75 M [X2] = 1.25 M [AX3] = 1.50 M

Do you predict that the number of moles of A2(g) will decrease, increase, or remain the same as this system approaches equilibrium at 300 K? Justify your answer by comparing the value of the reaction quotient Q with the value of the equilibrium constant K.

**Summary**

| Q vs. K | Ratio | Inequality Symbol Used | Consequence |
| --- | --- | --- | --- |
| Q is equal to K | products  reactants | K= Q | no shift |
| Q is less than K | products  reactants | K>Q | reactants convert to products until equilibrium is achieved |
| Q is more than K | products  reactants | K<Q | products convert to reactants until equilibrium is achieved |

**Ice Box Questions**

1) 1.0 mol Sulfur dioxide and 1.00 mol of oxygen are sealed in a 1.00 L rigid container at 1000K. When equilibrium is established, 0.925 mol of sulfur trioxide is formed. Calculate Keq for this reaction.

2) Suppose a tank initially contains H2S at a pressure of 10.0 atm and at a temperature of 800 K. When the reaction has come to equilibrium, the partial pressure of S2 vapor is 0.020 atm. Calculate Kp.

2 H2S(g) ↔ 2 H2(g) + S2(g)

3) A sample of hydrogen fluoride is synthesized when 3.000 mol hydrogen and 3.000 mol fluorine are mixed in a 3.000-L flask. The value of Kc at the temperature of the reaction is 1.15 x 102. Calculate the equilibrium concentrations of all species

H2(g) + F2(g) ↔ 2HF(g)

4) A sample of COCl2 is allowed to decompose. The value of Kc for the equilibrium is 2.2 x 10-10 at 100 oC.

If the initial concentration of COCl2 is 0.095M, what will be the equilibrium concentrations for each?

COCl2 (g) ↔ CO (g) + Cl2 (g)

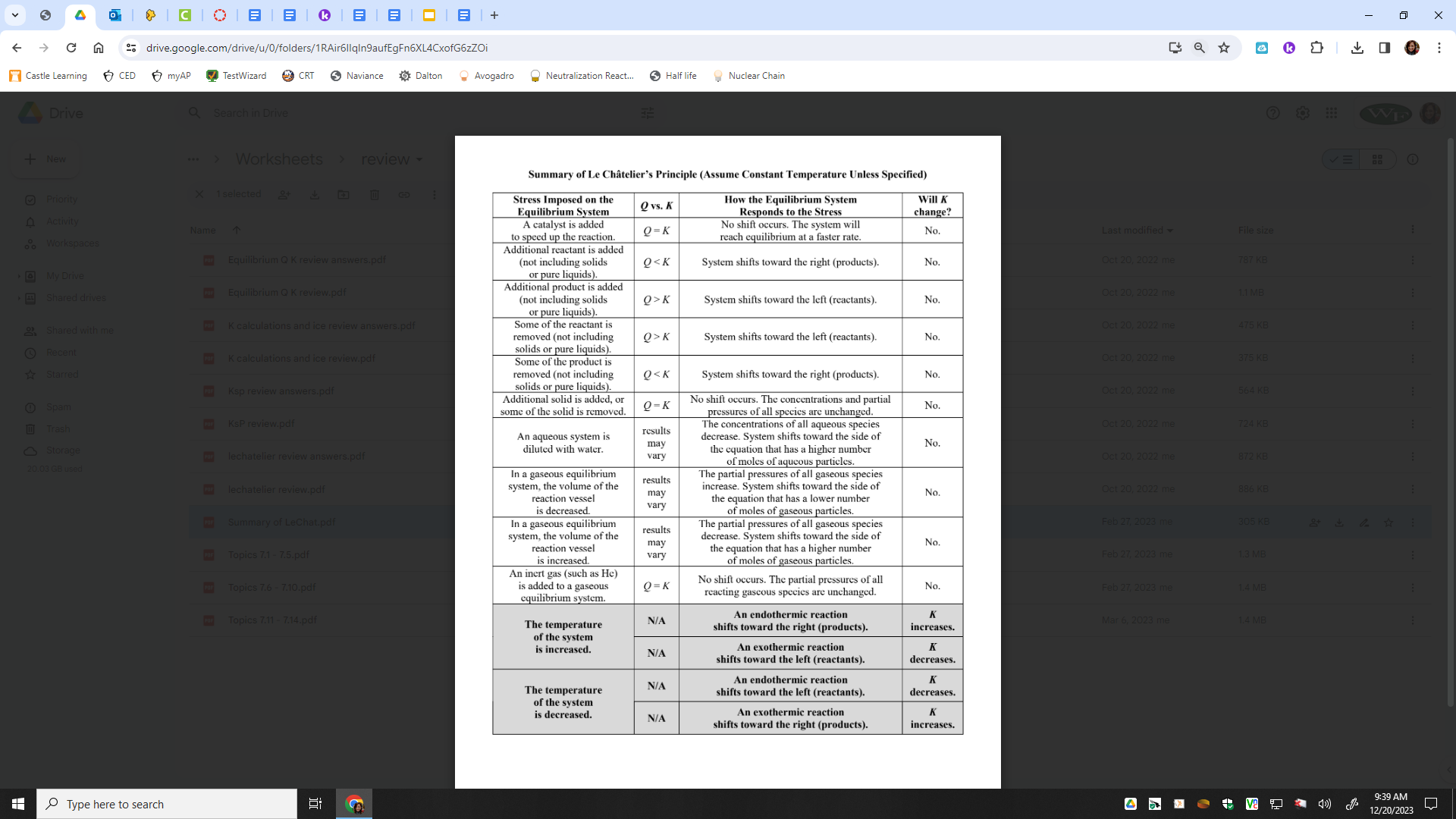
5) You have 1.00 M CH3COOH. Calculate the equilibrium concentrations of CH3COOH, H+, CH3COO-. Ka=1.8x10-5

CH3COOH(aq) ↔ CH3COO-(aq) + H+(aq)

6) If 0.160mol NO2 and 0.40mol N2O4 are placed in a 20.0L container and the reaction 2NO2 ↔ N2O4 is allowed to come to equilibrium at 352.5K, at equilibrium [NO2] = 0.0150M. What is the equilibrium concentration of N2O4? Calculate Kc for the reaction.

7) When heated, H2S gas is decomposed: 2H2S ↔ 2H2 +S2. A 3.40g sample of H2S is in a 1.25L container which is sealed and heated to 483K. At equilibrium 0.0372 mol S2 are present.

1. Write the expression for Kc.
2. Calculate the equilibrium concentration in mol/L at 483K for H2 and H2S.
3. Calculate the value of Kc at 483K.
4. Calculate the partial pressure of S2 at equilibrium.
5. For the reaction H2 + ½ S2 ↔ H2S at 483K, what is Kc?
6. Which reaction is most favorable? 2H2S ↔ 2H2 +S2 orH2 + ½ S2 ↔ H2S. Justify your answer.

****

**LeChatelier Practice**

2 SO3(g) ↔ 2 SO2(g) + O2(g)

1. Sulfur trioxide gas decomposes at high temperature to produce sulfur dioxide gas and oxygen gas according to the equation above. A sample of SO3(g) was added to a previously evacuated rigid reaction vessel. The reaction represented by the equation above was allowed to proceed until it reached equilibrium at 1000 K. The partial pressures were determined to be the following.

