Experiment 7.
LeChâtelier's Principle; Buffers

Experimental Procedure

- Objectives
- Introduction
- Experimental Procedure

OBJECTIVES

- To study the effects if concentration and temperature changes on the position of equilibrium in a chemical system
- To study the effect of strong acid and strong base addition on the pH of buffered and unbuffered systems
- To observe the common-ion effect on a dynamic equilibrium

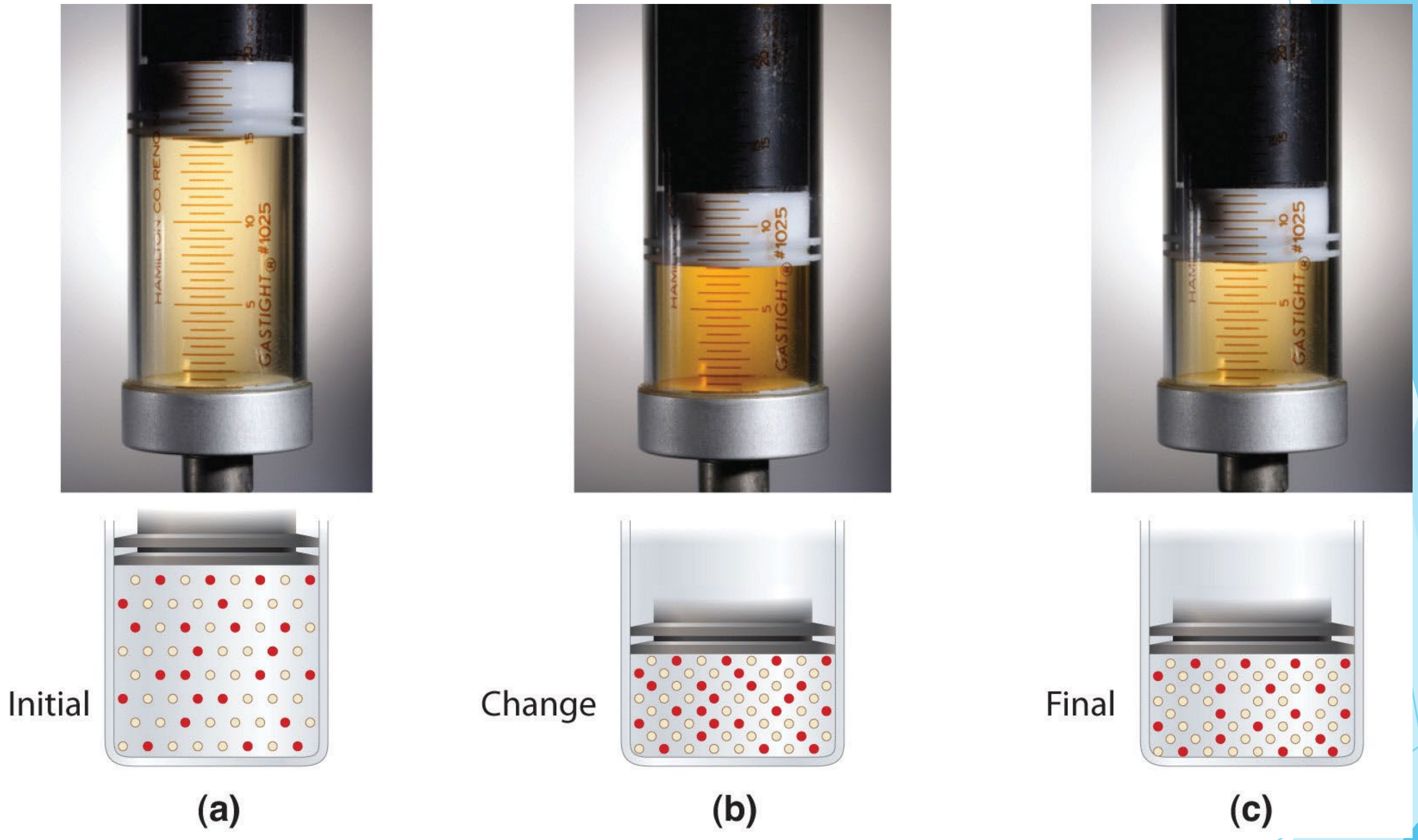
Introduction

Chemists use various strategies to increase the yield of the desired products of reactions. When synthesizing an ester, for example, how can a chemist control the reaction conditions to obtain the maximum amount of the desired product? Only three types of stresses can change the composition of an equilibrium mixture: (1) a change in the concentrations (or partial pressures) of the components by adding or removing reactants or products, (2) a change in the total pressure or volume, and (3) a change in the temperature of the system.

