container in a closed system

Pressure Change

The only state that fills its reacting container in every situation is a gas.
Thus, increasing or decreasing the volume of a reacting vessel will only initially affect the concentration of any gas state substance. Then, an equilibrium shift may affect the concentrations or amounts of the non-gaseous substances. (after)

A decrease in volume = an increase in pressure.
An increase in volume = a decrease in pressure.

A decrease in volume causes an increase in pressure, meaning that all gas concentrations immediately increase.
An increase in volume causes a decrease in pressure, meaning all gas concentrations immediately decrease.
Explain:
when volume is ↓ there are the same # of gas particles in a smaller amount of space; ∴ more gas particles/unit of space.
This means an ↑ in gas concentration (pressure).
(if vol. is ↑ same # of gas particles in larger space ∴ ↓ gas concentration (pressure))

A change in pressure **may** also cause a LeChatelier shift to occur.
↑ pressure If pressure of a system is increased, gas particles are packed tightly together, so what can you say about collisions? increased number of collisions
Therefore, what happens to both the forward and reverse rates? both increase
(similar to how temp Δ affects equilibrium) However, one rate may increase more than the other. The side of the equation with more gas particles will experience a greater rate increase, causing a shift to the other side (the side with less gas particles). Soon the rates re-balance, and a new equilibrium is established.

Example: "The Haber Process" $N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$

What happens to the pressure of the gases if the volume of the system is decreased? volume ↓ = pressure ↑ or [conc.]$_{(gas)}$ ↑
So what happens initially to all gas concentrations? all gas [conc.] will ↑
So what happens to the # of collisions? there will be more overall collisions
What happens to the rates? both rxn rates will increase due to an ↑ in [conc.] b/c there are gases on both sides of the reaction.

shift →

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

FWD rate ↑ more

How many gas molecules on the reactant side? $1N_{2(g)} + 3H_{2(g)}$ 4 molec total

How many gas molecules on the product side? $2NH_{3(g)}$ 2 molec. total

Thus, which rate will increase more? FWD Reactants will ↑ rate more due to more gas molecules on that side.

Therefore, a shift has occurred to what side? shift RIGHT, products favored.

Then, the rates will eventually re-balance and a new equilibrium will be established.

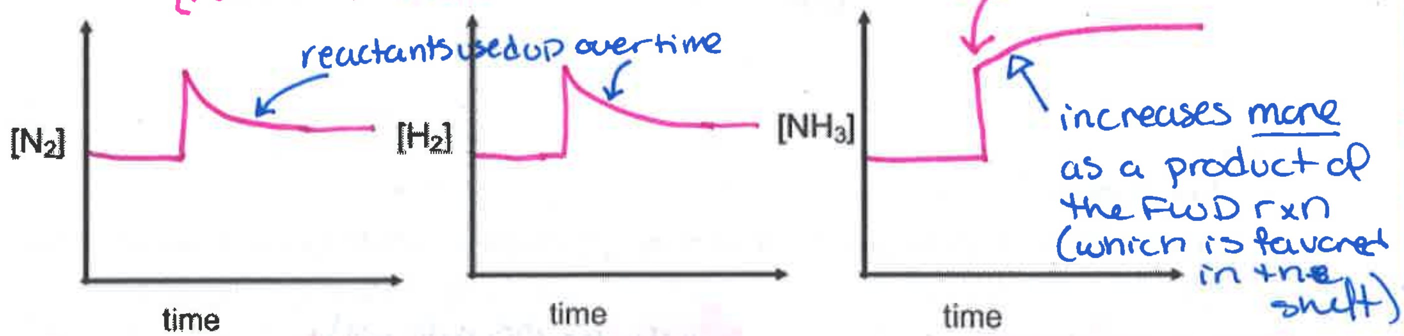
because they are getting used up faster than they are being produced. FWD rate ↑

$[N_2]$ and $[H_2]$ both initially increase, then due to the shift will decrease, but overall slightly increase.

