

Ch. 14 Chemical Equilibrium

14.1 Characteristics

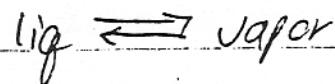
- ① not completely on product or reactant side - have some of each
 "product favored" - mostly product
 "reactant favored" - reactant

② "Dynamic Equilibrium"

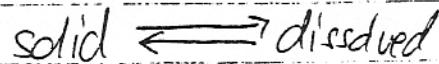
- forward rate = reverse rate
- reactions happen, but cancel, so that no overall change
- "Steady state"

③ Previous Examples

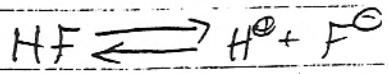
1. Vapor Pressure (closed container)



2. Saturated soln



3. Weak acid/weak electrolyte



④ Doesn't matter whether you start from left side or right side

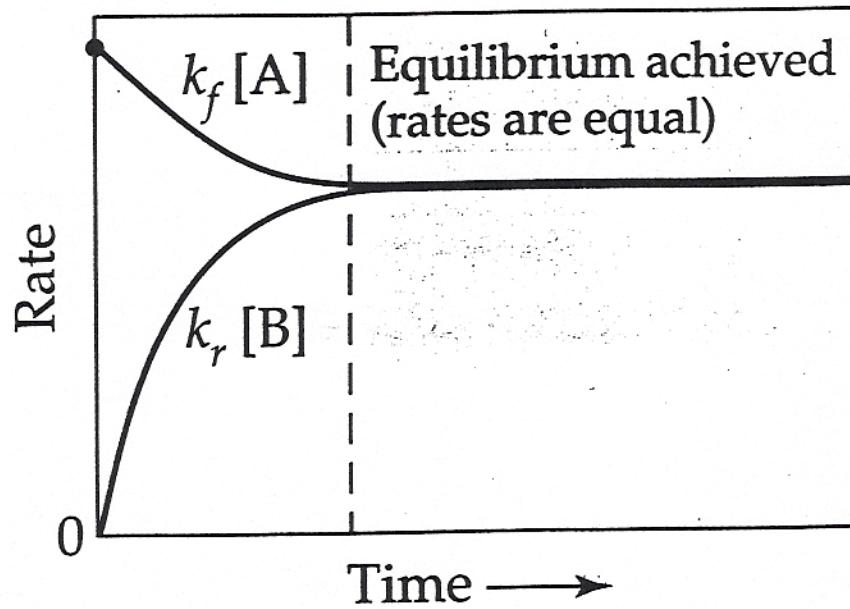
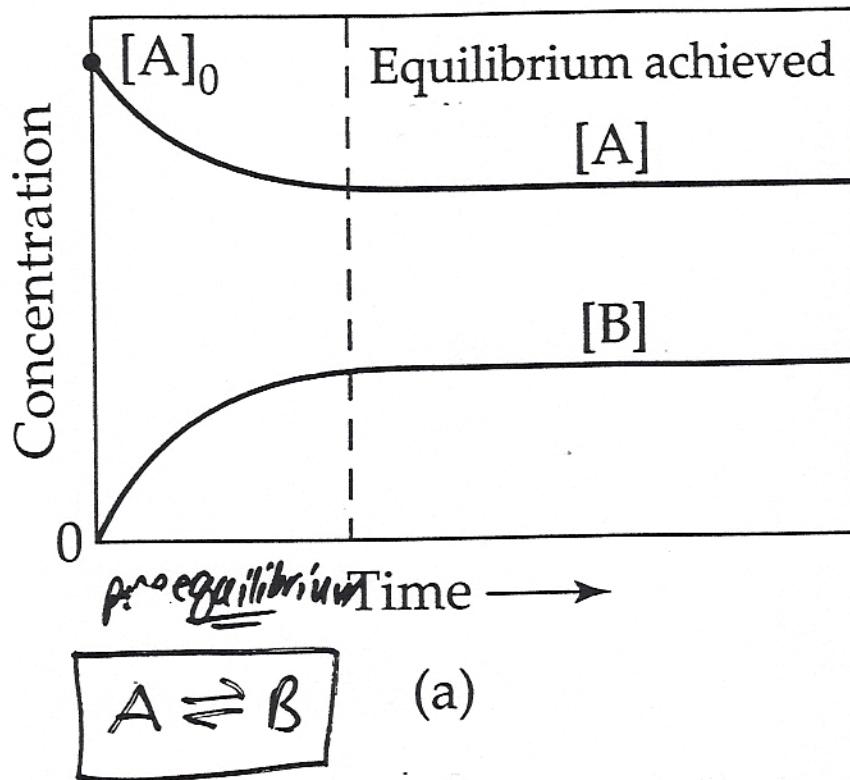
Fig T-117, 118, Brown