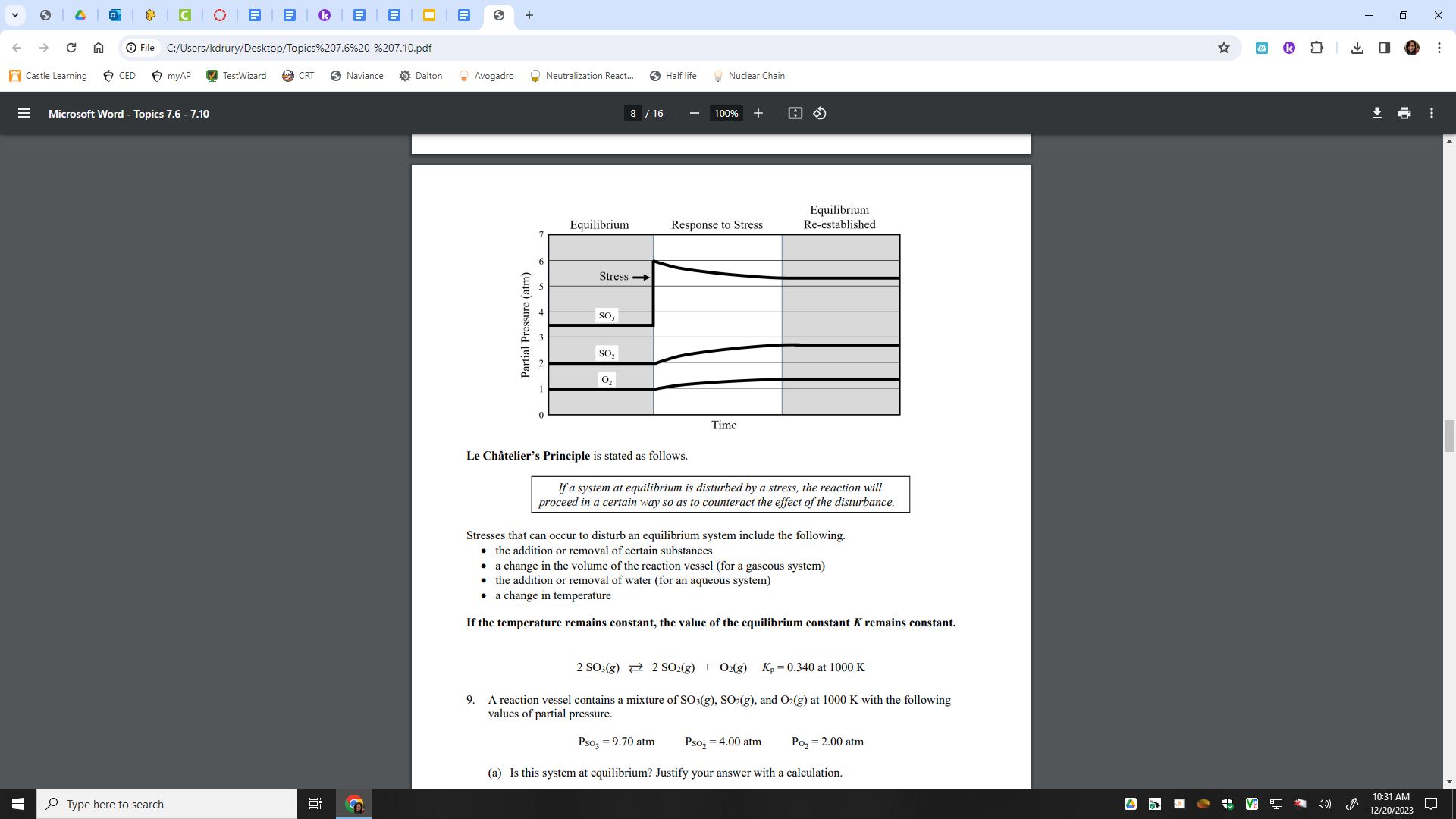
SO3 = 3.43 atm SO2 = 2.00 atm O2 = 1.00 atm

* 1. Write the equilibrium constant expression (Kp) for the reaction.
  2. Calculate the value of Kp at 1000 K.
  3. Additional SO3(g) is added to the reaction vessel at 1000 K until the partial pressure of SO3(g) is 6.00 atm. Calculate the value of Qp at the moment that additional SO3(g) is added.
  4. The addition of SO3(g) to the reaction vessel caused a disturbance in the equilibrium system that had already been established. As the system re-establishes equilibrium at 1000 K, which of the following statements should be true?

The partial pressure of SO2(g) will decrease until Qp = Kp.

The partial pressure of SO2(g) will increase until Qp = Kp.

* 1. When equilibrium is reestablished at 1000 K, the partial pressure of O2(g) in the reaction vessel is 1.34 atm. Calculate the partial pressures of SO3(g) and SO2(g) when equilibrium is reestablished.

****

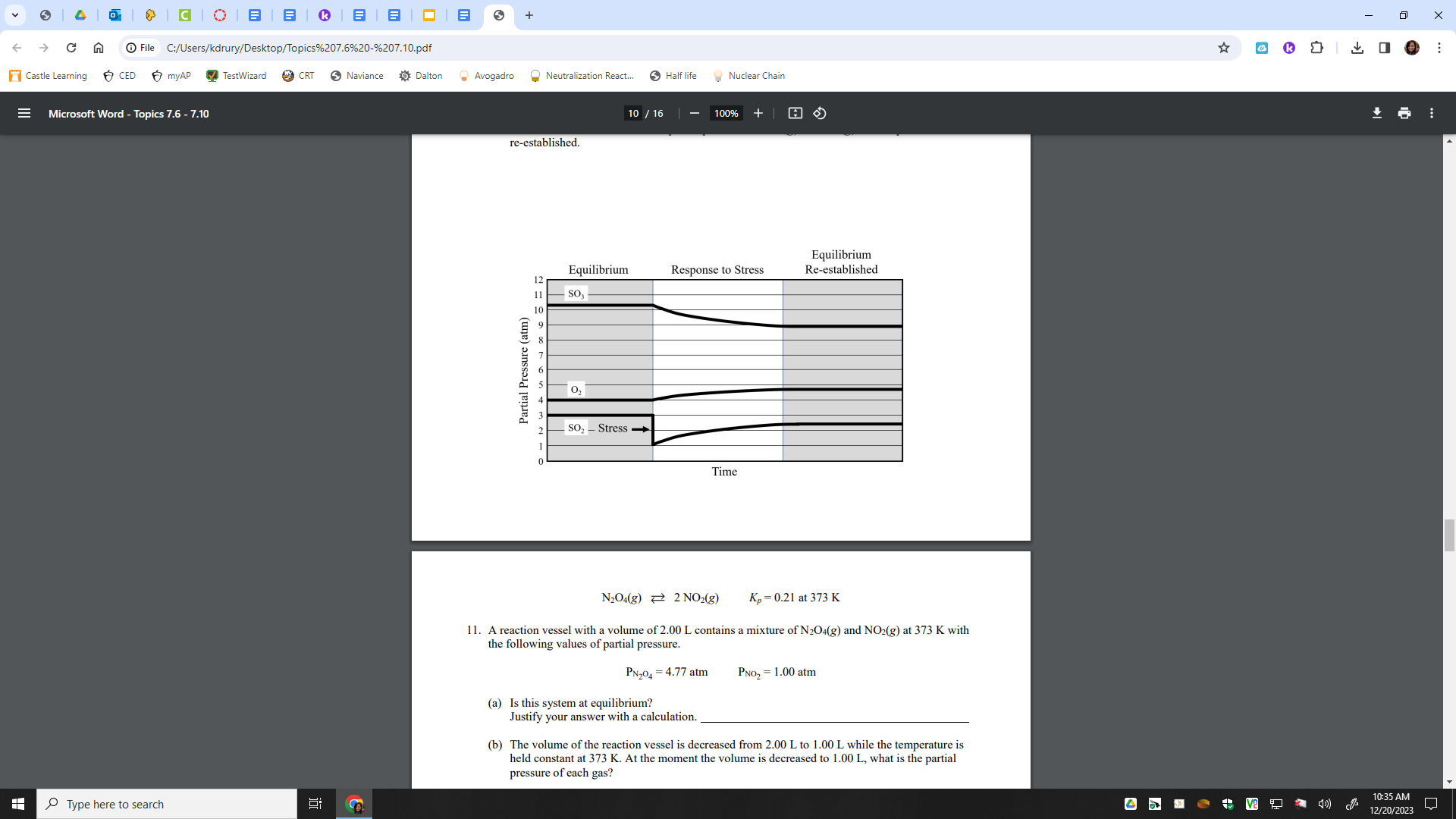
2 SO3(g) ↔ 2 SO2(g) + O2(g) Kp = 0.340 at 1000 K