LeChâtelier's Principle:

If an external stress (change in concentration, temperature, etc) is applied to a system in a state of dynamic equilibrium, the equilibrium shifts in the direction that minimizes the effect of that stress.

Changes in Total Pressure or Volume

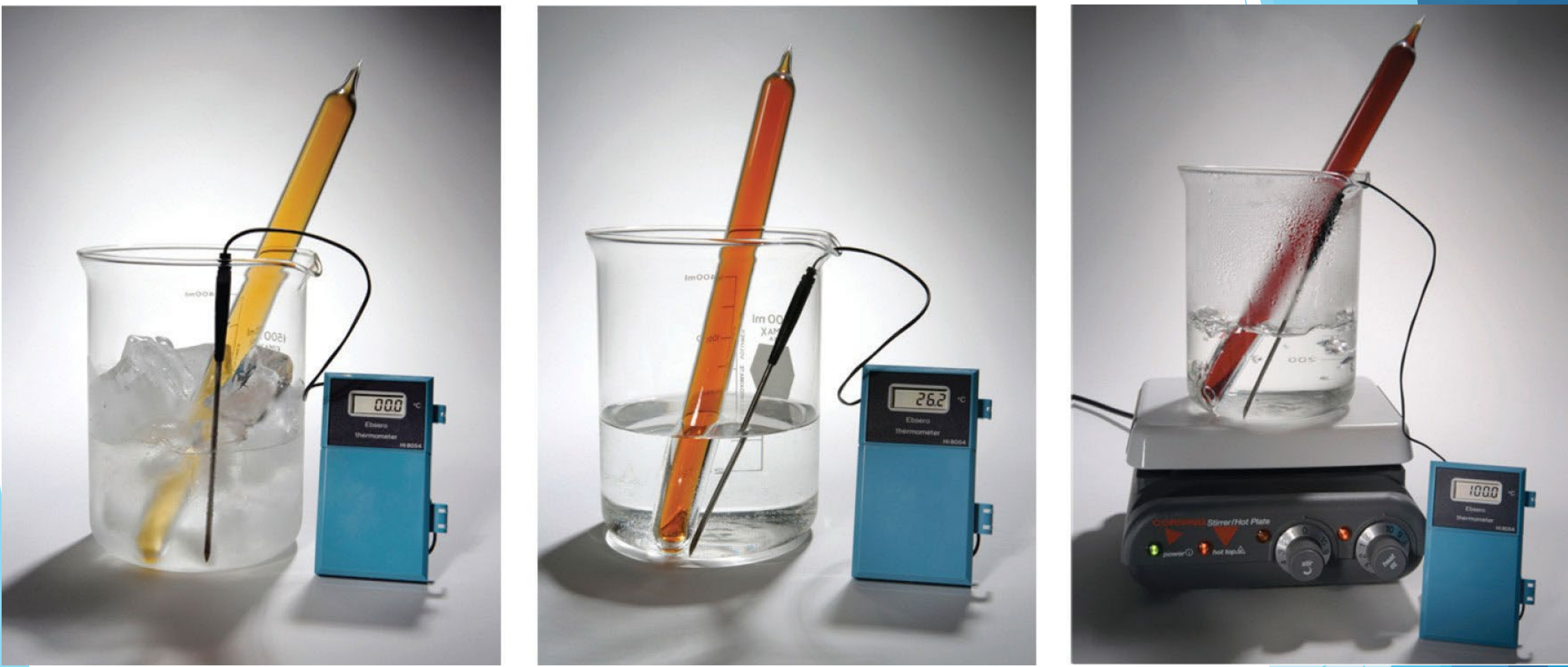


The Effect of Changing the Volume (and Thus the Pressure) of an Equilibrium Mixture of N_2O_4 and NO_2 at Constant Temperature

(a) The syringe with a total volume of 15 mL contains an equilibrium mixture of N_2O_4 and NO_2; the red-brown color is proportional to the NO_2 concentration.
(b) (b) If the volume is rapidly decreased by a factor of 2 to 7.5 mL, the initial effect is to double the concentrations of all species present, including NO_2. Hence the color becomes more intense.
(c) With time, the system adjusts its composition in response to the stress as predicted by Le Châtelier's principle, forming colorless N_2O_4 at the expense of red-brown NO_2, which decreases the intensity of the color of the mixture.

In general, if a balanced chemical equation contains different numbers of gaseous reactant and product molecules, the equilibrium will be sensitive to changes in volume or pressure. Increasing the pressure on a system (or decreasing the volume) will favor the side of the reaction that has fewer gaseous molecules and vice versa.