Fig 14.1 Moore

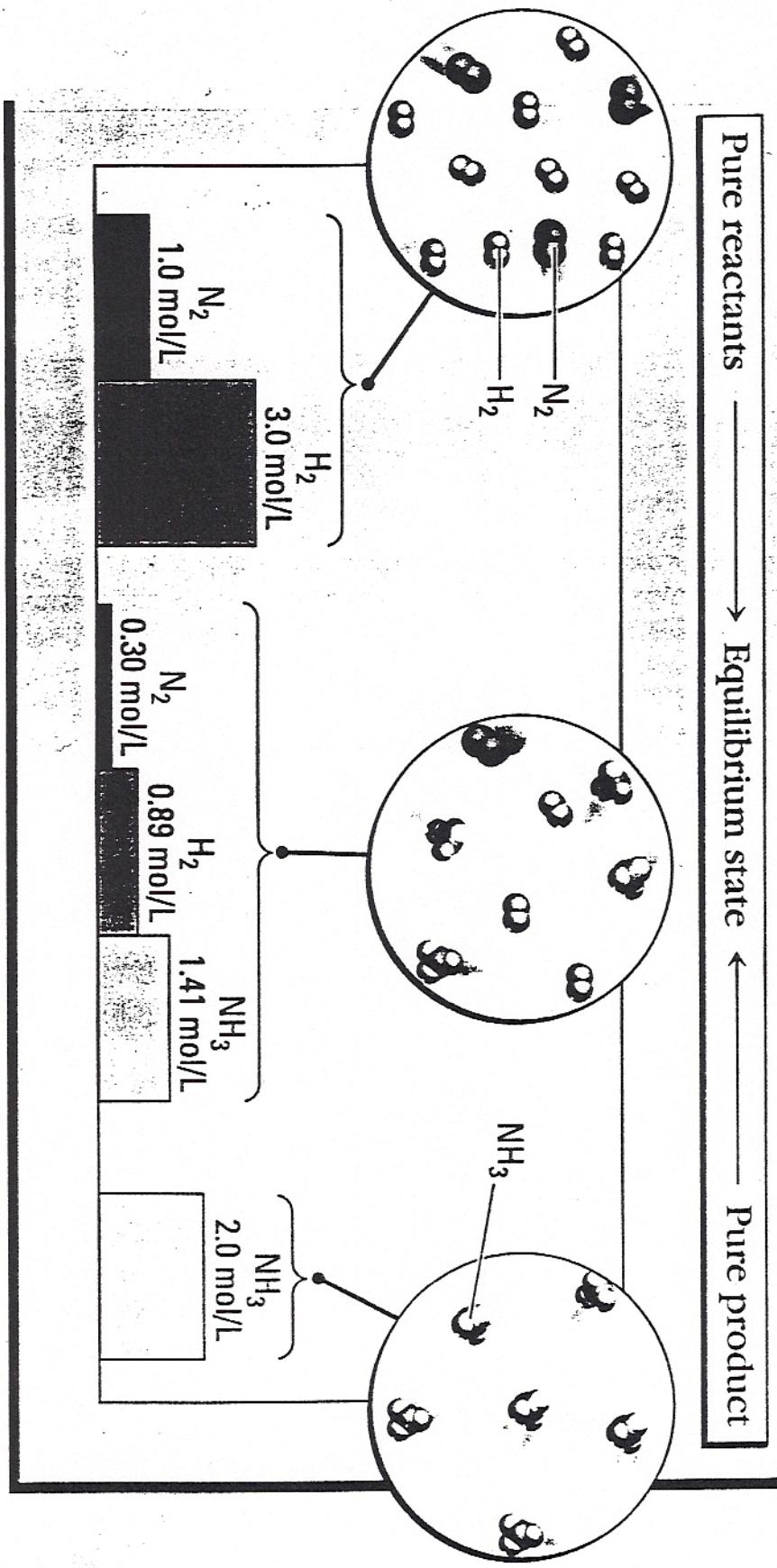
⑤ Catalysts Don't Change (just faster)

⑥ Temp Does Change

Fig. 15.3 Achieving Equilibrium, General



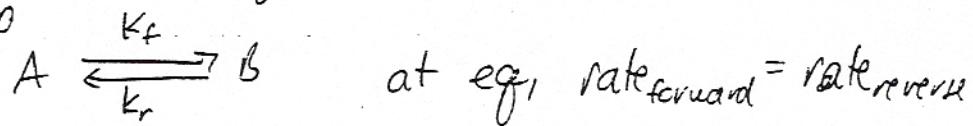
(b)



Moore/Stanitski/Jurs, Chemistry: The Molecular Science
Figure 14.1

14.2 The Equilibrium "Constant"

A. Intro

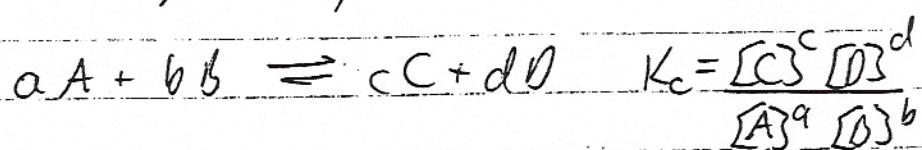


$$k_f[A] = k_r[B]$$

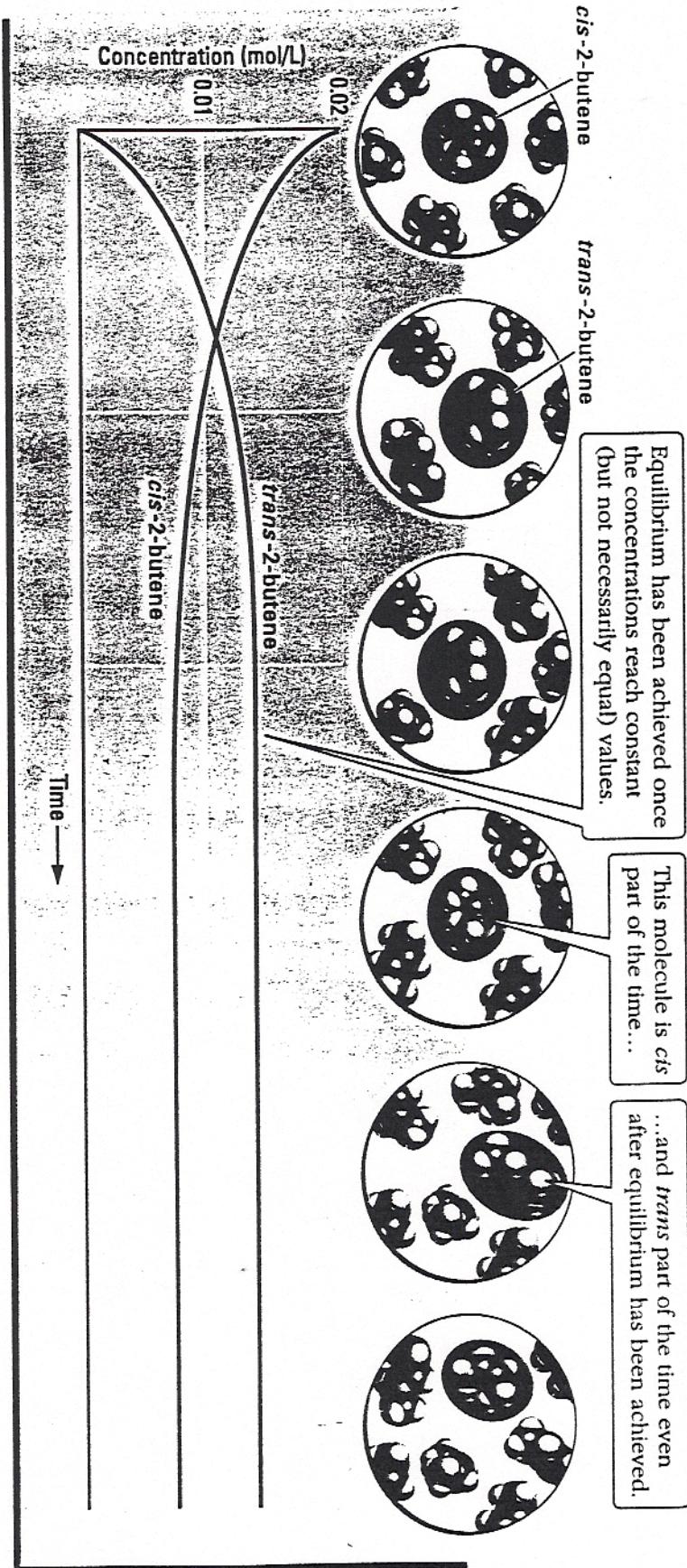
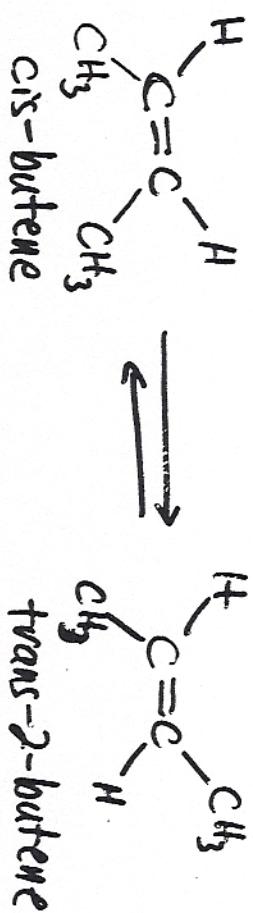
$$\frac{[B]}{[A]} = \frac{k_f}{k_r} = K_c$$