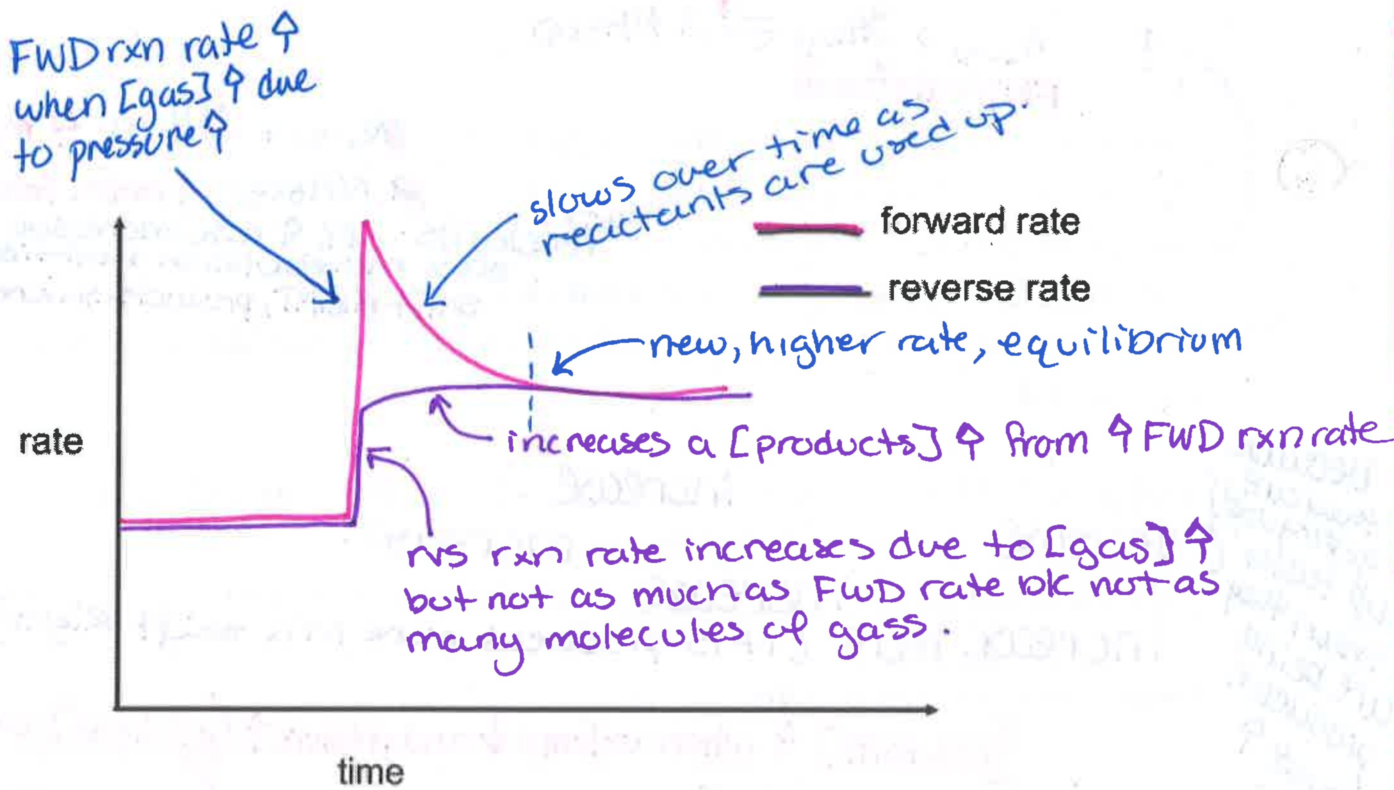
$[NH_3]$ will initially increase, then due to the shift will increase more (it is produced more in a shift Right)

Draw concentration graphs:

[reactant] ↑ when volume ↓ and pressure ↑ (all [gas] will increase)



Sketch a rate vs. time graph for the process:



LeChatelier:

An increase in pressure (initial change) causes a shift to the side with less gas particles (counteraction) until a new equilibrium is established.

FWD rate ↓ more

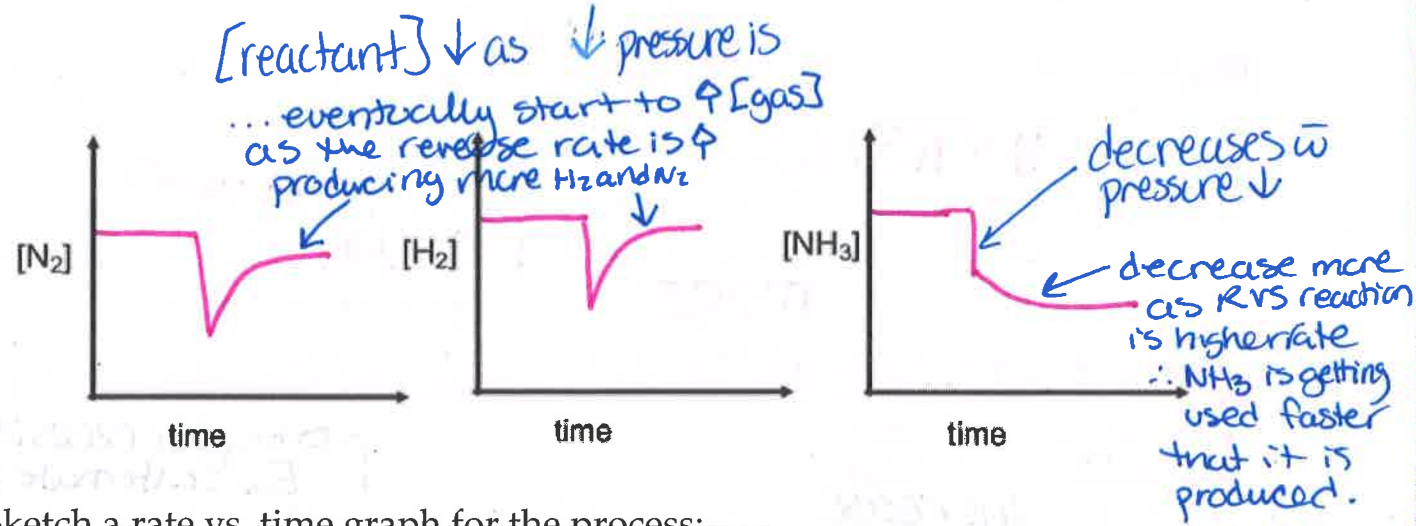
shift (as RVS rate will be higher) ↑ volume = ↓ pressure

