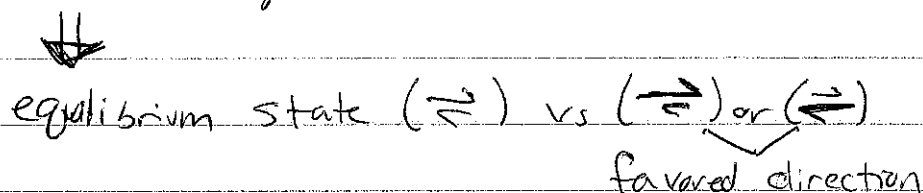Topic 7 Equilibrium

Definition: when a reaction takes place at the
same rate as its reverse reaction
∴ no net change has occurred
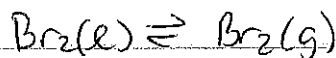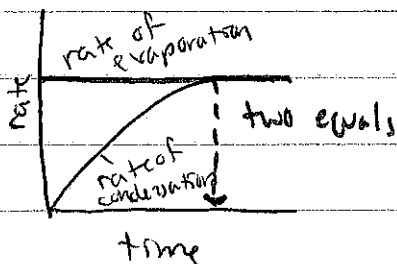⇓

equilibrium state ($\rightleftharpoons$) vs ($\rightleftharpoons$) or ($\rightleftharpoons$)
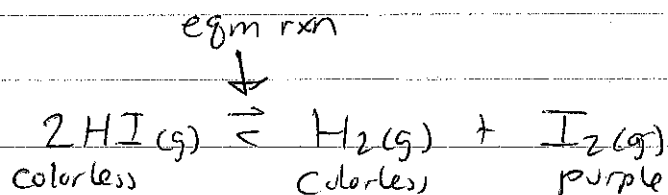favored direction

7.1 Equilibrium

Physical Systems

$Br_2(\ell) \rightarrow$ put into a closed container
· Volatile (b.p. close to room temp) ∴
movement to vapor (gas) occurs easily

$Br_2(\ell) \rightarrow$ evaporates (vapor) → upon interaction
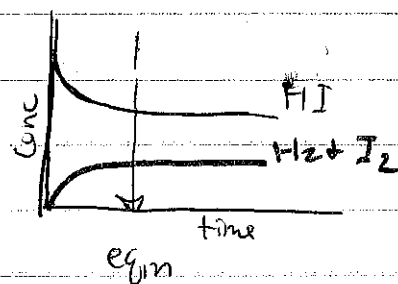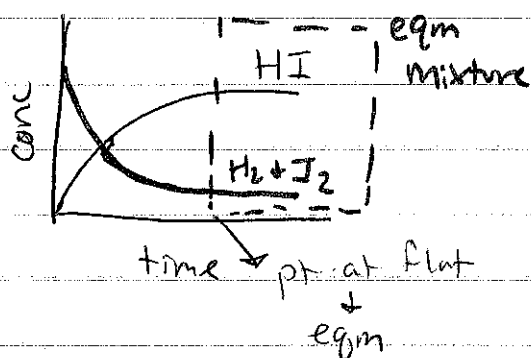w/ surface (ℓ), particles lose energy → condense (ℓ)

evaporation = condensation ⇛ equilibrium

$Br_2(\ell) \rightleftharpoons Br_2(g)$

Chemical systems

eqm rxn

$$2HI_{(g)} \rightleftharpoons H_2{(g)} + I_2{(g)}$$

colorless   colorless   purple

forward rxn = $R \rightarrow P$ ⟩ dynamic due to
reverse rxn = $P \rightarrow R$ ⟩ occurring at same time

★ start w/ only reactants or only products ⟹ under
   same conditions same eqm mixture will be
   created

Characteristics of eqm state

1. Dynamic: forward & backward rxn occurring at same
   rate (though never stopped)

2. achieved in closed system: prevents exchange w/ surroundings
   allows both R & P ability to react/recombine

3. R & P conc constant: produced & destroyed at same rate

4. no change in macroscopic properties: (color & density) do not change as dependent on conc in mixture

5. Reached from either direction: no matter starting pt all R, all P, or mix, eqm will be at same pt.

At eqm → constant conc does not necessairly mean equal
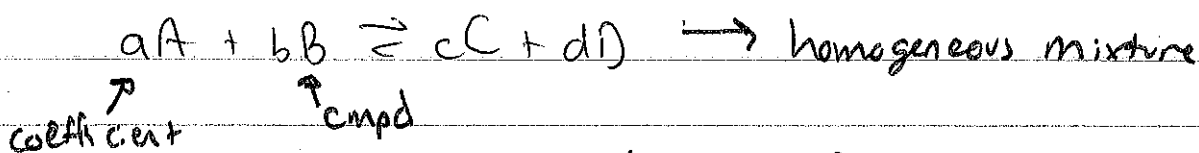 • one side will be favored (depends on rxn & conditions)
    ⇊
      eqm position   P → lie to right ⟩ determined
                     R → lie to left   mathematically