- ~~1~~ K_c is a constant
- ~~2~~ Each eq. has own "K"
- ~~3~~ Ratio of product/reactant concentration
- ~~4~~ Thing K tells us
 - a. at eq, product favored ($K > 1$) or reactants favored? ($K \leq 1$)
 - b. if initial ratio $\neq K$, in which direction will reaction go to achieve eq?
 - c. what will specific concentrations be at eq?

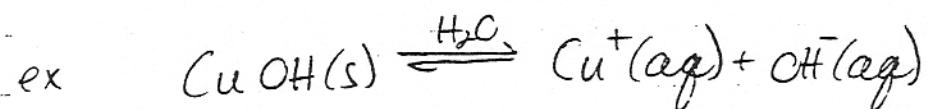
B. Writing K Expression



- ~~1~~ products over reactants
- ~~2~~ to the "coefficient" power
- ~~3~~ straight from balanced eqn. (don't need mech.)

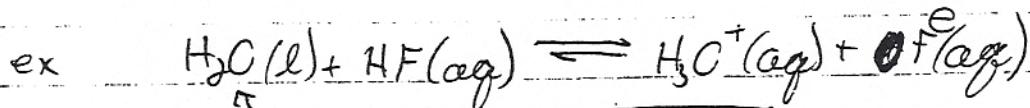


- C. Heterogeneous Equilibria: Do not include solids or liquids (solvents) in K expression \hookrightarrow (water!!)
- their conc. is constant, so just wrapped into K
 - only gases and "aqueous things" appear
- | | | |
|----------|---------|-----|
| $A(g)$, | $B(aq)$ | Yes |
| $C(l)$, | $D(s)$ | NO |



$$K = \frac{[\text{Cu}^+][\text{OH}^-]}{[\text{Cu(OH)}_3]} \quad \text{so} \quad K_c = [\text{Cu}^+][\text{OH}^-]$$

$\underbrace{[\text{Cu(OH)}_3]}_{\text{constant}}$



$$K_c = \frac{[\text{H}_3\text{C}^+][\text{F}^-]}{[\text{HF}]}$$

D. K's for Related Reactions

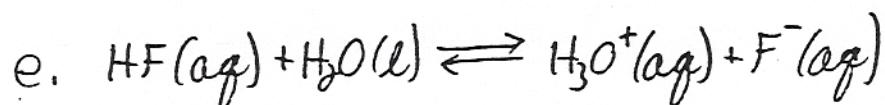
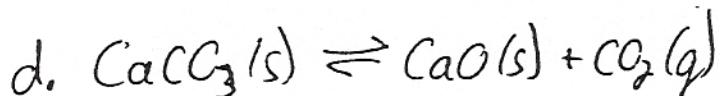
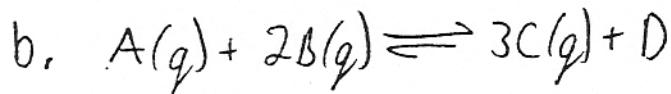
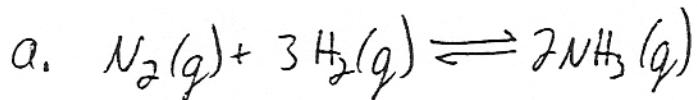
reverse direction: $\frac{1}{K_c} = K_c^{-1}$

$$aA \rightleftharpoons bB \quad K_c = \frac{[\text{B}]^b}{[\text{A}]^a} \quad K_{\text{reverse}} = \frac{[\text{A}]^a}{[\text{B}]^b} = \frac{1}{K_c}$$

$\times 2$

$$2aA \rightleftharpoons 2bB \quad K_{x2} = K_c^2 = \frac{[\text{B}]^{2b}}{[\text{A}]^{2a}}$$

① Write K_c Expressions



② If $A + B \rightleftharpoons C \quad K_c = 10^4$

What is K for $C \rightleftharpoons A + B$?