1. A reaction vessel contains a mixture of SO3(g), SO2(g), and O2(g) at 1000 K with the following values of partial pressure. SO3 = 10.29 atm SO2 = 3.00 atm O2 = 4.00 atm
   1. Is this system at equilibrium? Justify your answer with a calculation.
   2. Some of the SO2(g) is removed from the reaction vessel at 1000 K, reducing the partial pressure of SO2(g) to a value of 1.00 atm. Calculate the value of Qp at the moment that the SO2(g) is removed.
   3. The removal of SO2(g) from the reaction vessel caused a disturbance in the equilibrium system that had already been established. As the system re-establishes equilibrium at 1000 K, which of the following statements should be true?

The partial pressure of O2(g) will decrease until Qp = Kp.

The partial pressure of O2(g) will increase until Qp = Kp.

* 1. When equilibrium is reestablished at 1000 K, the partial pressure of O2(g) in the reaction vessel is 4.70 atm. Calculate the partial pressures of SO3(g) and SO2(g) when equilibrium is reestablished.

****

**AP Practice LeChatelier**

1. For the system 2 SO2*(g)* + O2*(g)* ↔ 2 SO3*(g)* , Δ*H* is negative for the production of SO3. Assume that one has an equilibrium mixture of these substances. Predict the effect of each of the following changes on the value of the equilibrium constant and on the number of moles of SO3 present in the mixture at equilibrium. Briefly account for each of your predictions. (Assume that in each case all other factors remain constant.)

1. Decreasing the volume of the system.
2. Adding oxygen to the equilibrium mixture.

(c) Raising the temperature of the system.

NH4Cl*(s)* ↔ NH3*(g)* + HCl*(g)* Δ*H* = +42.1 kilocalories

2. Suppose the substances in the reaction above are at equilibrium at 600K in volume V and at pressure P. State whether the partial pressure of NH3*(g)* will have increased, decreased, or remained the same when equilibrium is reestablished after each of the following disturbances of the original system. Some solid NH4Cl remains in the flask at all times. Justify each answer with a one-or-two sentence explanation.

(a) A small quantity of NH4Cl is added.

1. The temperature of the system is increased.
2. The volume of the system is increased.
3. A quantity of gaseous HCl is added.

(e) A quantity of gaseous NH3 is added.

NH4HS*(s)* ↔ NH3*(g)* + H2S*(g)* ΔHº = +93 kilojoules

3. The equilibrium above is established by placing solid NH4HS in an evacuated container at 25ºC. At equilibrium, some solid NH4HS remains in the container. Predict and explain each of the following.

(a) The effect on the equilibrium partial pressure of NH3 gas when additional solid NH4HS is introduced

1. The effect on the equilibrium partial pressure of NH3 gas when additional solid H2S is introduced
2. The effect on the mass of solid NH4HS present when the volume of the container is decreased

(d) The effect on the mass of solid NH4HS present when the temperature is increased.

**AP Equilibrium**

1. Sulfuryl chloride, SO2Cl2, is a highly reactive gaseous compound. When heated, it decomposes as follows: SO2Cl2*(g)* → SO2*(g)* + Cl2*(g)*. This decomposition is endothermic. A sample of 3.509 grams of SO2Cl2 is placed in an evacuated 1.00 liter bulb and the temperature is raised to 375K.

(a) What would be the pressure in atmospheres in the bulb if no dissociation of the SO2Cl2*(g)* occurred?

(b) When the system has come to equilibrium at 375K, the total pressure in the bulb is found to be 1.43 atmospheres. Calculate the partial pressures of SO2, Cl2, and SO2Cl2 at equilibrium at 375K.

(c) Give the expression for the equilibrium constant (either Kp or Kc) for the decomposition of SO2Cl2*(g)* at 375K. Calculate the value of the equilibrium constant you have given, and specify its units.

(d) If the temperature were raised to 500K, what effect would this have on the equilibrium constant?

2. At elevated temperatures, SbCl5 gas decomposes into SbCl3 gas and Cl2 gas as shown by the following equation: SbCl5*(g)* ↔ SbCl3*(g)* + Cl2*(g)*

(a) An 89.7 gram sample of SbCl5 (molecular weight 299.0) is placed in an evacuated 15.0 liter container at 182ºC.

i) What is the concentration in M of SbCl5 in the container before any decomposition occurs?

ii) What is the pressure in atmospheres of SbCl5 in the container before any decomposition occurs?

(b) If the SbCl5 is 29.2 percent decomposed when equilibrium is established at 182ºC, calculate the value for either equilibrium constant Kp or Kc, for this decomposition reaction. Indicate whether you are calculating Kp or Kc.

(c) In order to produce some SbCl5, a 1.00 mole sample of SbCl3 is first placed in an empty 2.00 liter container maintained at a temperature different from 182ºC. At this temperature, Kc, equals 0.117. How many moles of Cl2 must be added to this container to reduce the number of moles of SbCl3 to 0.700 mole at equilibrium?

2 NaHCO3*(s)* ↔ Na2CO3*(s)* + H2O*(g)* + CO2*(g)*

3. Solid sodium hydrogen carbonate, NaHCO3, decomposes on heating according to the equation above.

(a) A sample of 100. grams of solid NaHCO3 was placed in a previously evacuated rigid 5.00-liter container and heated to 160ºC. Some of the original solid remained and the total pressure in the container was 7.76 atmospheres when equilibrium was reached. Calculate the number of moles of H2O*(g)* present at equilibrium.

(b) How many grams of the original solid remain in the container under the conditions described in (a)?

(c) Write the equilibrium expression for the equilibrium constant, KP, and calculate its value for the reaction under the conditions in (a).

(d) If 110. grams of solid NaHCO3 had been placed in the 5.00-liter container and heated to 160ºC, what would the total pressure have been at equilibrium? Explain

CO2*(g)* + H2*(g)* ↔ H2O*(g)* + CO*(g)*

4. When H2*(g)* is mixed with CO2*(g)* at 2,000 K, equilibrium is achieved according to the equation above. In one experiment, the following equilibrium concentrations were measured.