K_c → eqm constant

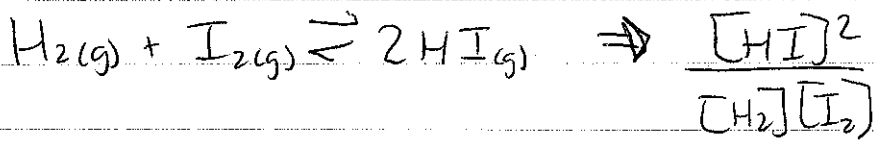 • it is a fixed value for a particular rxn at a specified T ∴ is Temp dependent
  • Every rxn has its own particular value for K_c

eqm constant expression (use stoichiometric rxn)

$$aA + bB \rightleftharpoons cC + dD \longrightarrow \text{homogeneous mixture}$$

coefficient↗   ↑cmpd

↙ coefficient from rxn

$$K_c = \frac{[C]^c_{eqm} [D]^d_{eqm}}{[A]^a_{eqm} [B]^b_{eqm}} \longleftarrow \text{conc at eqm}$$

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \implies \frac{[HI]^2}{[H_2][I_2]}$$

exp 1 $\frac{(0.156)^2}{(0.0222)(0.0222)}$ exp 2 $\frac{(0.280)^2}{(0.0350)(0.0450)}$ exp3 $\frac{(0.100)^2}{(0.0156)(0.0135)}$

$\quad = 49.4$ $\quad\quad = 49.8$ $\quad\quad = 49.4$
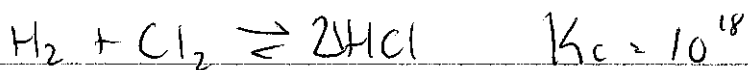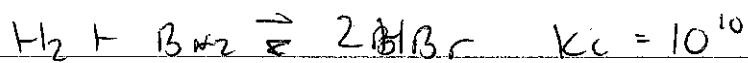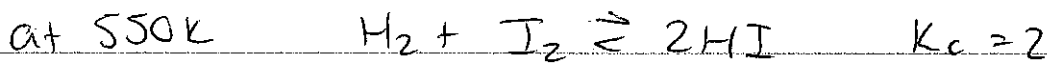
eqm data = constant value (w/in limits)

$\downarrow$

K_c - no unit as it represents an activity

example : pg 316

$K_c \gg 1$ products favored $\left(\frac{[P]}{[R]} = \frac{large \#}{small \#}\right)$

rxn goes towards completion

$K_c \ll 1$ reactants favored $\left(\frac{small \#}{large \#}\right)$

rxn barely starts

at 550K $H_2 + I_2 \rightleftharpoons 2HI$ $K_c = 2$

$H_2 + Br_2 \rightleftharpoons 2HBr$ $K_c = 10^{10}$

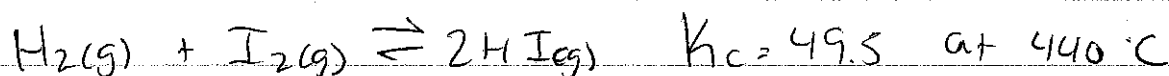$H_2 + Cl_2 \rightleftharpoons 2HCl$ $K_c = 10^{18}$

all products favored but HCl favored most

$\star$ magnitude of K_c does not relate to rate just nature of eqm mixture

$Q \rightarrow$ rxn quotient , predicts direction of rxn

- determines $[R]$ + $[P]$ at 1 moment when rxn
  is not at eqm
- value of Q changes in direction of K_c

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad K_c = 49.5 \quad \text{at } 440°C$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