$$N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$$

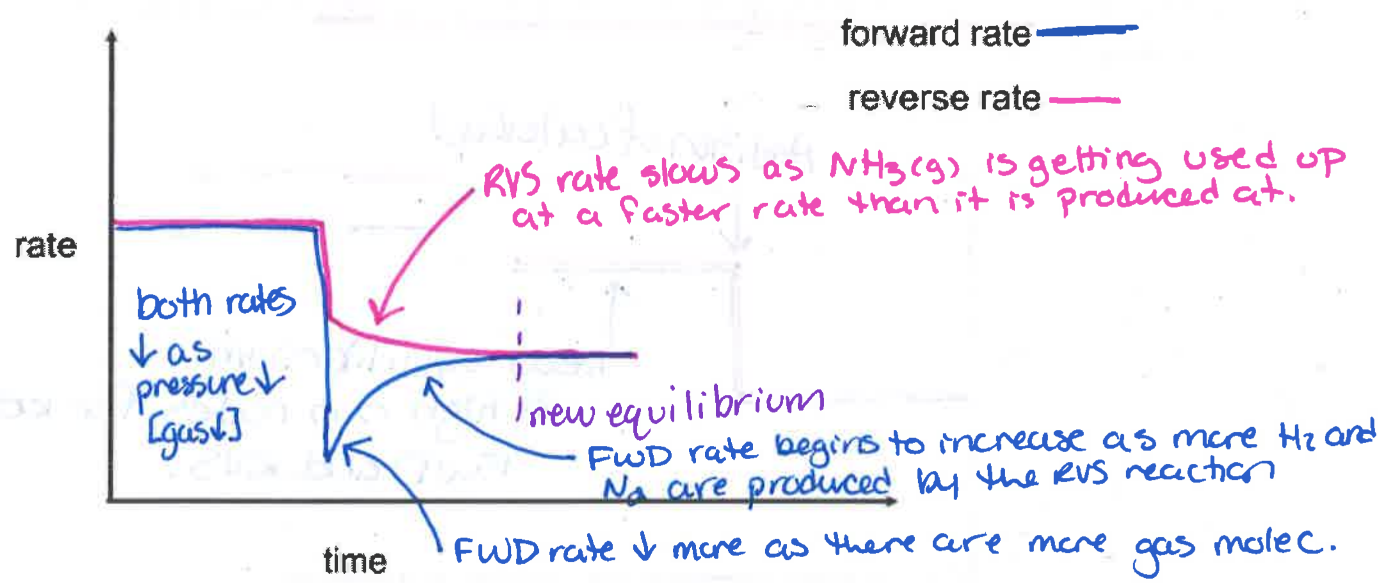
ie: ↓ [conc] gas

An increase in volume will cause a decrease in pressure (all gas concentrations immediately decrease). Both rates will decrease, but since the reactant side has more gas particles, the forward rate will be affected more, so it will decrease more than the reverse rate, causing a shift to the LEFT (reactants) (the side with more gas particles).

Draw concentration vs. time graphs for the process:



Sketch a rate vs. time graph for the process:



LeChatelier:
A decrease in pressure (initial change) causes a shift to the side with more gas particles (counteraction) until a new equilibrium is established.

Why would a pressure change not cause a shift for the system below?

$$\underbrace{1\,H_{2(g)} + 1\,CO_{2(g)}}_{2} \Leftrightarrow \underbrace{1\,H_2O_{(g)} + 1\,CO_{(g)}}_{2}$$

There are equal numbers of gas particles on each side, so no shift will occur.

([gas] changes due to a change in volume will occur.)