[H2] = 0.20 mol/L [CO2] = 0.30 mol/L [H2O] = [CO] = 0.55 mol/L

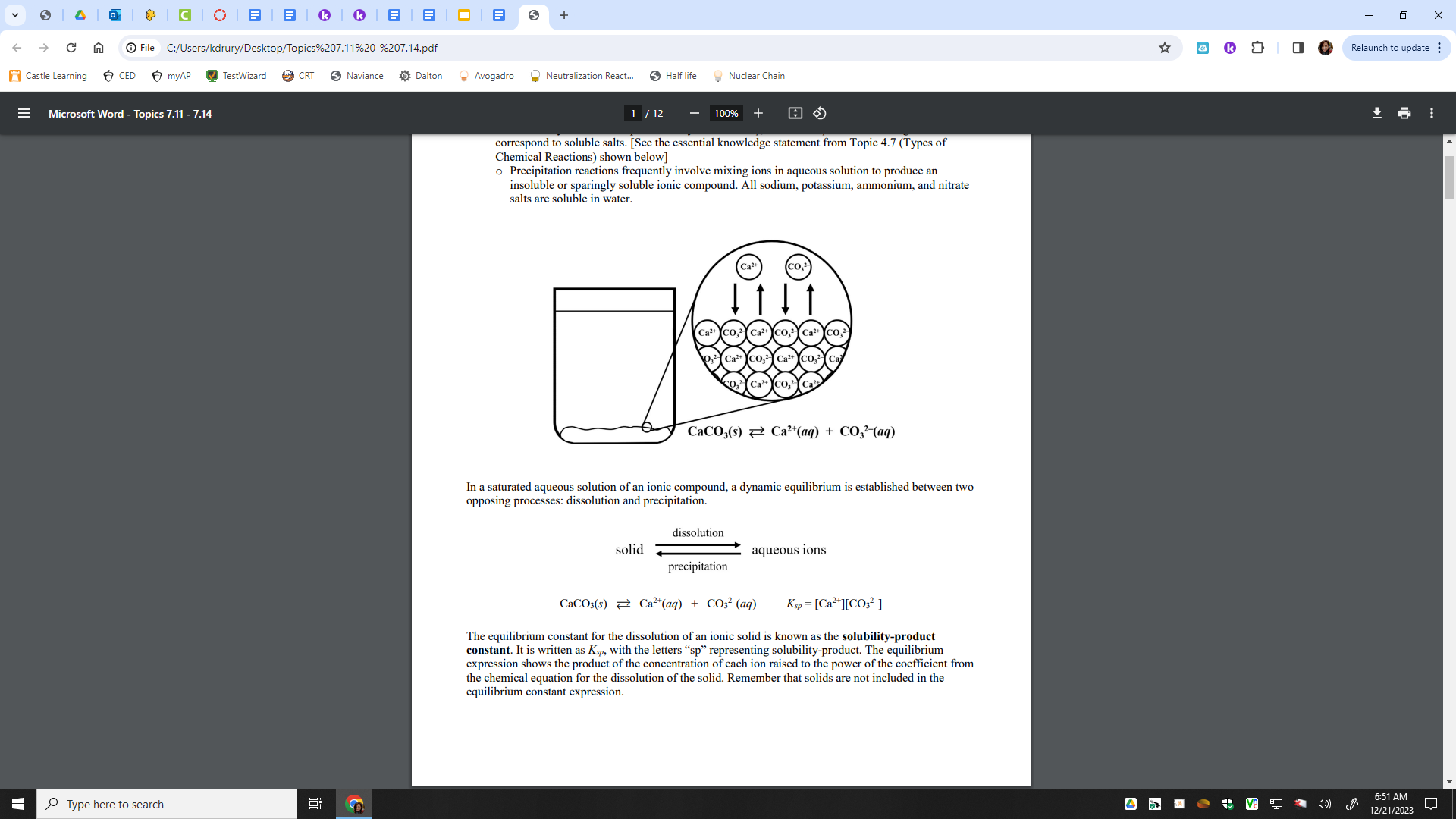
(a) What is the mole fraction of CO*(g)* in the equilibrium mixture?

(b) Using the equilibrium concentrations given above, calculate the value of *Kc*, the equilibrium constant for the reaction.

(c) When the system is cooled from 2,000 K to a lower temperature, 30.0 percent of the CO*(g)* is converted back to CO2*(g)*. Calculate the value of *Kc* at this lower temperature.

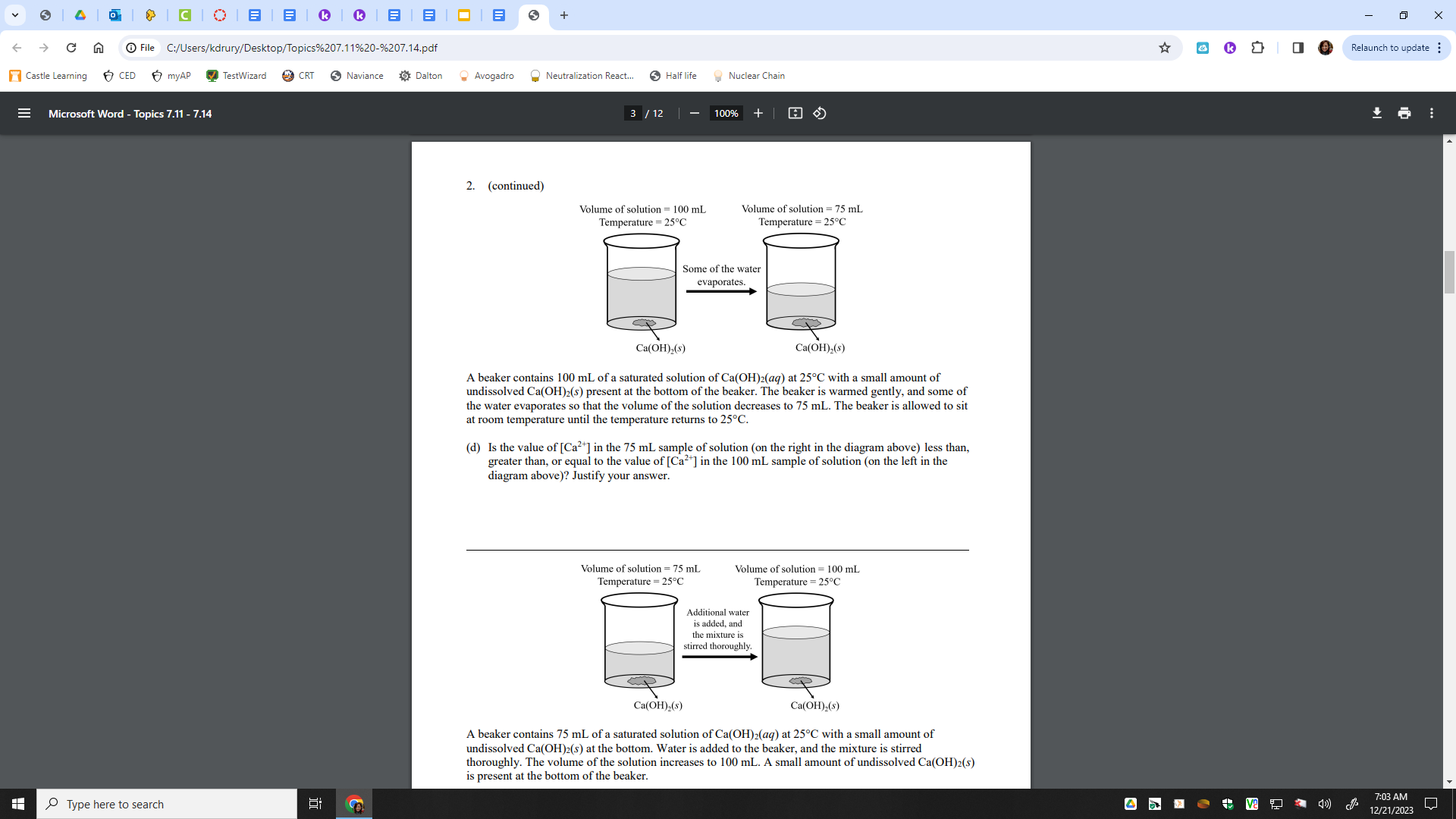
(d) In a different experiment, 0.50 mole of H2*(g)* is mixed with 0.50 mole of CO2*(g)* in a 3.0-liter reaction vessel at 2,000 K. Calculate the equilibrium concentration, in moles per liter, of CO*(g)* at this temperature.

