

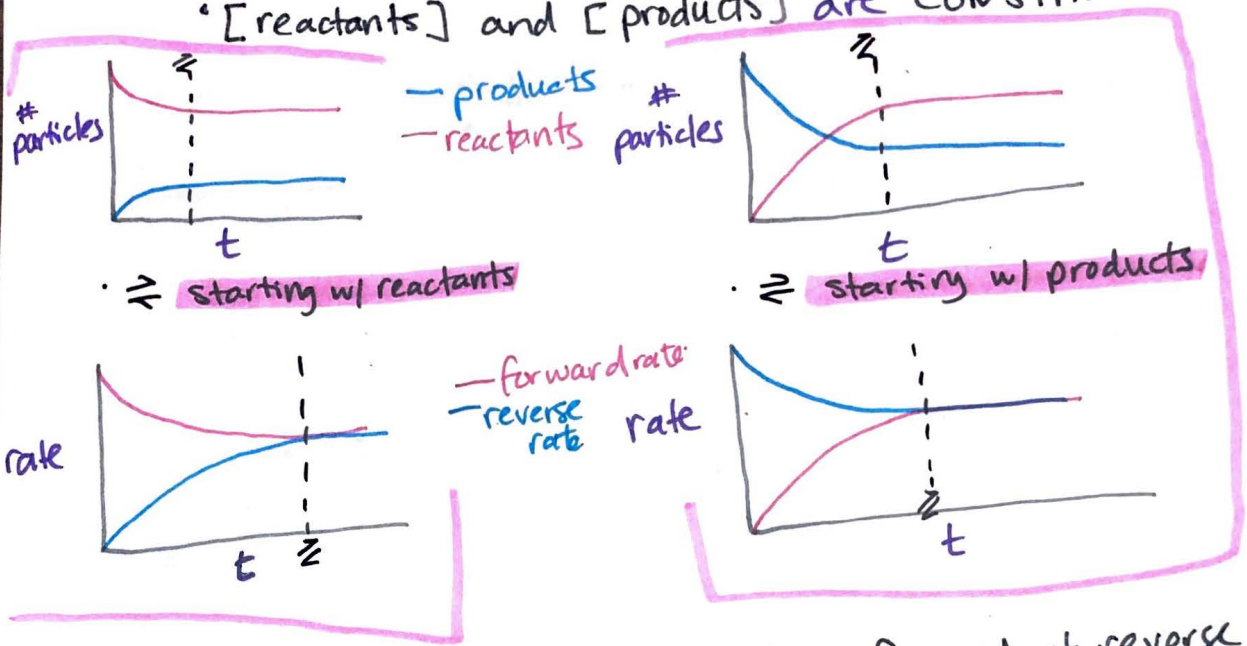
# Unit 2: Equilibrium $\rightleftharpoons$

- must occur in closed system so gas can't escape

- reversible rxn
- forward + reverse  $E_a$  are low  $\rightarrow$  spontaneous

## Characteristics of $\rightleftharpoons$

- can be achieved from either direction (start w/ products or reactants)
- @  $\rightleftharpoons$  rates of forward + reverse are EQUAL
- [reactants] and [products] are CONSTANT



Dynamic - [R] + [P] constant but forward + reverse reactions still occur (microscopic) but at SAME rate  $\therefore$  no observable change (Macroscopic)

## Le Chatelier's Principle

If  $\rightleftharpoons$  system is subject to a change (stress) processes occur to counteract the change until a new  $\rightleftharpoons$  is established

types of stresses:

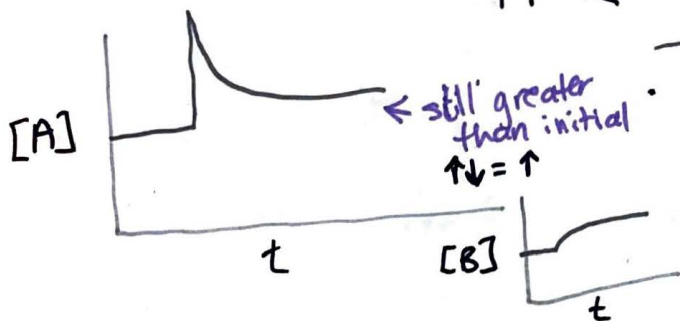
1. concentration (only for g and aq substances)
2. temperature (endo vs. exo)
3. pressure (for g vol. and gas pressure related inversely)
4. catalyst

\* no change in [ ]  
\* both forward + reverse rates  $\uparrow$  the same amount.