Changes in Temperature



The Effect of Temperature on the Equilibrium between Gaseous N_2O_4 and NO_2

(center) A tube containing a mixture of N_2O_4 and NO_2 in the same proportion at room temperature is red-brown due to the NO_2 present.
(left) Immersing the tube in ice water causes the mixture to become lighter in color due to a shift in the equilibrium composition toward colorless N_2O_4.
(right) In contrast, immersing the same tube in boiling water causes the mixture to become darker due to a shift in the equilibrium composition toward the highly colored NO_2.

The effect of increasing the temperature on a system at equilibrium can be summarized as follows: increasing the temperature increases the magnitude of the equilibrium constant for an endothermic reaction, decreases the equilibrium constant for an exothermic reaction, and has no effect on the equilibrium constant for a thermally neutral reaction.

Experimental Procedure

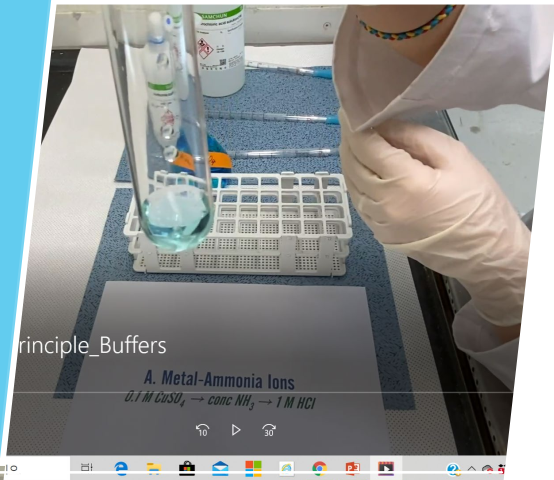
Overview

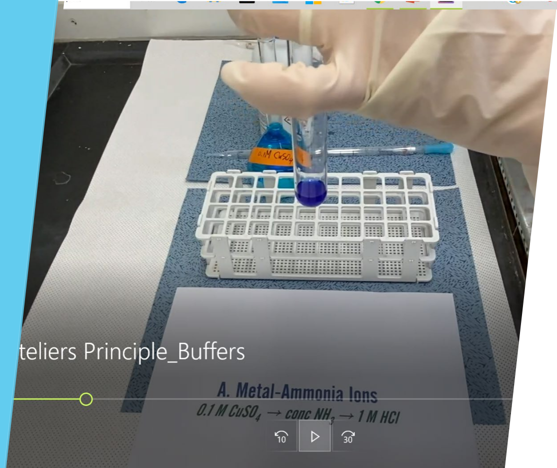
A large number of qualitative tests and observations are performed. The effects that concentration changes and temperature changes have on a system at equilibrium are observed and interpreted using LeChâtelier's principle. The functioning of a buffer system and the effect of a common ion on equilibria are observed.

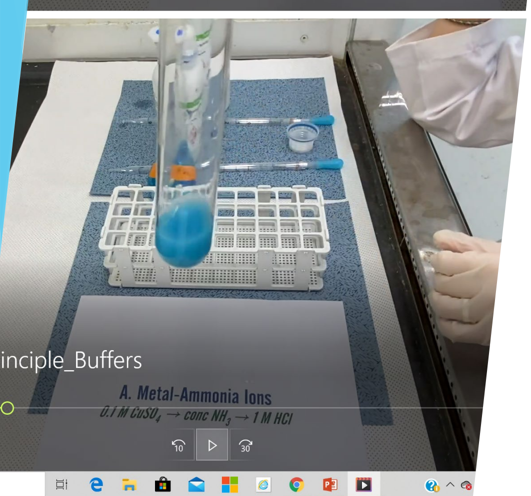
Perform this experiment with a partner. At each circled superscript (1–21) in the procedure, stop and record your observation on the Report Sheet. Discuss your observation with your lab partner and TA. Account for the changes in appearance of the solution after each addition in terms of LeChâtelier's principle.

Part A.

Metal–Ammonia Ions





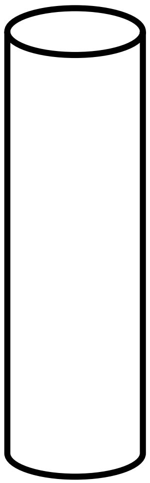


1. Formation of metal–ammonia ions. Place ~ 1mL (<20 drops) of **0.1 M $CuSO_4$** in a small, clean test tube. (1) Add drops of conc NH_3 (Caution: strong ordor, do not inhale) until a color change occurs and the solution is clear (not colorless). (2)

2. Shift of equilibrium. Add drops of 1 M HCl until the color again changes. (3)

Part B. Multiple Equilibria with the Silver Ion

Summary



1–1) ~ 0.5 mL of 0.1 M Na_2CO_3

1–2) ~ 0.5 mL (≤10 drops) 0.01 M $AgNO_3$

1–3) Add drops of 6 M HNO_3 until a chemical change occurs.