**Ksp and (Molar) Solubility**



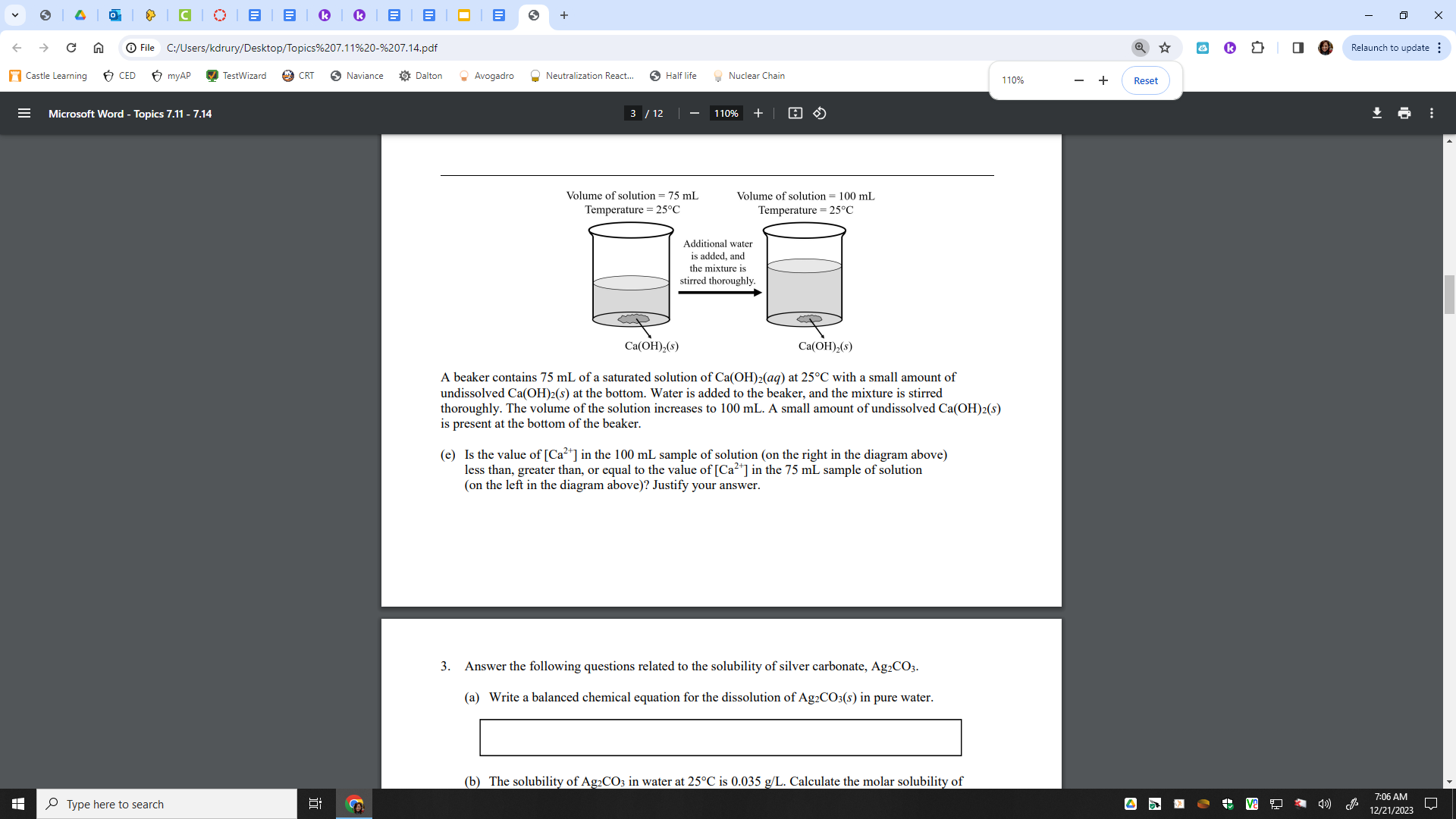
Ksp is known as the solubility product constant. It is constructed and calculated the same as Kc but specifically for “insoluble” salts. The concentrations, measured in M, used to calculate the Ksp are also known as “Molar Solubility” whereas “Solubility” is measured in g/L.

1. Write the Ksp for the reaction above.
2. Explain the equilibrium system represented in terms of concentration of reactants and products and the rates of the forward and reverse reactions.
3. If the solubility of CaCO3 is 0.015g/L at 298K, calculate the Molar Solubility.
4. Calculate the Ksp of CaCO3.
5. Compare the solubility of CaCO3 to Ca(OH)2 (Ksp=5.0x10-6).



A beaker contains 100 mL of a saturated solution of Ca(OH)2(aq) at 25°C with a small amount of undissolved Ca(OH)2(s) present at the bottom of the beaker. The beaker is warmed gently, and some of the water evaporates so that the volume of the solution decreases to 75 mL. The beaker is allowed to sit at room temperature until the temperature returns to 25°C.

1. Is the value of [Ca2+] in the 75 mL sample of solution (on the right in the diagram above) less than, greater than, or equal to the value of [Ca2+] in the 100 mL sample of solution (on the left in the diagram above)? Justify your answer.

A beaker contains 75 mL of a saturated solution of Ca(OH)2(aq) at 25°C with a small amount of undissolved Ca(OH)2(s) at the bottom. Water is added to the beaker, and the mixture is stirred thoroughly. The volume of the solution increases to 100 mL. A small amount of undissolved Ca(OH)2(s) is present at the bottom of the beaker. 

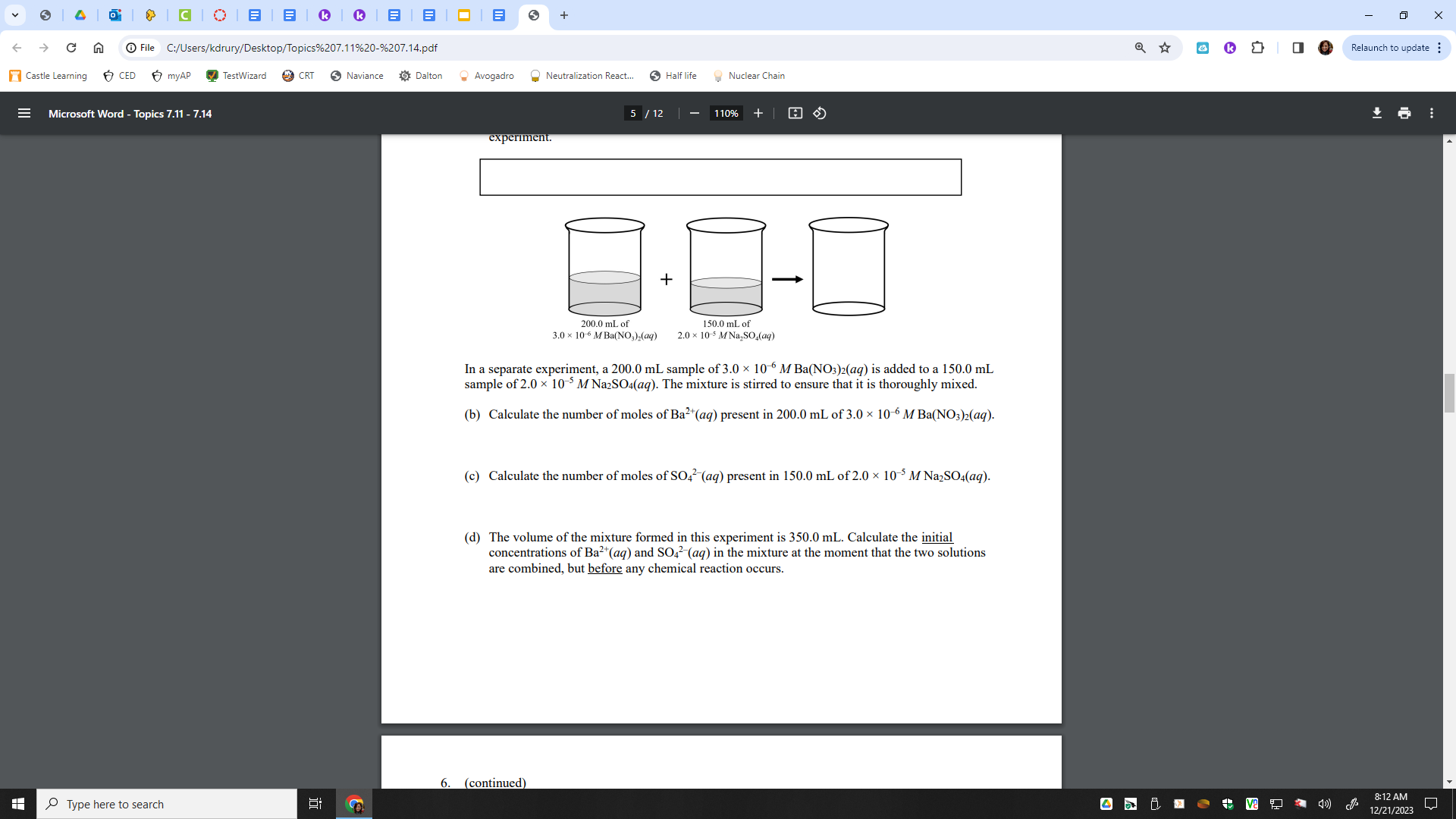
1. Is the value of [Ca2+] in the 100 mL sample of solution (on the right in the diagram above) less than, greater than, or equal to the value of [Ca2+] in the 75 mL sample of solution (on the left in the diagram above)? Justify your answer.