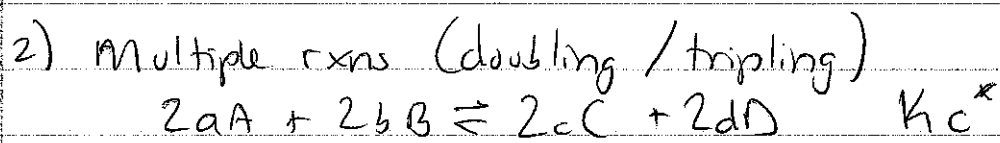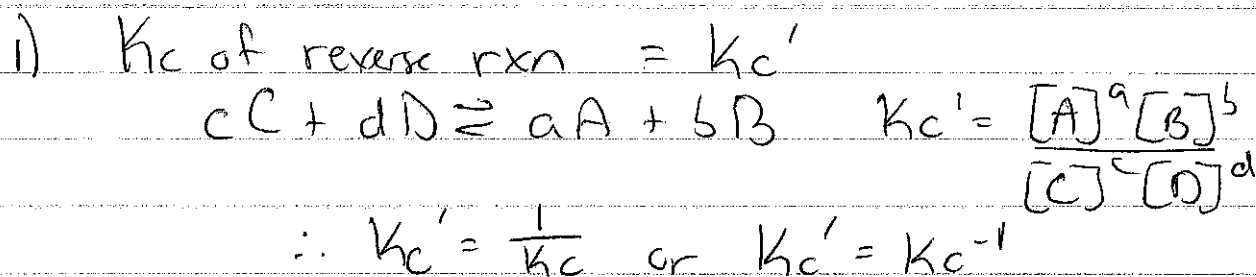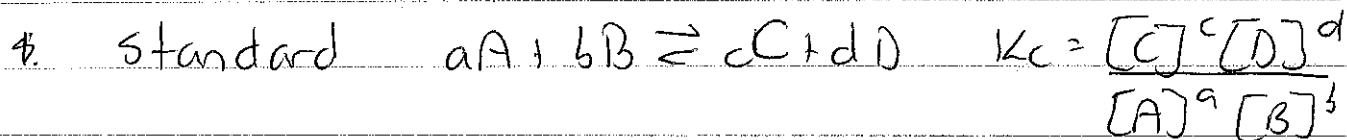time #1 $\quad Q = \dfrac{(0.100)^2}{(0.0500)(0.0500)} = 4.00 \quad Q < K_c \therefore \text{favor}[P]$

time #2 $\quad Q = \dfrac{(0.300)^2}{(0.0850)(0.0350)} = 103 \quad Q > K_c \text{ favor}[R]$

if $\quad Q = K_c \quad$ rxn at eqm (no net rxn)

$\quad\quad Q < K_c \quad$ proceeds right (products)

$\quad\quad Q > K_c \quad$ proceeds left (reactants)

example pg 319

Manipulating K_c for diff rxn equations

for changes made to standard eq.

4. Standard $\quad aA + bB \rightleftharpoons cC + dD \quad K_c = \dfrac{[C]^c [D]^d}{[A]^a [B]^b}$

1) K_c of reverse rxn $= K_c'$

$cC + dD \rightleftharpoons aA + bB \quad K_c' = \dfrac{[A]^a [B]^b}{[C]^c [D]^d}$

$\therefore K_c' = \dfrac{1}{K_c} \quad$ or $\quad K_c' = K_c^{-1}$

2) Multiple rxns (doubling / tripling)

$2aA + 2bB \rightleftharpoons 2cC + 2dD \quad K_c^{\ast}$

$K_c^x = \dfrac{[C]^{2c} [D]^{2d}}{[A]^{2a} [B]^{2b}} = K_c^2 \ (K_c^3, etc.)$

3) ½ing rxn coefficients $\rightarrow \sqrt{exp} \rightarrow \sqrt{K_c}$

4) adding 2 rxns $\rightarrow$ multiply 2 exp $\rightarrow K_c^i \times K_c^{ii}$
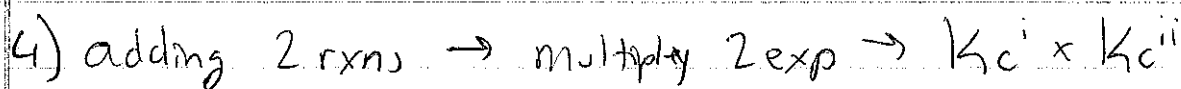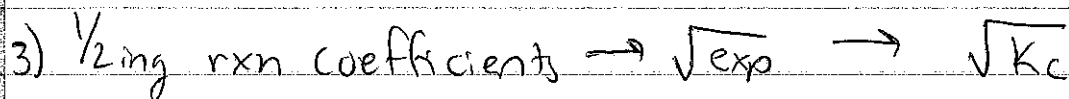
example pg 321

Le Châtlier's Principle

- a system at eqm when subjected to change will respond in such a way as to minimize the effect of the change

add → adjust to remove it (vice versa)
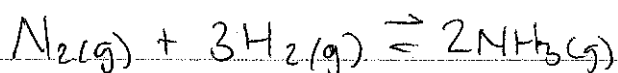   ↓
new eqm (diff than before)

1) changes in concentration

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

- add H_2 (reactant) ↑ conc : decrease $[N_2]$ & $[H_2]$ in
  1:3 ratio increasing $[NH_3]$ in 1:2 ratio
  → favor products b/c add reactants want to
     remove in order to re-equilibrate

- remove NH_3 (product) ↓ conc : decrease $[N_2]$ & $[H_2]$
  to ↑ $[NH_3]$
  → favor products b/c removed product, need to
     replace, pushes rxn in forward direction

✻ K_c remains unchanged in both cases b/c only affected by T

Remove R   P   Add   R   P

✻ no matter effect new eqm is achieved (new ratio
  but same K_c)