2–1) ~ 5 drops of 0.1 M HCl

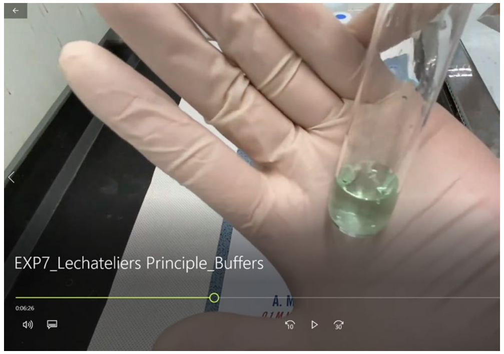
2–2) Add drops of conc NH_3 until evidence of a chemical change occurs. (At this point, the solution should be "Clear and colorless.")

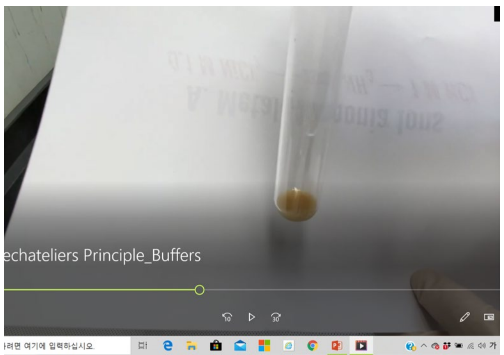
2–3) Reacidify with 6 M HNO_3.

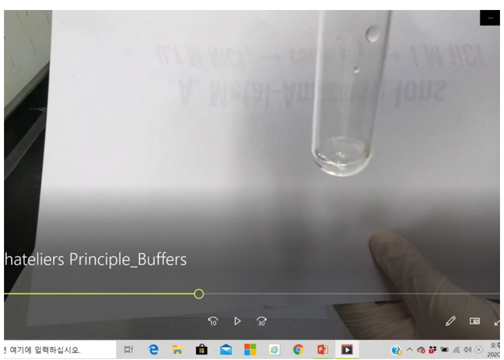
2–4) Add excess conc NH_3.

3–1) Add drops of 0.1 M KI

4–1) Add drops of 0.1 M Na_2S until evidence of chemical change has occurred.