**Additional Examples:** Write the Equilibrium expression for each question and then solve:

1. If the molar solubility of CaF2 is 1.24 x 10-3 M, calculate the Ksp.
2. The Ksp for LaF3 is 2 x 10-19.
   1. What is the molar solubility of LaF3 in M?
   2. What is the solubility in g/L?
3. The Ksp for Cr(OH)3 is 1.6 x 10-30. Calculate the molar solubility of Cr(OH)3 and the ion concentrations.
4. The Ksp for Calcium Phosphate is 2.0 x 10-29. Calculate the molar solubility and ion concentrations.
5. A 1.00L solution is saturated at 25 C with Lead (II) Iodide containing 0.54g of PbI2. Calculate the Ksp.
6. Soluble barium compounds are poisonous; however, barium sulfate is routinely ingested as a suspended solid to improve the contrast in x-ray images. Calculate the concentration of dissolved barium per liter of water in equilibrium with solid barium sulfate. The Ksp is 1.1x10-10.

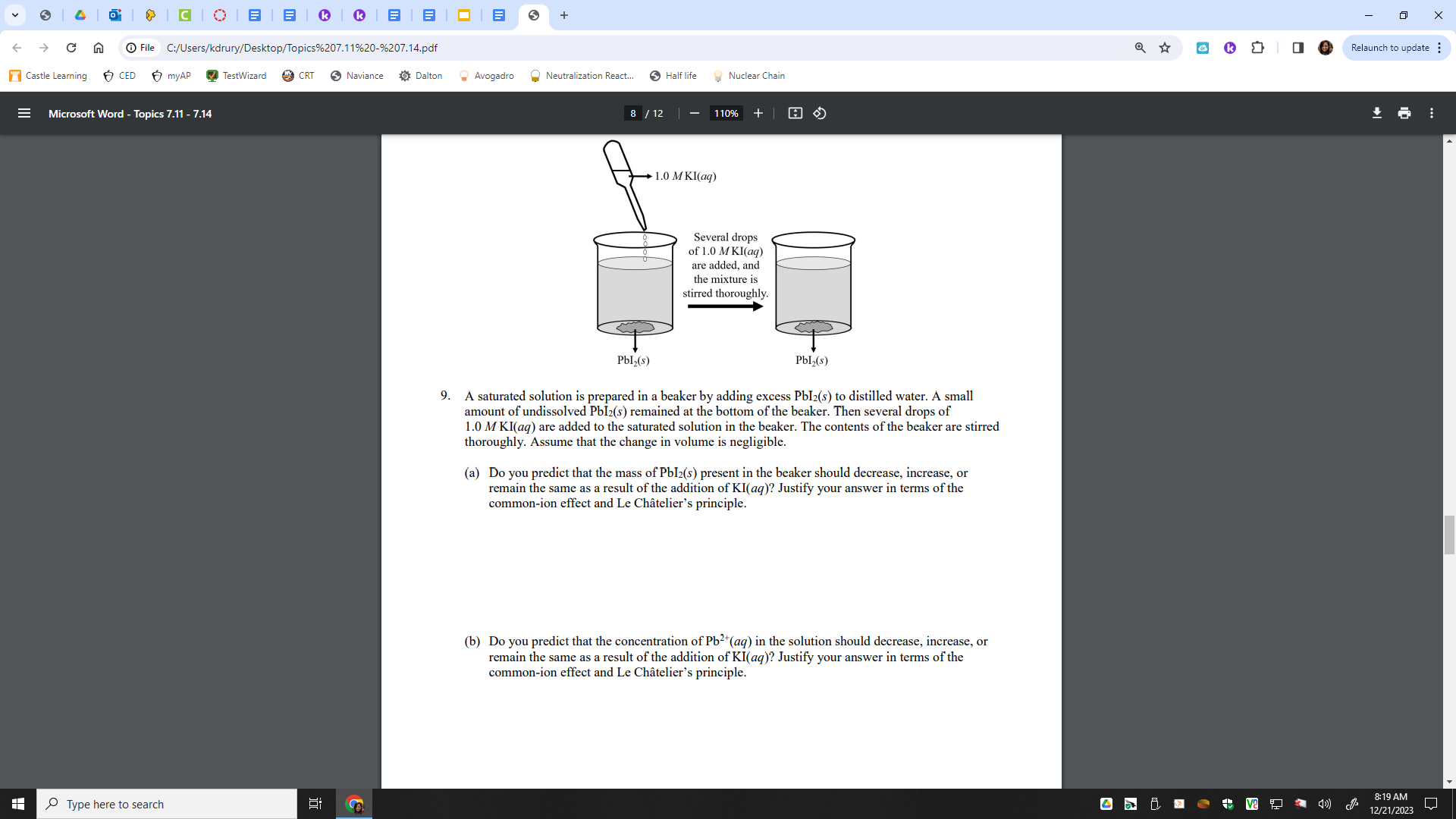
| Compound | CaF2 | SrF2 | BaF2 |
| --- | --- | --- | --- |
| Ksp at 25C | 3.9x10-11 | 4.3x10-9 | 1.8x10-7 |

1. Saturated solutions of each compound listed in the table above were prepared at 25°C. Use the information in the table above to answer the following questions.
   1. Which compound has the smallest value for molar solubility in water at 25°C? Justify your answer.
   2. Calculate the value of [F– ] (in mol/L) in a saturated solution of the compound that you selected in part (a).