1. Concentration: - add or remove (could be through precipitation)  
 - affect # collisions  $\therefore$  rate

$\uparrow [ ]$  will shift (counteraction) to opposite side to decrease (stress)

$\downarrow [ ]$  will shift to same side to increase



**add more A**

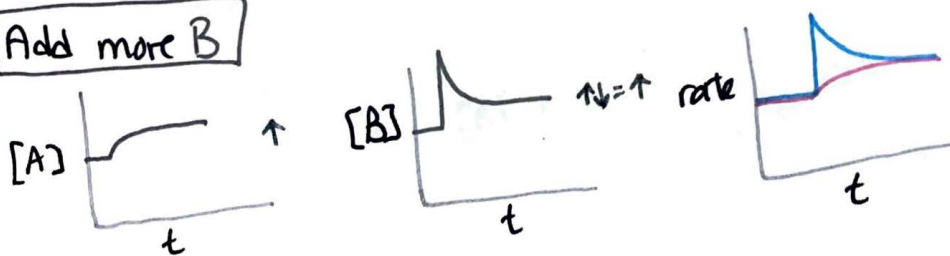
•  $[A]$  increases STRESS will shift RIGHT to  $\downarrow [A]$  and establish new  $\rightleftharpoons$   
 • **RATE** - forward initially greater b/c more particles ( $\therefore$  collisions) then decreases as forming more products and reverse rate increase until the are EQUAL

- forward rate  
 - rev rate

\*note\* for  $[ ]$  only spike is for molecule directly affected \*

\*note\* both rates higher b/c overall more molec. present

**Add more B**



$\uparrow [ ]$  summary:

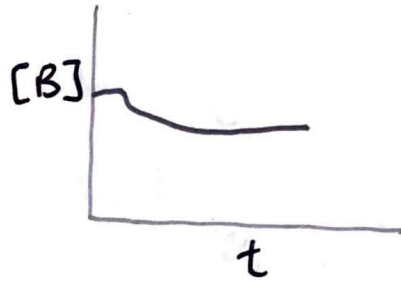
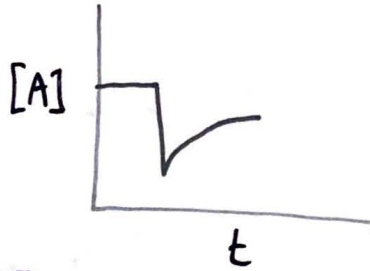
- $\uparrow [ ]$  will cause spike in molec. directly affected then shift to opp. side to  $\downarrow [ ]$  and establish new  $\rightleftharpoons$
- rate of molec.  $\uparrow$  will all  $\uparrow$  due to more collisions, then  $\downarrow$  due to shift.
  - if [reactant]  $\uparrow$ , forward rate  $\uparrow$  then  $\downarrow$  and reverse slowly  $\uparrow$
  - if [product]  $\uparrow$ , reverse rate  $\uparrow$  then  $\downarrow$  and forward rate slowly  $\uparrow$





Concentration decreases:

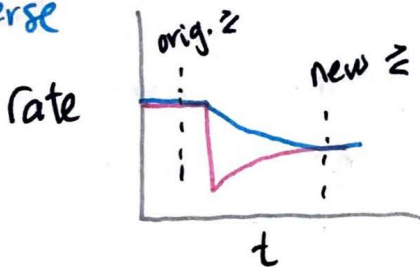
Remove A  
(or ppt. A)



[A] drops sharply (spike down) which is stress then shift to LEFT to make more A ( $\downarrow \uparrow = \downarrow$ )

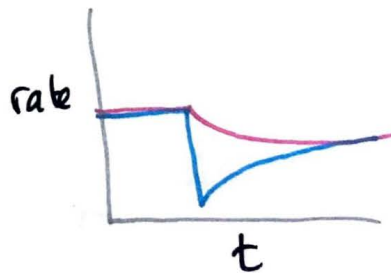
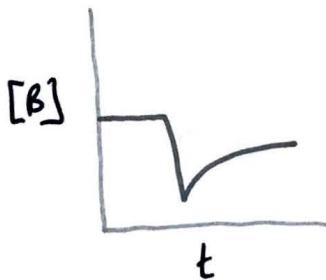
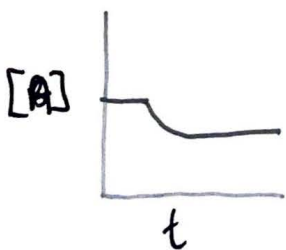
[B] slowly  $\downarrow$  ( $\downarrow$ )

-forward  
-reverse



- both rates Drop because less molec.
- $\therefore$  less collisions
- forward spikes down then due to shift slowly  $\uparrow$  but still Lower than before ( $\downarrow \uparrow = \downarrow$ )
- due to shift LEFT reverse rate slowly  $\downarrow$  as molec. are used to make more A