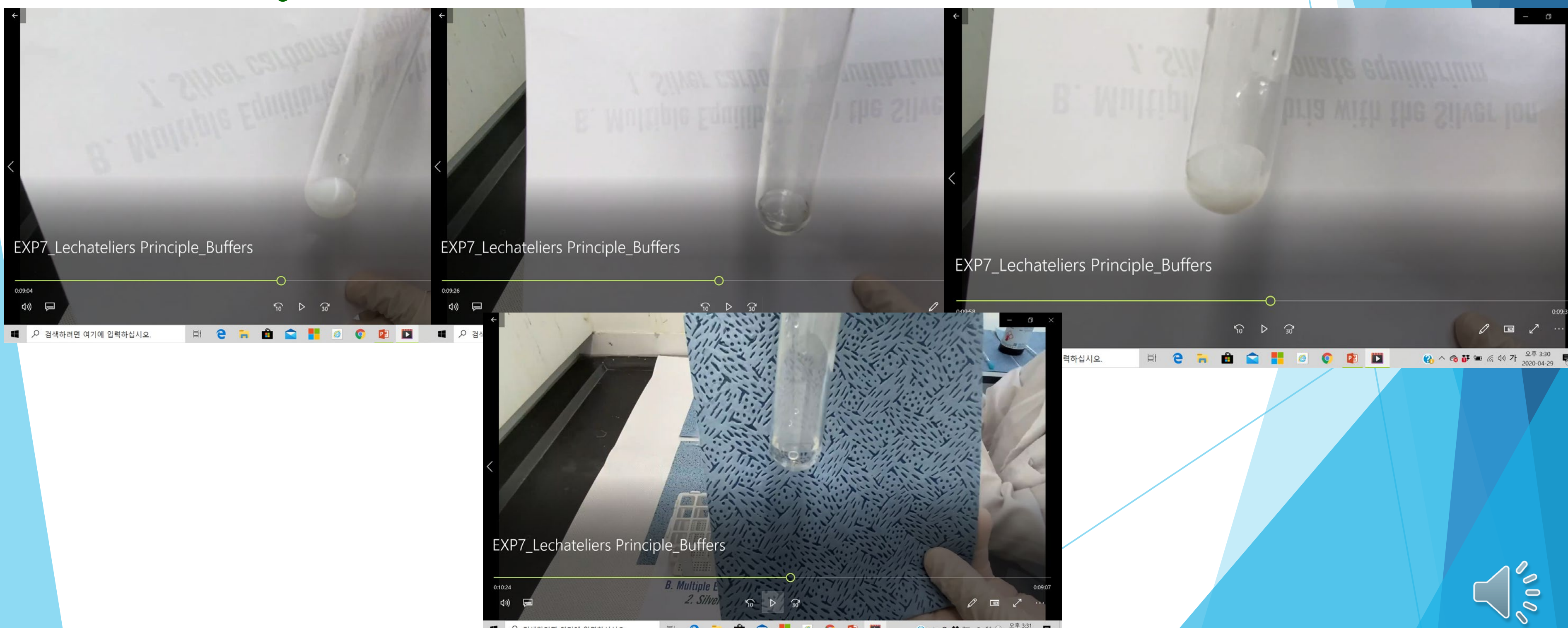






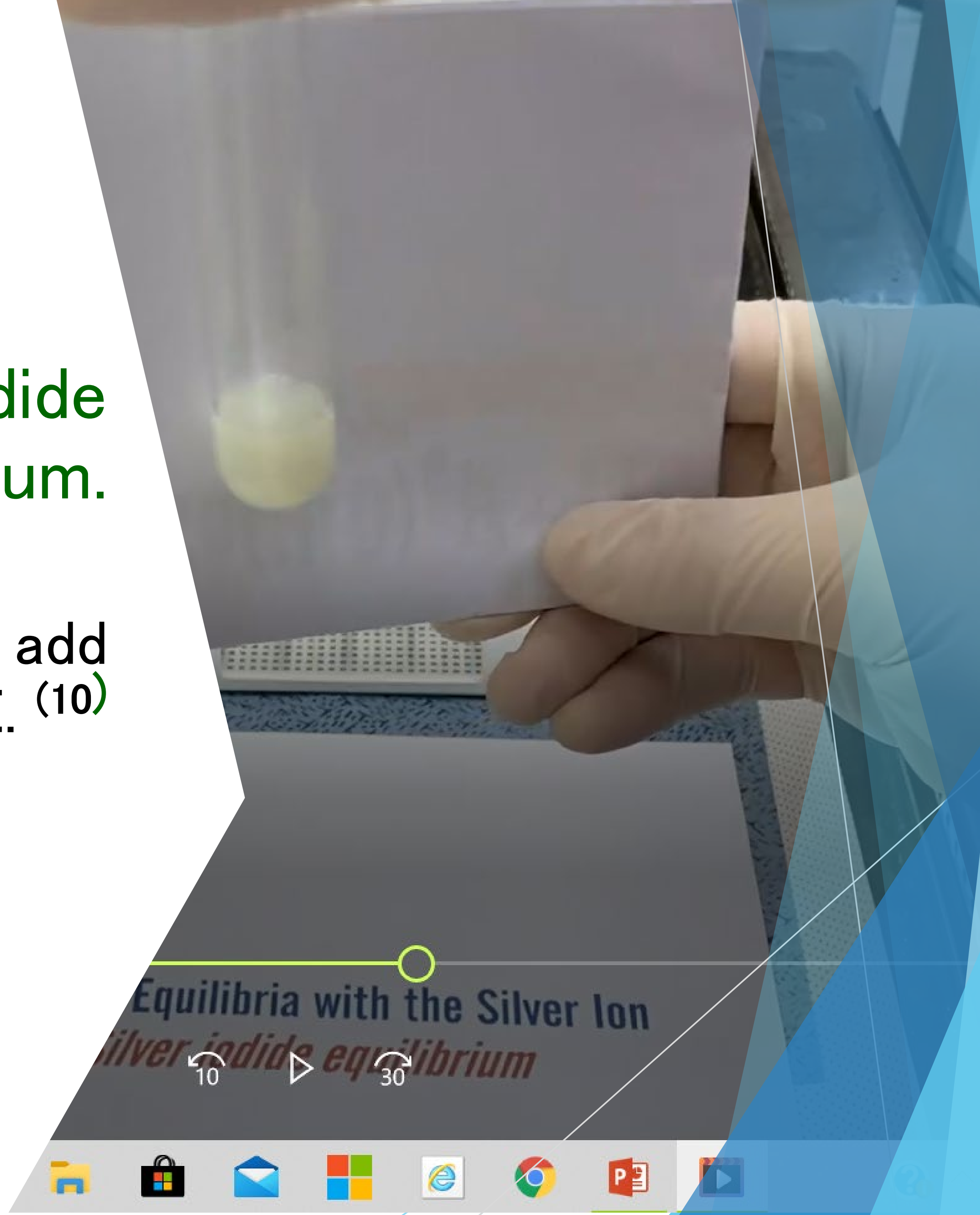
1. **Silver carbonate equilibrium**. In a 150-mm test tube add ~ ½ mL (≤10 drops) of 0.01 M $AgNO_3$ to ~ 1/2mL of 0.1 M Na_2CO_3. (4) Add drops of 6 M HNO_3 (Caution: 6 M HNO_3 reacts with the skin!) to the precipitate until evidence of a chemical change occurs. (5)