1. A student adds an excess amount of Na2SO4(aq) to a solution of Ba(NO3)2(aq), resulting in the formation of a precipitate.
   1. Write the net ionic equation for the reaction that occurred in this experiment.
   2. In a separate experiment, a 200.0 mL sample of 3.0 × 10–6 M Ba(NO3)2(aq) is added to a 150.0 mL sample of 2.0 × 10–5 M Na2SO4(aq). The mixture is stirred to ensure that it is thoroughly mixed. Calculate the number of moles of Ba2+(aq) present in 200.0 mL of 3.0 × 10–6 M Ba(NO3)2(aq).
   3. Calculate the number of moles of SO4 2–(aq) present in 150.0 mL of 2.0 × 10–5 M Na2SO4(aq).
   4. The volume of the mixture formed in this experiment is 350.0 mL. Calculate the initial concentrations of Ba2+(aq) and SO4 2–(aq) in the mixture at the moment that the two solutions are combined, but before any chemical reaction occurs.
   5. Use your answers to part (d) to calculate the value of the reaction quotient (Qsp) for BaSO4.
   6. The value of Ksp for BaSO4 is 1.1 × 10–10. Will a precipitate of BaSO4(s) be formed in this experiment? Justify your answer by comparing Qsp with Ksp.
2. A solution of NaF is added dropwise to a solution that is 0.0144M Ba2+. At what concentration will BaF2 precipitate? Ignore changes in volume. Ksp = 1.7x10-7.
3. A solution of Barium chromate is prepared by dissolving 6.3x10-3 g of this yellow solid in 1.00L of hot water. Will solid barium chromate precipitate upon cooling according to the Ksp? If so, how much will precipitate? Ksp=2.1x10-10.
4. Summarize:

|  | saturated, unsaturated, supersaturated? | precipitate, dissolve more, equilibrium? |
| --- | --- | --- |
| Q=Ksp |  |  |
| Q>Ksp |  |  |
| Q<Ksp |  |  |



1. A saturated solution is prepared in a beaker by adding excess PbI2(s) to distilled water. A small amount of undissolved PbI2(s) remained at the bottom of the beaker. Then several drops of 1.0 M KI(aq) are added to the saturated solution in the beaker. The contents of the beaker are stirred thoroughly. Assume that the change in volume is negligible.
   1. Do you predict that the mass of PbI2(s) present in the beaker should decrease, increase, or remain the same as a result of the addition of KI(aq)? Justify your answer in terms of the common-ion effect and Le Châtelier’s principle.
   2. Do you predict that the concentration of Pb2+(aq) in the solution should decrease, increase, or remain the same as a result of the addition of KI(aq)? Justify your answer in terms of the common-ion effect and Le Châtelier’s principle.

**Ksp and pH**

Mg(OH)2(s) ⇄ Mg2+(aq) + 2 OH– (aq) Ksp = 5.6 × 10–12

1. The dissolution of Mg(OH)2(s) in water is represented by the equation above. A saturated solution is prepared in a beaker by adding excess Mg(OH)2(s) to distilled water. A small amount of undissolved Mg(OH)2(s) remained at the bottom of the beaker.
   1. Several drops of concentrated NaOH(aq) are added to a saturated solution of Mg(OH)2(aq), and the mixture is stirred thoroughly. Assume that the change in volume is negligible. The addition of NaOH(aq) causes the concentration of Mg2+(aq) in the solution to decrease. Explain this result in terms of Le Châtelier’s principle.
   2. Several drops of concentrated HNO3(aq) are added to a saturated solution of Mg(OH)2(aq), and the mixture is stirred thoroughly. Assume that the change in volume is negligible. The addition of HNO3(aq) causes the mass of Mg(OH)2(s) present in the mixture to decrease. Explain this result in terms of Le Châtelier’s principle.

The following information describes relationships between [H+ ], [OH– ], and pH. Calculations involving pH will be featured in Unit 8 (Acids and Bases). When an acid is added to water, [H+ ] increases, and the pH decreases. When a base is added to water, [OH– ] increases, and the pH increases.

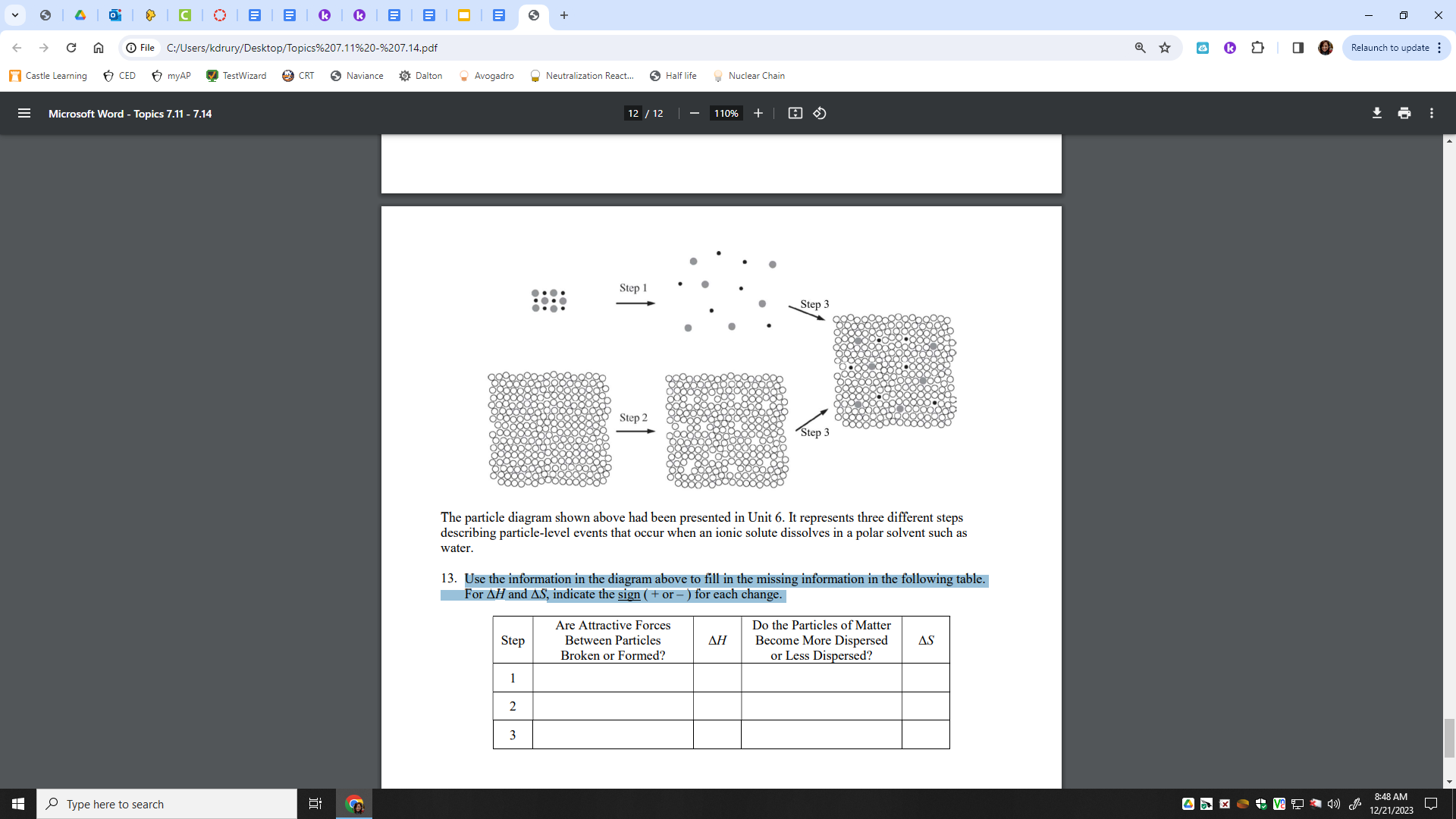
Ni(OH)2(s) ⇄ Ni2+(aq) + 2 OH– (aq) Ksp = 5.5 × 10–16

1. The dissolution of Ni(OH)2(s) in water is represented by the equation above.
   1. How will a change in pH decrease the solubility of Ni(OH)2 in an aqueous solution? Justify your answer in terms of Le Châtelier’s principle.
   2. How will a change in pH increase the solubility of Ni(OH)2 in an aqueous solution? Justify your answer in terms of Le Châtelier’s principle.