③ $A \rightleftharpoons B \quad$ Find $\{B\}/\{A\}$ ratios

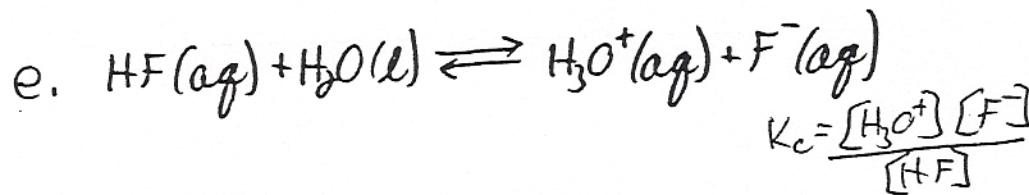
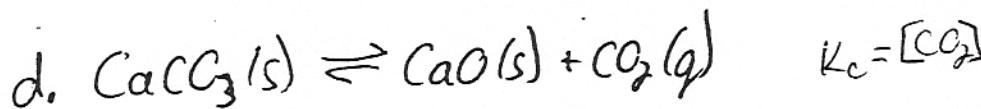
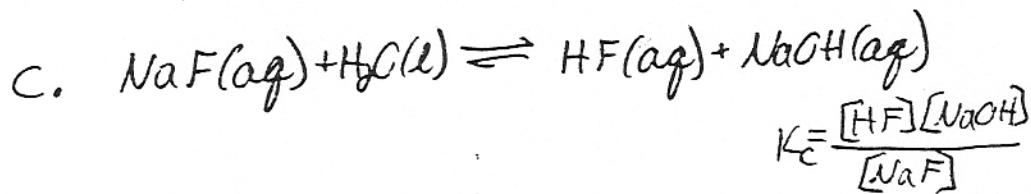
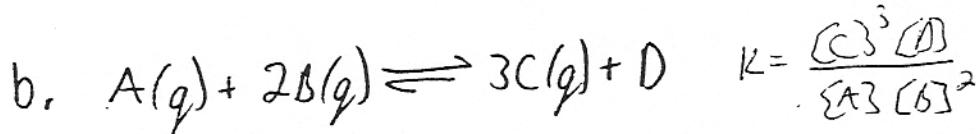
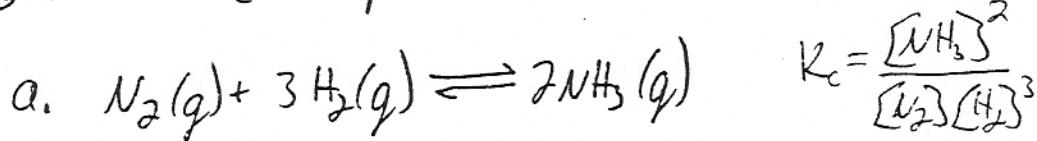
a. $K_c = 10^3$

b. $K_c = 10^{-3}$

Jasperse Chem 160 Ch.14 In Class
Problems

(14-4)

① Write K_c Expressions



② If $A+B \rightleftharpoons C$ $K_c = 10^4$

What is K for $C \rightleftharpoons A+B$? $K_c = 1/10^4 = 10^{-4}$

③ $A \rightleftharpoons B$ Find $[B]/[A]$ ratios

a. $K_c = 10^3$ $1000/1$

b. $K_c = 10^{-3}$ $1/1000$

14.3 Calculating K_c

- need all equilibrium concentrations, plug into K_c

A. Given eq. concs (easy) (14.6, p. 1, 2)

B. Given initial concentrations and at least one final concentration (medium)

① Write balanced egn, K_c

② Make "ICE" table, enter knowns

Initial

Change

Equilibrium

③ Find change for chemical whose final conc is known

④ Use stoich to determine changes of others

⑤ From initial concs and deduced changes, determine all ~~not~~ eq. concs.

⑥ Solve for K

(Practice: 14.6 #3-4)

Note: ~~E~~ "E" must be in molarity, moles/liter

If info given in "moles" or "grams" plus volume, will need to convert,

Using the "ICE" Method to Calculate K, Given Initial Concentrations and One Final Concentration

1. Write balanced equation, and expression for K_c
2. Make an "ICE" table, and enter the knowns
 - a. Initial
 - b. Change
 - c. Equilibrium
3. Find the Change for the chemical whose final concentration is known
4. Use stoichiometric relationship to determine the change in concentrations for the others
5. From the initial concentrations and the deduced changes, determine all equilibrium concentrations
6. With all equilibrium concentrations now known, plug into the K_c expression and solve for K
7. Check: Does Answer Make Any Sense?
 - Note: equilibrium concentrations must be in Molarity, moles/liter. If information is given in grams or moles plus solvent volume, you will need to convert into molarity.

Using the "ICE" Method to Calculate Equilibrium Concentrations, Given Only Initial Concentrations and K_c

1. Write balanced equation, and expression for K_c
2. Make an "ICE" table, and enter the known initial concentrations
 - a. Initial
 - b. Change
 - c. Equilibrium
3. Use "x" to define the change of one substance. Use stoichiometric relationships to determine the changes in the concentrations for the others, in terms of "x".
4. Calculate the equilibrium concentrations of all chemicals in terms of initial concentrations and "x", and enter them in the table.
 - If K is small so that "x" is likely to be small, the simplifying assumption that $[A]_{\text{initial}} - "x" = [A]_{\text{initial}}$ is often justified, and can greatly simplify the math.
5. Solve for "x" (This is the hard part!)
6. Once "x" is known, solve for the actual equilibrium concentrations
7. Check: Does Answer Make Any Sense? If you made the "simplifying assumption", was it justified?

(14-6)

① For $A \rightleftharpoons B+C$, find K_c if $[A] = 0.26$

$$[B] = 0.26$$

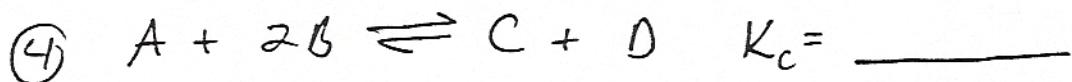
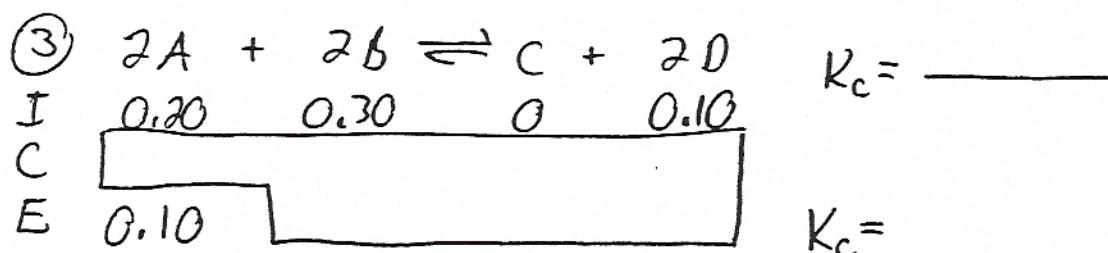
$$[C] = 0.93$$