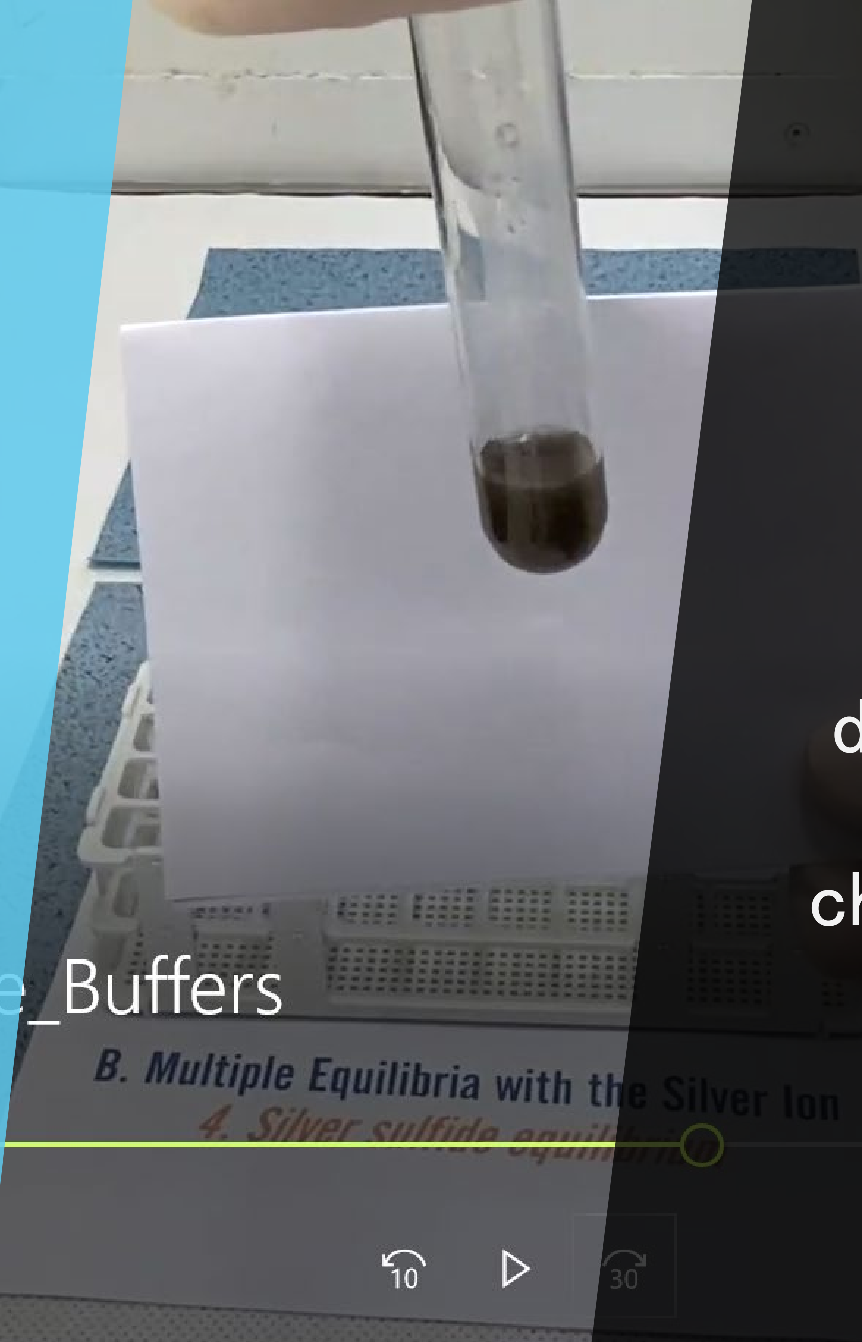
2. Silver chloride equilibrium. To the clear solution from **PART B.1**, add ~ 5 drops of 0.1M HCl.(6) Add drops of conc NH_3(Caution! Avoid breathing vapors and avoid skin contact) until evidence of a chemical change.(7)[At this point, the solution should be "clear and colorless."] Reacidify the solution with 6 M HNO_3 (Caution!) and record your observations.(8) What happens if excess conc NH_3 is again added? Try it. (9)