Remove B  
(or ppt. B)

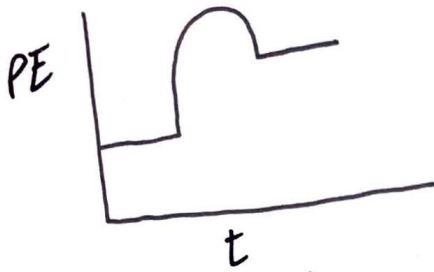


[A] -  $\downarrow$  due to shift R

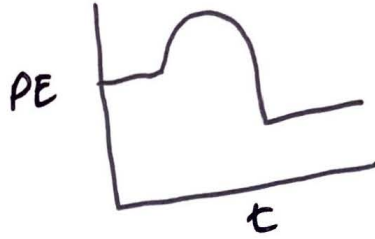
[B] -  $\downarrow \uparrow = \downarrow$

rate: less product molec.  $\therefore$  reverse rate drops then due to shift increases. Still lower than initial b/c less molec.  $\therefore$  less collisions. Forward slowly drops due to shift ( $A \rightarrow B$ )

## 2. Temperature



- endothermic
  - $\Delta H = \text{positive}$
  - energy is a REACTANT
- MORE dependent on Energy  
 $\therefore \uparrow$  in temp favors the endothermic reaction

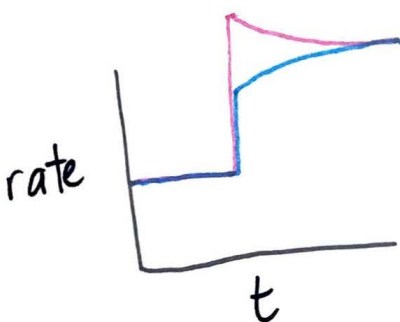
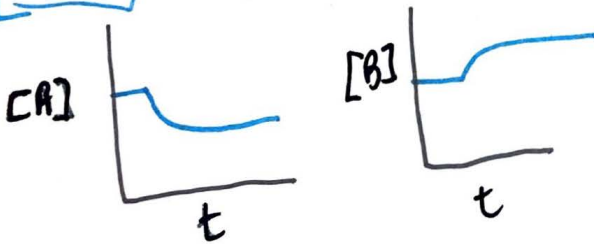


- exothermic
  - $\Delta H = \text{negative}$
  - energy is a PRODUCT
- LESS dependent on Energy  
 $\therefore \downarrow$  in temp favors exothermic reaction

★ With Temperature change there is NO spikes in [ ] ★



- forward is endo
- reverse is exo

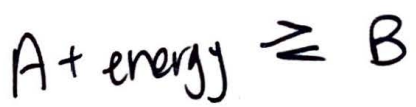


- forward (endo)
- reverse (exo)

- $\uparrow$  in temp.  $\therefore$  Both rates immediately  $\uparrow$
- since ENDO depends more on energy it will  $\uparrow$  more then slope down due to shift.
- reverse (exo) slowly  $\uparrow$  due to  $\uparrow$  production of B

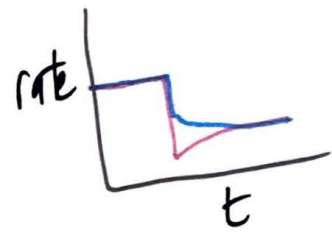
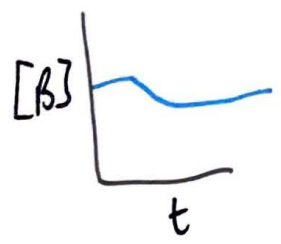
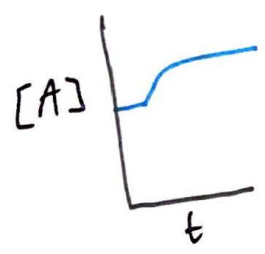
↓ in Temp

· favors the EXOTHERMIC direction ∴ shift LEFT



← shift exo

- forward (endo)  
- rev (exo)



- ↓ in temp ∴ BOTH rates drop immediately
- ENDO will drop MORE then due to shift LEFT will ↑ as more A produced.
- EXO (reverse) will drop then slowly decrease due to  $B \rightarrow A$

↑ temp → shift Endothermic direction

↓ temp → shift Exothermic direction

- endothermic more dependant on energy ∴ will ↑ more (w/ ↑ temp) or ↓ more (w/ ↓ temp)