② For $A + 2B \rightleftharpoons 2C + D$ find K_c if $[A] = 0.15$

$$[B] = 0.18$$

$$[C] = 20 \times 10^{-4}$$

$$[D] = 30 \times 10^{-6}$$



I	0.20	0.20	0	0
C	↓			
E	0.15			

$K_c = \underline{\hspace{2cm}}$

(14-6)

① For $A \rightleftharpoons B+C$, find K_c if $[A] = 0.26$

$$K_c = \frac{[B][C]}{[A]} = \frac{(0.26)(0.93)}{0.26} = 0.93$$

$[B] = 0.26$

$[C] = 0.93$

② For $A + 2B \rightleftharpoons 2C + D$ find K_c if $[A] = 0.15$

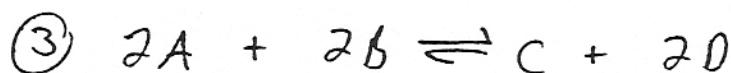
$$K_c = \frac{[C]^2 [D]}{[A][B]^2} = \frac{(2.0 \times 10^{-4})^2 (3.0 \times 10^{-6})}{(0.15)(0.18)^2}$$

$[B] = 0.18$

$[C] = 2.0 \times 10^{-4}$

$[D] = 3.0 \times 10^{-6}$

$K_c = 2.47 \times 10^{-11}$

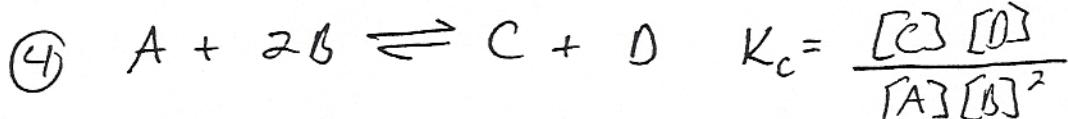


I	0.20	0.30	0	0.10
C	-0.10	-0.10	+0.05	+0.10
E	0.10	0.20	0.05	0.20

$K_c = \frac{[C][D]^2}{[A]^2[B]^2}$

$K_c = \frac{(0.05)(0.20)^2}{(0.10)^2(0.20)^2}$

$K_c = 5.0$



I	0.20	0.20	0	0
C	-0.05	-0.10	+0.05	+0.05
E	0.15	+0.10	+0.05	+0.05

$K_c = \frac{(0.05)(0.05)}{(0.15)(0.10)^2}$

$K_c = 1.67$

14.4 Meaning of K_c

- ① $K_c \gg 1$ Product favored
 - ② $K_c \ll 1$ Reactants favored
 - ③ $K_c \approx 1$ Significant quantities of both products + reactants
↳ calcs required
- many cases where $K_c \ll 1$, but small amount of product still very important

14.5 Using K_c

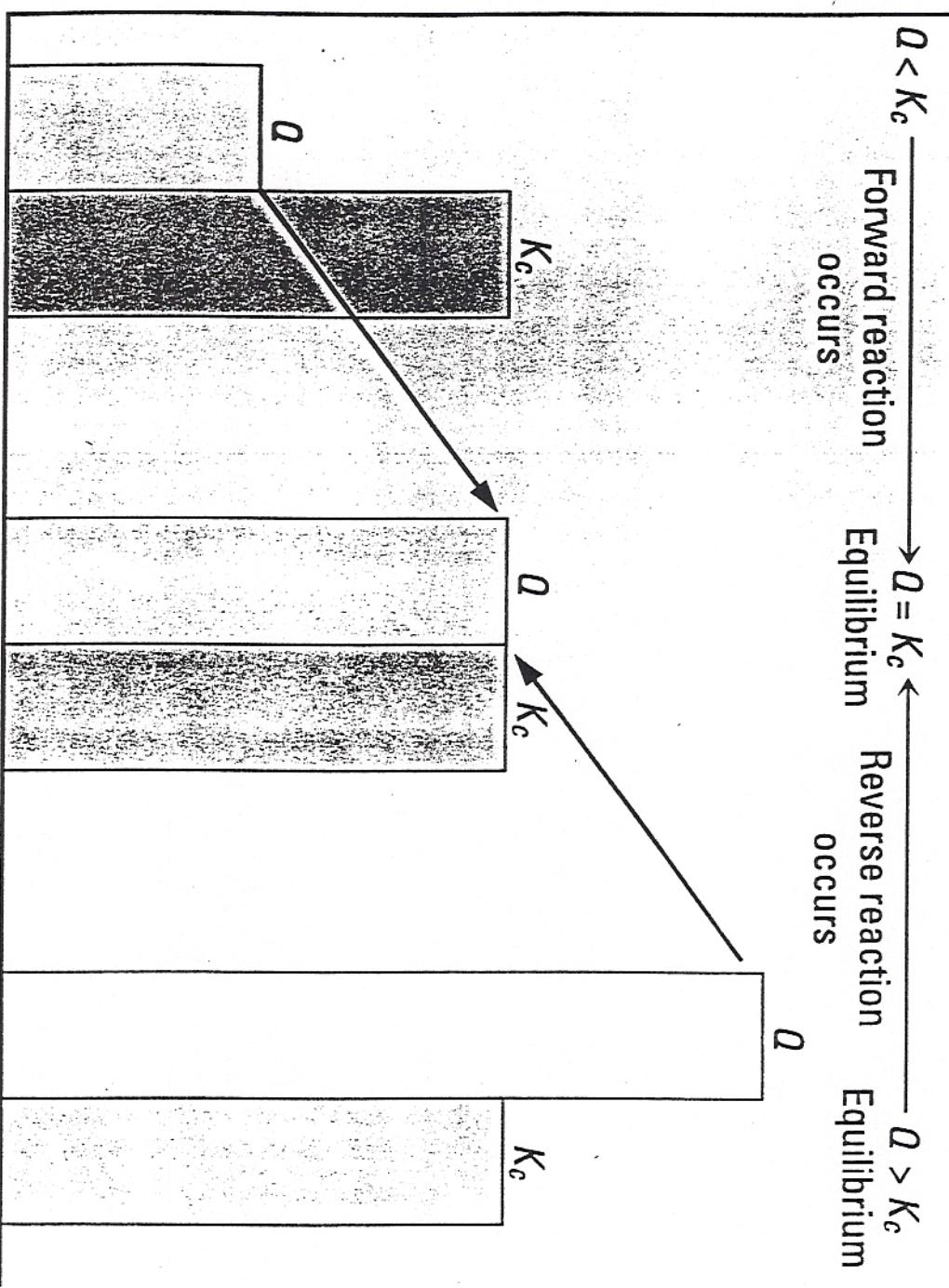
- A. Predicting the Direction of a Reaction,
Given Info About Actual Situation