3. Silver iodide equilibrium.

After trying it, add drops of 0.1 M KI. [10]





4. Silver sulfide equilibrium. To the mixture from **PART B.3**, add drops of 0.1 M Na_2S until evidence of chemical change has occurred.(11)

Part C.
A Buffer System

	1	2
A	Buffer + HCl	Buffer + NaOH
B	H_2O + HCl	H_2O + NaOH

1. Preparation of buffered and unbuffered systems.

Transfer 10 mL of 0.10 M CH_3COOH to A1 and A2 of labeled 50-mL beaker. Use a pH meter to determine the pH of the solution. (12) Now add 10 mL of 0.10 M $NaCH_3CO_2$ to each beaker. (13) Measure the pH of the solution. (14)

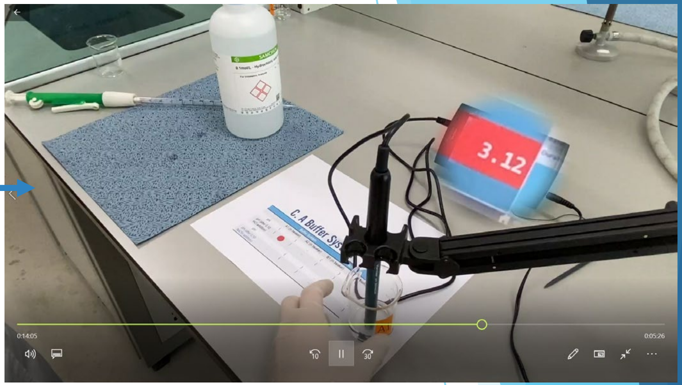
Place 20-mL of distilled water into beaker B1 and B2 of labeled 50-mL beaker. Measure the pH of the distilled water.

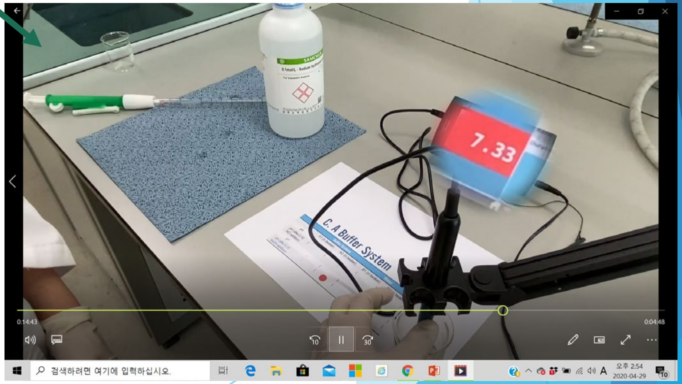
2. **Effect of strong acid.** Add 5 mL of 0.10 M HCl to A1 and B1 beaker, estimate the pH, and record each pH change.(15)

3. **Effect of strong base.** Add 5 mL of 0.10 M NaOH to A2 and B2 beaker, estimate the pH, and record each pH change.(16)

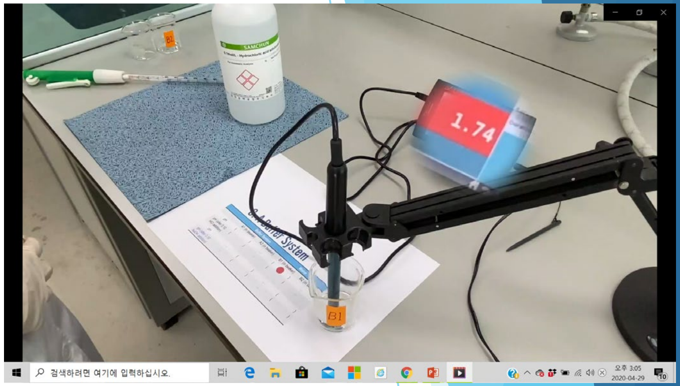
4. **Effect of a buffer system.** Explain the observed pH change for a buffered system(as compared with an unbuffered system) when a strong acid or strong base is added to it.(17)

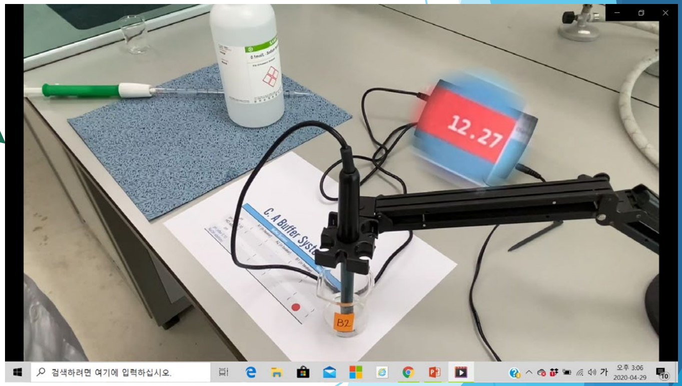
Buffer System		
	A1 (in beaker)	A2 (in beaker)
pH	( )	…
pH (after 0.10 HCl addition)	( )	…
pH	…	( )
pH (after 0.10 NaOH addition)	…	( )