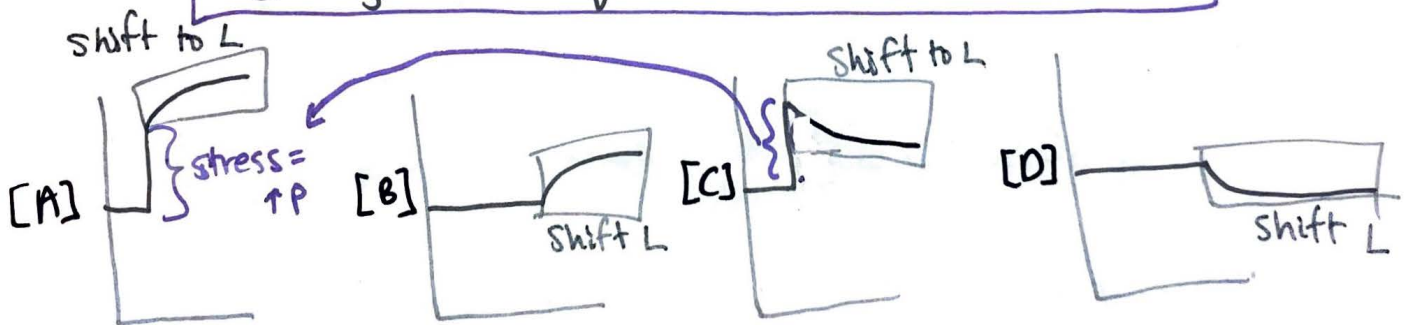
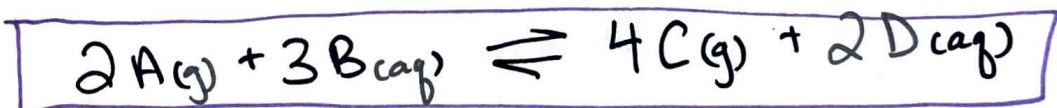
### 3. Pressure - only for GAS

↑ Pressure = ↓ Volume

↓ Pressure = ↑ Volume

- will immediately affect ALL gas concentrations then IF a shift will affect gas and aq concentrations
- shift will be to counteract change in pressure ∴ will need DIFFERENT # of GAS molec. on each side

↑ pressure: - all gas [ ] immediately ↑ (↓ in volume) - then if possible, will shift to side with Less gas molec. and will see change in [gas] & [aq] substances



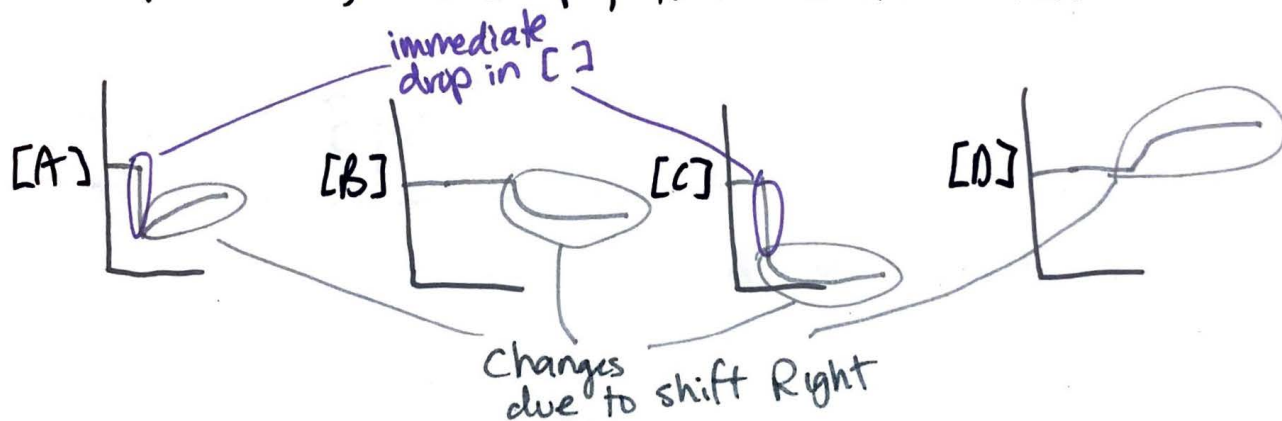
- ↑ pressure - ALL gas ↑
- will shift to side with FEWER gas molec. to ↓ pressure (counteraction)
- shift LEFT
- @ shift ALL gas + aq will change

↓ in Pressure (or ↑ volume)

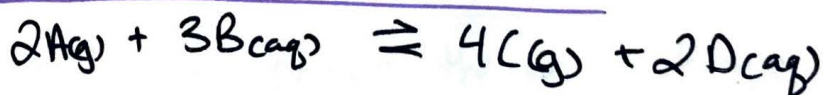
- All [gas] immediately (spike) drop
- will (if possible) shift to side with more gas molec. to ↑ pressure (counteraction) and [gas] and [aq] will change