K = equilibrium Q = actual ratios (same format)

if $Q = K$ you're at eq, won't change

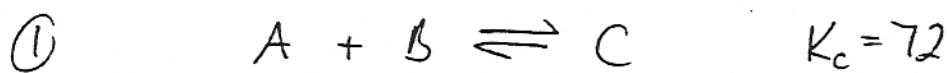
$Q < K$ not " " , short on product, reactants will go to products to achieve eq

$Q > K$ excess product, will proceed to left



Moore/Sitko/Jurs, Chemistry: The Molecular Science
Figure 14.5

(14-8)

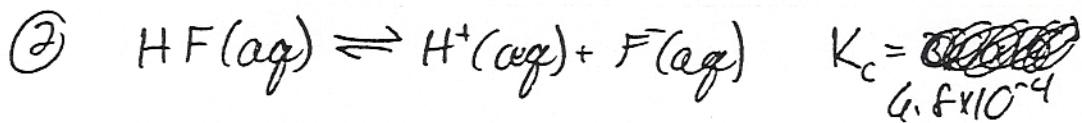


Suppose $[A]$, $[B]$, + $[C]$, all begin at 0.33M :

a. what is Q ?

b. Which direction will the reaction go to achieve equilibrium?

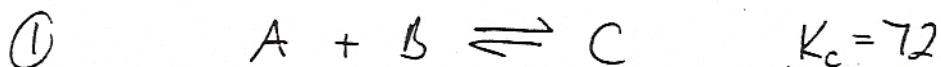
c. What will happen to the concentrations of:



a. Find $[H^+]$ if $[HF] = 0.10$ and $[F^-] = 0.10$

b. Find $[F^-]$ if $[HF] = 0.20$ and $[H^+] = 10^{-3}$

(14-8)



Suppose $[A]$, $[B]$, + $[C]$ all begin at 0.33M :

a. what is Q ? $Q = \frac{[C]}{[A][B]} = \frac{0.33}{(0.33)(0.33)} = \boxed{1.0}$

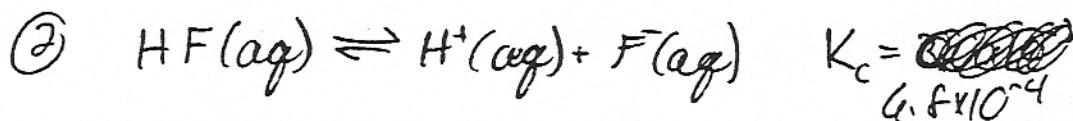
b. which direction will the reaction go to achieve equilibrium? Forwards

$$Q < K$$

c. what will happen to the concentrations

of:

$[A]$	\downarrow
$[B]$	\downarrow
$[C]$	\uparrow



a. Find $[\text{H}^+]$ if $[\text{HF}] = 0.10$ and $[\text{F}^-] = 0.10$

$$K = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} \quad 6.8 \times 10^{-4} = \cancel{\frac{[\text{H}^+] \cdot 0.10}{0.10}} \quad \boxed{\text{H}^+ = 6.8 \times 10^{-4}}$$

b. Find $[\text{F}^-]$ if $[\text{HF}] = 0.20$ and $[\text{H}^+] = 10^{-3}$

$$6.8 \times 10^{-4} = \frac{(10^{-3}) \cancel{[\text{F}^-]}}{0.20} = \boxed{0.136\text{M}}$$

B. Calculating Eq. Conc.

1. If some eq. conc. are given (easy)
 (14.8 p#2) Plug + chug

2. If only initial conditions are given:
 use ICE

- * ① Write balanced egn, K_c
- ② Make "ICE" table, enter knowns
- ③ Use "x" to define change of one substance. Use stoich to calculate other changes in terms of x
- ④ Calculate eq. concs. in terms of x, and enter them in table
- rd part! \Rightarrow ⑤ Solve for "x", then use "x" to calculate other things. (targets)
- ~~sometimes \Rightarrow~~ ~~no simplifications~~ ⑥ Check: does answer make any sense?

Note: Some hard math! Quadratics are tough!

* Great simplifying assumption: changes "x" are often small, so something with nonzero original concentration can be approximated to be unchanged