**Ksp and Gibbs Free Energy**

1. Fill in the following table. For ΔH and ΔS, indicate the sign ( + or – ) for each change.

| Phase Change | Are Attractive Forces Between Particles Broken or Formed? | ΔH | Do the Particles of Matter Become More Dispersed or Less Dispersed? | ΔS |
| --- | --- | --- | --- | --- |
| melting  (solid → liquid) |  |  |  |  |
| freezing  (liquid → solid) |  |  |  |  |
| evaporation (liquid → gas) |  |  |  |  |
| condensation  (gas → liquid) |  |  |  |  |

****

1. The diagram above represents 3 different steps describing particle-level events that occur when an ionic solute dissolves in a polar solvent such as water. Use the information in the diagram above to fill in the following table. For ΔH and ΔS, indicate the sign ( + or – ) for each change.

| Step | Are Attractive Forces Between Particles Broken or Formed? | ΔH | Do the Particles of Matter Become More Dispersed or Less Dispersed? | ΔS |
| --- | --- | --- | --- | --- |
| 1 |  |  |  |  |
| 2 |  |  |  |  |
| 3 |  |  |  |  |

**AP Solubility FRQ**

1. At 25ºC the solubility product constant, Ksp, for strontium sulfate, SrSO4, is 7.6×10-7. The solubility product constant for strontium fluoride, SrF2, is 7.9×10-10.

(a) What is the molar solubility of SrSO4 in pure water at 25ºC?

1. What is the molar solubility of SrF2 in pure water at 25ºC?

(c) An aqueous solution of Sr(NO3)2 is added slowly to 1.0 litre of a well-stirred solution containing 0.020 mole F- and 0.10 mole SO42- at 25ºC. (You may assume that the added Sr(NO3)2 solution does not materially affect the total volume of the system.)

i. Which salt precipitates first?

ii. What is the concentration of strontium ion, Sr2+, in the solution when the first precipitate begins to form?

2. H2S + H2O ↔ H3O+ + HS– K1 = 1.0×10–7

HS– + H2O ↔ H3O+ + S2– K2 = 1.3×10–13

H2S + 2 H2O ↔ 2 H3O+ + S2– K = 1.3×10–20

Ag2S*(s)* ↔ 2 Ag+ + S2– Ksp= 5.5×10–51

1. Calculate the concentration of H3O+ of a solution which is 0.10 molar in H2S.
2. Calculate the concentration of the sulfide ion, S2–, in a solution that is 0.10 molar in H2S and 0.40 molar in H3O+.
3. Calculate the maximum concentration of silver ion, Ag+, that can exist in a solution that is 1.5×10–17 molar in sulfide ion, S2–.

**AP Chemistry: Equilibrium Multiple Choice**

| 76. HgO(s) + 4 I− + H2O ⇄ HgI42− + 2 OH−; ∆H < 0  Consider the equilibrium above. Which of the following changes will increase the concentration of HgI42−? |
| --- |
| (A) Increasing the concentration of OH− (B) Adding 6 M HNO3 |
| (C) Increasing the mass of HgO present (D) Increasing the temperature (E) Adding a catalyst |
| 29. In which of the following systems would the number of moles of the substances present at equilibrium NOT be shifted by a change in the volume of the system at constant temperature? |
| (A) CO(g) + NO(g) ⇄ CO2(g) + 1/2 N2(g) (B) N2(g) + 3 H2(g) ⇄ 2 NH3(g) |
| (C) N2(g) + 2 O2(g) ⇄ 2 NO2(g) (D) N2O4(g) ⇄ 2 NO2(g) |
| (E) NO(g) + O3(g) ⇄ NO2(g) + O2(g) |
| 48. PCl3(g) + Cl2(g) ⇄ PCl5(g) + energy |
| Some PCl3 and Cl2 are mixed in a container at 200 °C and the system reaches equilibrium according to the equation above. Which of the following causes an increase in the number of moles of PCl5 present at equilibrium? |
| I. Decreasing the volume of the container |
| II. Raising the temperature |
| III. Adding a mole of He gas at constant volume |
| (A) I only (B) II only (C) I and III only (D) II and III only (E) I, II, and III |
| 51. 4 HCl(g) + O2(g) ⇄ 2 Cl2(g) + 2 H2O(g)  Equal numbers of moles of HCl and O2 in a closed system are allowed to reach equilibrium as represented by the equation above. Which of the following must be true at equilibrium? |
| I. [HCl] must be less than [Cl2]. |
| II. [O2] must be greater than [HCl]. |
| III. [Cl2] must equal [H2O]. |
| (A) I only (B) II only (C) I and III only (D) II and III only (E) I, II, and III |
| 65. The solubility of CuI is 2 x 10−6 molar. What is the solubility product constant, Ksp, for CuI? |
| (A) 1.4 x 10−3 (B) 2 x 10−6 (C) 4 x 10−12 (D) 2 x 10−12 (E) 8 x 10−18 |
| 73. 2 SO2(g) + O2(g) ⇄ 2 SO3(g)  When 0.40 moles of SO2 and 0.60 moles of O2 are placed in an evacuated 1.00-liter flask, the reaction represented above occurs. After the reactants and the product reach equilibrium and the initial temperature is restored, the flask is found to contain 0.30 moles of SO3. Based on these results, the expression for the equilibrium constant, Kc, of the reaction is… |
| (A) (0.30)2 / [(0.45)(0.10)2] (B) (0.30)2 / [(0.60)(0.40)2] (C) (2 x 0.30) / [(0.45)(2 x 0.10)] |
| (D) (0.30) / [(0.45)(0.10)] (E) (0.30) / [(0.60)(0.40)] |
| 54. 2NO(g) + O2(g) ⇄ 2 NO2(g) ; ∆H < 0  Which of the following changes alone would cause a decrease in the value of Keq for the reaction represented above? |
| (A) Decreasing the temperature (B) Increasing the temperature |
| (C) Decreasing the volume of the reaction vessel (D) Increasing the volume of the reaction vessel |
| (E) Adding a catalyst |
| 2 SO3*(g)* ⇄ 2 SO2*(g)* + O2*(g)*  41. After the equilibrium represented above is established, some pure O2*(g)* is injected into the reaction vessel at constant temperature. After equilibrium is reestablished, which of the following has a lower value compared to its value at the original equilibrium?  (A) *Keq* for the reaction  (B) The total pressure in the reaction vessel  (C) The amount of SO3*(g)* in the reaction vessel  (D) The amount of O2*(g)* in the reaction vessel  (E) The amount of SO2*(g)* in the reaction vessel |
| 37. HCO3−(aq) + OH− (aq) ⇄ H2O(l) + CO32− (aq) ΔH° = −41.4kJ When the reaction represented by the equation above is at equilibrium at 1 atm and 25°C, the ratio [CO32−] can be increased by doing which of the following? [HCO3−]  (A) Decreasing the temperature (B) Adding acid (C) Adding a catalyst (D) Diluting the solution with distilled water (E) Bubbling neon gas through the solution |
| 42. H2(g) + Br2(g) ⇄ 2HBr(g) At a certain temperature, the value of the equilibrium constant, K, for the reaction represented above is 2.0 × 105. What is the value of K for the reverse reaction at the same temperature?  (A) −2.0 × 10−5 (B) 5.0 × 10−6 (C) 2.0 × 10−5  (D) 5.0 × 10−5 (E) 5.0 × 10−4 |
| 1. In a saturated solution of Zn(OH)2 at 25°C , the value of [OH−] is 2.0 × 10−6M. What is the value of the solubility-product constant, Ksp, for Zn(OH)2 at 25°C ?   (A) 4.0 × 10−18 (B) 8.0 × 10−18 (C) 1.6 × 10−17 (D) 4.0 × 10−12 (E) 2.0 × 10−6 |
| 36. CuO(s) + H2(g) ⇄ Cu(s) + H2O(g) ; ∆H = − 2.0 kilojoules |
| When the substances in the equation above are at equilibrium at pressure P and temperature T, the equilibrium can be shifted to favor the products by… |
| (A) increasing the pressure by means of a moving piston at constant T. |
| (B) increasing the pressure by adding an inert gas such as nitrogen. |
| (C) decreasing the temperature. |
| (D) allowing some gases to escape at constant P and T. |
| (E) adding a catalyst. |