↓ pressure, all drop, then shift RIGHT

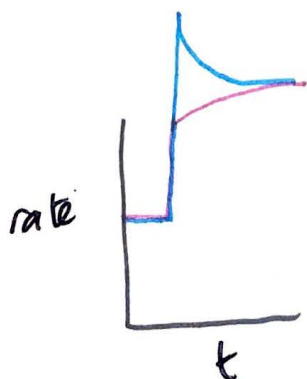


### Pressure and Rate



↑ Pressure

- all rates ↑ due to more collisions
- shift LEFT

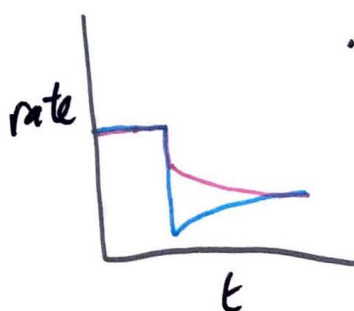


- forward  
- reverse

- reverse rate ↑ more b/c more gas, then ↓ due to shift L and forward ↑ until new  $\rightleftharpoons$

↓ Pressure

- rates ↓ due to less collisions
- shift RIGHT



- reverse rate ↓ more b/c more gas molec. ∴ ↑ due to shift R and forward slowly ↓

Completion,  $\rightleftharpoons$ , or NO Reaction  
C E NR

- ENTHALPY (total potential Energy content, 'H')

- easier to lose energy than gain
- will favor the EXOTHERMIC direction

- ENTROPY (state of randomness/disorder)

- in the universe there are more disordered states than ordered states  $\therefore$  reactions tend toward increasing disorder or to the side with more gas molec. (g > aq > l > s)

$K_{eq}$  - Equilibrium Constant

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$$

• do not include (l) and (s) states

$K_{eq} > 1$  : [product] higher/  
products favored

$K_{eq} < 1$  : [reactant] higher/  
reactants favored

Only thing (stress) that changes the value of the  $K_{eq}$  is

Temperature

- $\uparrow$  temp will shift Endothermic
- $\downarrow$  temp will shift Exothermic



1.)  $\uparrow$  temp, shift endo, shift R  $\therefore [B] \uparrow$  and  $K_{eq} \uparrow$

2.)  $\downarrow$  temp, shift exo, shift L  $\therefore [A] \uparrow$  and  $K_{eq} \downarrow$



## Type 1 Keq Problem

LOOK FOR: Q gives ALL eq. data

- Steps:
- ① write keq expression
  - ② plug [eq] into equation and solve

TRICKS: • could give volume + moles and you must put into M

## Type 2 Keq Problem

LOOK FOR: [ ]<sub>i</sub> and [ ]<sub>eq</sub>

- STEPS:
- ① write equation and set-up ICE table
  - ② insert [ ] given into table
  - ③ find the Change (between [ ]<sub>i</sub> and [ ]<sub>eq</sub> of same substance) and apply to all others  
+ recall: Change is where you use coefficients
  - ④ get all Equilibrium values
  - ⑤ set up keq expression, plug in values and solve keq.

## Type 3 Keq Problem

LOOK FOR: Q gives some [ ]<sub>i</sub> and keq value  $\Rightarrow$  will use  $x$  in change

- Steps:
- ① write eq. and set-up ICE table
  - ② plug-in [ ]<sub>i</sub> (start w/ reactants then products zero and vice versa)
  - ③ use  $-x$  and  $+x$  in change (recall: coefficients cant here)
  - ④ get [EQ] with #'s and  $x$ 's + write keq expression
  - ⑤ plug into keq expression and let  $x = \Delta[ ]$
  - ⑥ solve for  $x$  and use to answer question

## Type 4 Key Problem

LOOK FOR: Trial key, so look for things like:

'is this at  $\rightleftharpoons$ ?' 'which way does the system need to shift to attain  $\rightleftharpoons$ ?'  
'What will happen to the [X] as it approaches  $\rightleftharpoons$ ?'  
'all [ ] and key value will be given

STEPS:

- 1) Set-up trial key expression
- 2) plug-in [ ]'s given
- 3) solve for trial key
- 4) compare to actual key
  - if not = not at  $\rightleftharpoons$
  - if trial key < actual must  $\uparrow$   $\therefore$  shift RIGHT
  - if trial key > actual must  $\downarrow$   $\therefore$  shift LEFT
- 5) use comparison & shift direction to answer any questions