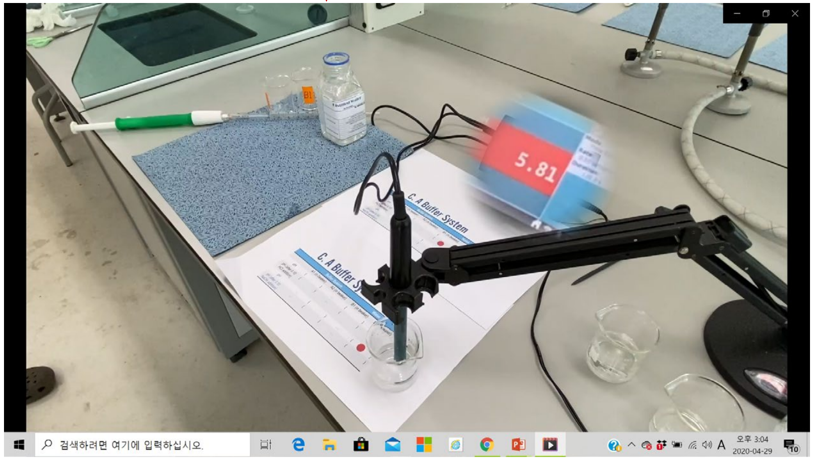




Water		
	B1 (in beaker)	B2 (in beaker)
pH	(　　　)	...
pH (after 0.10 HCl addition)	(　　　)	...
pH	...	(　　　)
pH (after 0.10 NaOH addition)	...	(　　　)





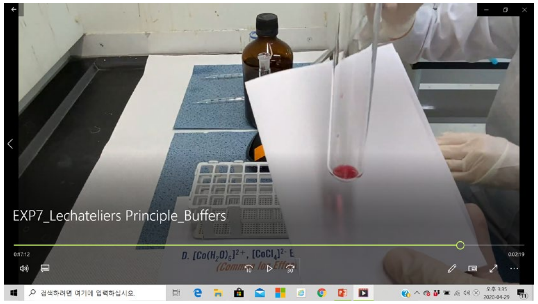


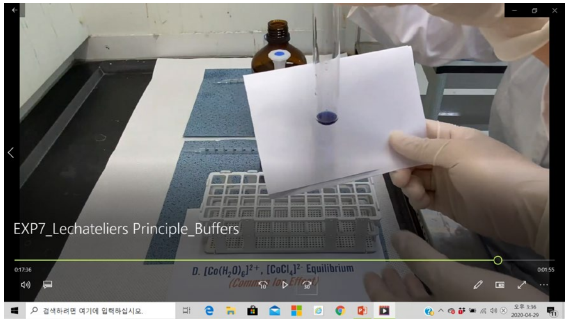
Part D.

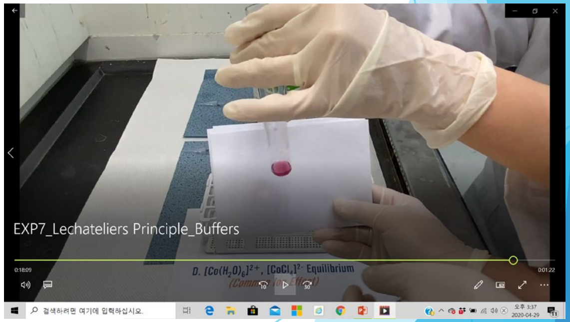
Equilibrium (Common-Ion effect)

$[Co(H_2O)_6]^{2+}$, $[CoCl_4]^{2-}$

1. Effect of concentrated HCl. Place about 10 drops of 1.0 M $CoCl_2$ in a 75-mm test tube.[18] Add drops of conc HCl (Caution: Avoid inhalation and skin contact) until a color change occurs.[20] Slowly add water to the system and stir.[20]







Part E.

Equilibrium (Temperature effect)

$[Co(H_2O)_6]^{2+}$, $[CoCl_4]^{2-}$

1. **What does heat do?** Place about 1.0 mL of $CoCl_2$ in a 75-mm test tube into the boiling water bath. Compare the color of the hot solution with that of the original cool solution.[21]