$$\text{ex } 0.20 - x \approx 0.20$$

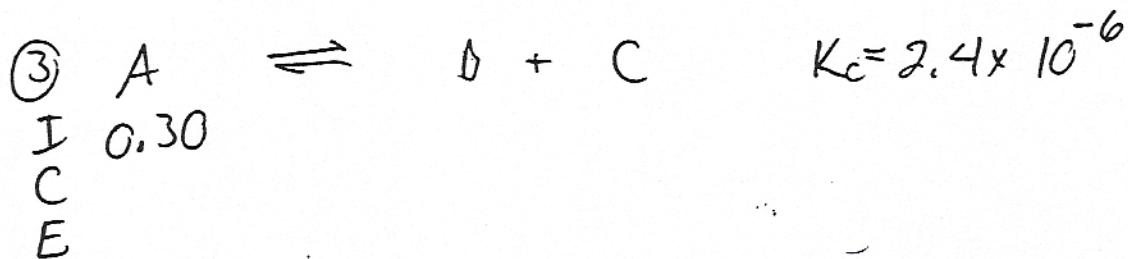
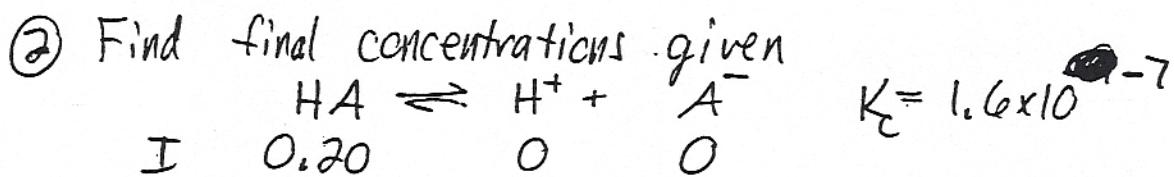
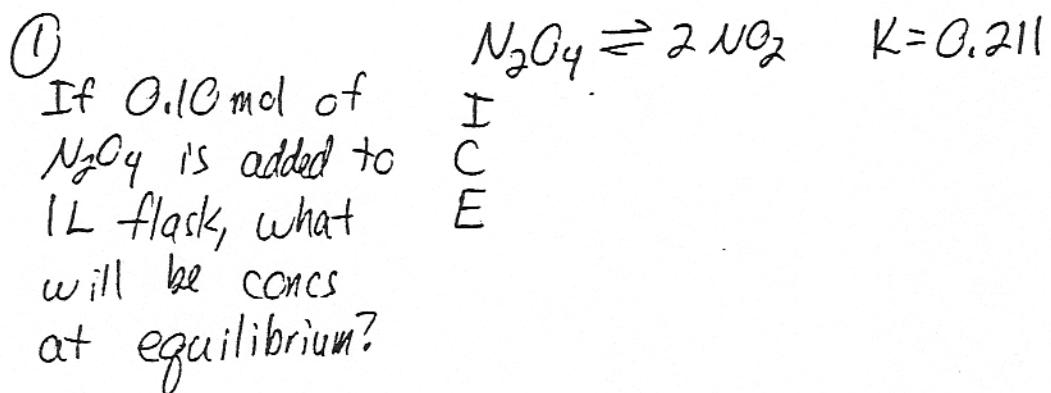
-check at end. If $x > 5\%$ of number, the assumption causes trouble

Using the "ICE" Method to Calculate K, Given Initial Concentrations and One Final Concentration

1. Write balanced equation, and expression for K_c
2. Make an "ICE" table, and enter the knowns
 - a. Initial
 - b. Change
 - c. Equilibrium
3. Find the Change for the chemical whose final concentration is known
4. Use stoichiometric relationship to determine the change in concentrations for the others
5. From the initial concentrations and the deduced changes, determine all equilibrium concentrations
6. With all equilibrium concentrations now known, plug into the K_c expression and solve for K
7. Check: Does Answer Make Any Sense?
 - Note: equilibrium concentrations must be in Molarity, moles/liter. If information is given in grams or moles plus solvent volume, you will need to convert into molarity.

Using the "ICE" Method to Calculate Equilibrium Concentrations, Given Only Initial Concentrations and K_c

1. Write balanced equation, and expression for K_c
2. Make an "ICE" table, and enter the known initial concentrations
 - a. Initial
 - b. Change
 - c. Equilibrium
3. Use "x" to define the change of one substance. Use stoichiometric relationships to determine the changes in the concentrations for the others, in terms of "x".
4. Calculate the equilibrium concentrations of all chemicals in terms of initial concentrations and "x", and enter them in the table.
 - If K is small so that "x" is likely to be small, the simplifying assumption that $[A]_{\text{initial}} - x = [A]_{\text{initial}}$ is often justified, and can greatly simplify the math.
5. Solve for "x" (This is the hard part!)
6. Once "x" is known, solve for the actual equilibrium concentrations
7. Check: Does Answer Make Any Sense? If you made the "simplifying assumption", was it justified?



14-10

①

If 0.10 mol of N_2O_4 is added to 1 L flask, what will be concs at equilibrium?

$$= \frac{-0.211 \pm \sqrt{0.211^2 - 4(0.0211)}}{8} = 0.0509$$

$$\text{so } [N_2O_4] = 0.10 - 0.0509 = 0.0491 \text{ M}$$

$$[NO_2] = 2x = 2 \times 0.0509 = 0.102 \text{ M}$$



$$K = 0.211$$

$$\begin{array}{ccc} I & 0.10 & 0 \\ C & -x & +2x \\ E & 0.10-x & 2x \end{array}$$

$$0.211 = \frac{[NO_2]^2}{[N_2O_4]}$$

$$0.211 = \frac{(2x)^2}{0.10-x}$$

$$0.0211 - 0.211x = 4x^2$$

$$0.0211 - 0.211x - 4x^2 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-0.211 \pm \sqrt{(0.211)^2 - 4(4)(-0.0211)}}{8}$$

$$= \frac{-0.211 \pm \sqrt{0.382}}{8}$$

② Find final concentrations given

Can bypass quadratic

$$\begin{array}{ccc} I & 0.20 & 0 \\ C & -x & +x \\ E & 0.20-x & x & x \end{array}$$

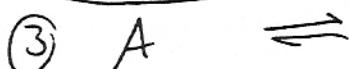
$$K_c = 1.6 \times 10^{-7}$$

$$K_c = \frac{[H^+][A^-]}{[HA]}$$

$$1.6 \times 10^{-7} = \frac{x^2}{0.20}$$

$$x^2 = 3.2 \times 10^{-8}$$

$$x = 1.78 \times 10^{-4}$$



$$\begin{array}{ccc} I & 0.30 & 0 \\ C & -x & +x \\ E & 0.30-x & x & x \end{array}$$