2) Changes in pressure
   - affects gases only where change in # molecules occur

   ↑ pressure move to side w/ fewer molecules
   ↓ pressure move to side w/ more molecules favored

   if equal # of (g) molecules on each side, pressure
   has no effect
   * K_c will be unchanged as long as T stays same

3) change in temperature
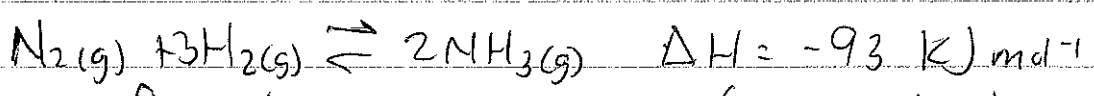   * K_c is temp dependent $(\Delta T = \Delta K_c)$

   enthalpy changes
      ΔH (-) exothermic ΔH (+) endothermic

      forward & reverse rxn are equal & opposite
         $f = \Delta H (+)$ then $R = \Delta H (-)$

      $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$ $\Delta H = -93$ KJ mol^{-1}
      forward rxn — exothermic (releases heat)
         (↓ temp, favor products (release more heat)
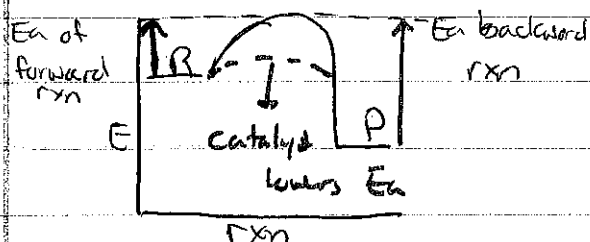   (↑ temp, favor reactants (take heat in)

            problem — ↓ temp too much, rate slows sig.

   ↑ temp (to ↑ rate), ↑ K_c for endo rxn
                        ↓ K_c for exo

4) Addition of a catalyst

- catalyst lowers E_a for both forward/reverse rxns ∴ rate of both rxn ↑ at same amt

no effect on eqm position (K_c), but speeds up attainment of eqm state

Summary

|		
1) conc	change in eqm position	Kc no change
2) pressure	↳ if # of (g) molec changes	↓
3) temp	changes	changes
4) catalyst	no change	no change

Industrial Applications

goal: obtain highest yield ∴ apply Le Chatilier's principle to push rxn to right

① yield   ⟩ ideal mix, may compensate
② rate   (cost - benefit)

The Haber Process: production of ammonia (NH_3)

Use: fertilizers (ammonium nitrate), plastics (nylon), refrigerants, explosives

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -93 \ KJmol^{-1}$$
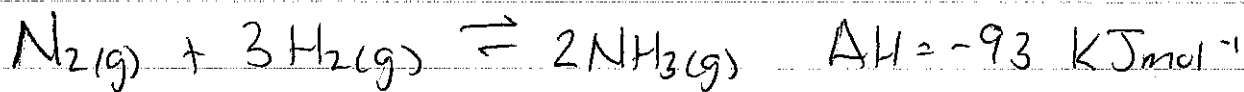
Optimum conditions:
1) conc: R need to be in 1:3 ratio
   product is removed as formed, pulling eqm to right (↑ yield)
2) pressure: forward rxn, fewer (g) molecules, favored by high pressure (20,000 kPa)
3) temp: forward rxn exothermic, favored at low temps (too low = uneconomic) (450°C)
4) catalyst: speed up rxn, compensate for moderate temp used (Fe catalyst w/ Al + MgO or Ruthenium to ↓ energy requirement)

The Contact process: production of H_2SO_4

Use: fertilizer's, detergents, dyes, explosives, drugs plastics

1) combustion of sulfur $\qquad$ $S(s) + O_2(g) \rightarrow SO_2(g)$

ROS★ 2) oxidation of sulfur dioxide $\qquad$ $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

3) $SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(aq)$

↳ Conditions:

- pressure: forward rxn, fewer (g) molecules (200 kPa)
- temp: forward rxn exo (~196 kJ mol^{-1}), moderate temp used (450°C)
- catalyst: Vanadium (V) oxide (V_2O_5)

Production of Methanol

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -90 \text{ kJ mol}^{-1}$$
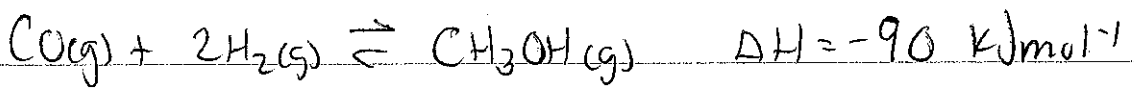
Conditions:

- pressure: fewer molecules of forward rxn (5-10×10^3 kPa)
- temp: exothermic (250°C)
- catalyst: $Cu \cdot ZnO \cdot Al_2O_3$ mixture