Addition of an inert (unreactive) gas to an equilibrium will not affect the [reactants] or [products] enough to cause a significant change, and will not cause a shift in any kind.

(dec. volume)

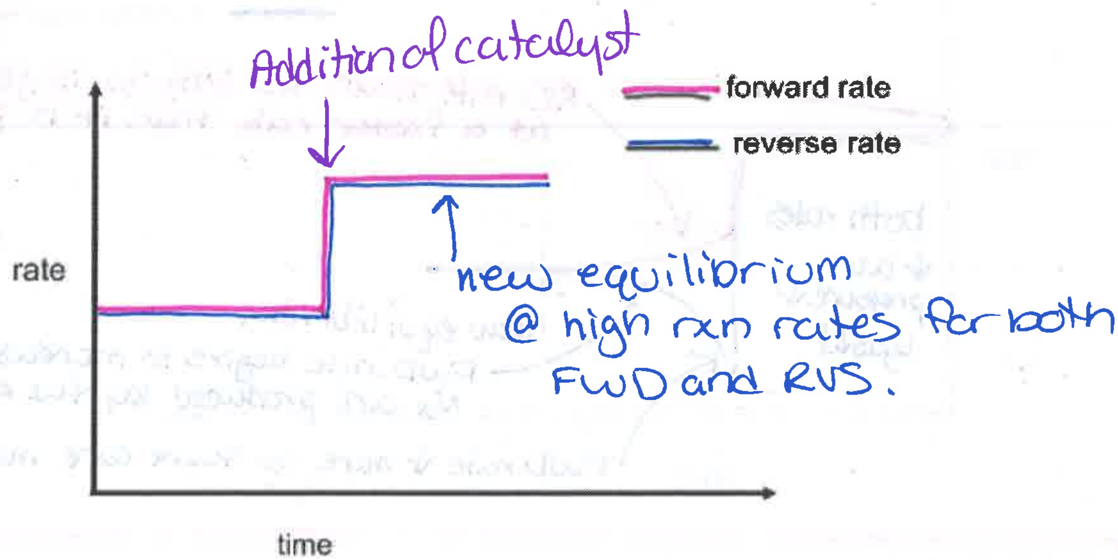
Conclusion: An increase in pressure will cause all gas concentrations to initially __INCREASE__ and then a shift to the side with __LESS__ gas particles will ensue. A decrease in pressure will cause all gas concentrations to initially __DECREASE__, and then a shift to the side with __MORE__ gas particles will ensue. Addition of an inert gas will not affect the equilibrium.

(inc. volume)

Addition of a Catalyst

by decreasing the Ea (alternate pathway)

Catalysts __increase__ both forward and reverse reaction rates EQUALLY, therefore at no time do rates differ, so there is no shift. Keep in mind that both rates are higher than they were before. Graph the rate change below:



Important Concepts for Shifts:

1) Equilibrium shifts will only affect the concentrations of gases and aqueous substances. The **amounts** of solid and liquid will be affected by shifts, but not their **concentrations**. In solids and liquids, concentrations are always constant because if you lose some mass, you also lose a proportional volume, so the concentration doesn't change. If you increase the mass, you increase volume proportionally.

2) If more solid or liquid is added to an equilibrium mixture (or if some is removed), **NO** shift will occur and equilibrium will be maintained. Adding

solid or liquid will cause a rate increase, but both the forward and reverse rates increase equally (they both decrease equally for a solid or liquid removal). The explanation behind why this is so is very advanced and difficult to conceptualize (it is beyond the scope of Chemistry 12)... so don't ask... it hurts my brain.

Assignment 3

1) finish Hebden p. 54 #17-23

2) Complete the table: $Ag_2CrO_{4(s)}$ + heat ⇔ $2Ag^+_{(aq)}$ + $CrO_4^{2-}{}_{(aq)}$

Stress	Shift	$[Ag_2CrO_4]$	$[Ag^+]$	$[CrO_4^{2-}]$
Add $Ag_2CrO_{4(s)}$				
Decrease temperature				
Increase pressure				
Decrease $Ag^+_{(aq)}$				
Increase $CrO_4^{2-}{}_{(aq)}$				

3) Complete the table: $BaCO_{3(s)}$ + heat ⇔ $BaO_{(s)}$ + $CO_{2(g)}$

Stress	Shift	$[BaCO_3]$	$[BaO]$	$[CO_2]$
Add $BaCO_{3(s)}$				
Increase temperature				
Decrease pressure				
Decrease volume				
Add $CO_{2(g)}$				
Remove $CO_{2(g)}$				

4) Complete the table: $CO_{(g)}$ + $H_2O_{(g)}$ ⇔ $CO_{2(g)}$ + $H_{2(g)}$ $\Delta H = -41 kJ$