$$K_c = 2.4 \times 10^{-6}$$

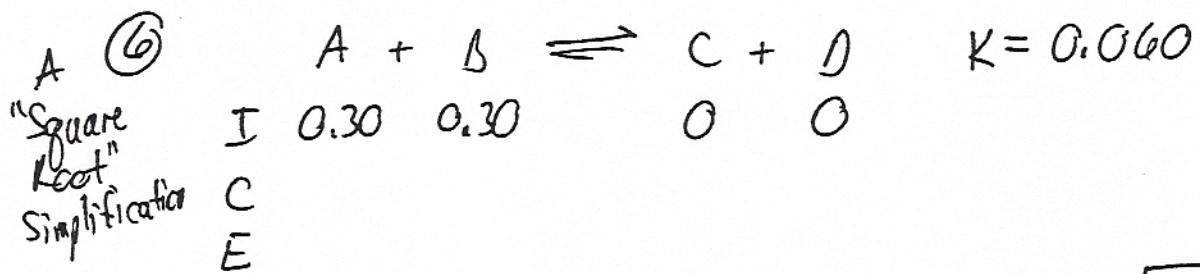
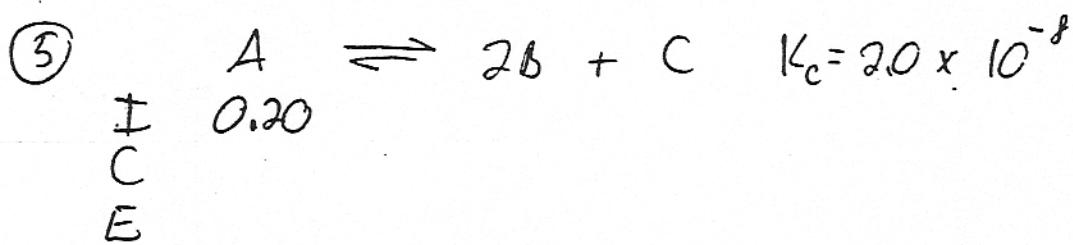
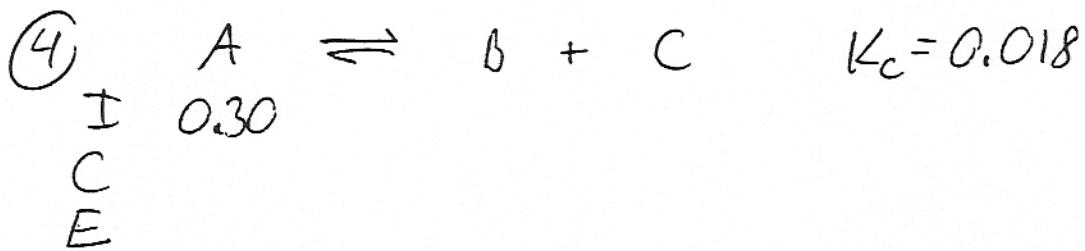
$$2.4 \times 10^{-6} = \frac{x^2}{0.30}$$

$$x = 8.48 \times 10^{-4}$$

$$[E] = 0.30$$

$$8.48 \times 10^{-4} \quad 8.48 \times 10^{-4}$$

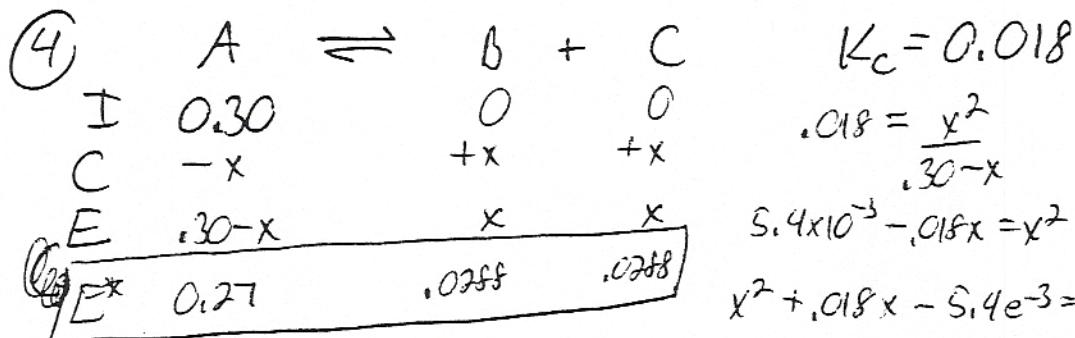
(14-11)



$$K = 0.060 = \underline{\quad}$$

take square
root of everything $\sqrt{0.060} = \sqrt{\underline{\quad}}$

(14-11)



In this case, K_c too big to justify simplifying assumption.

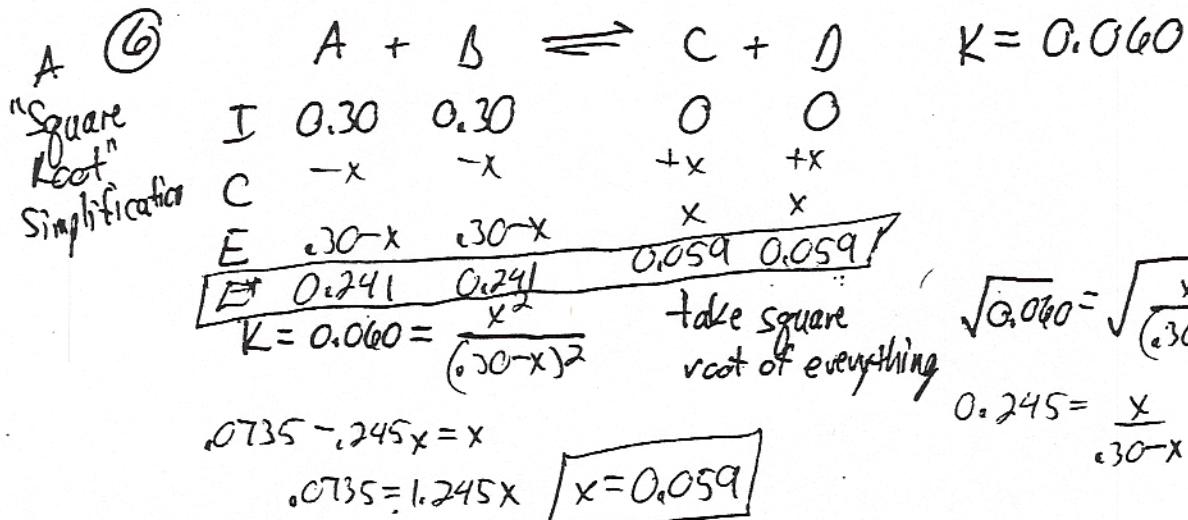
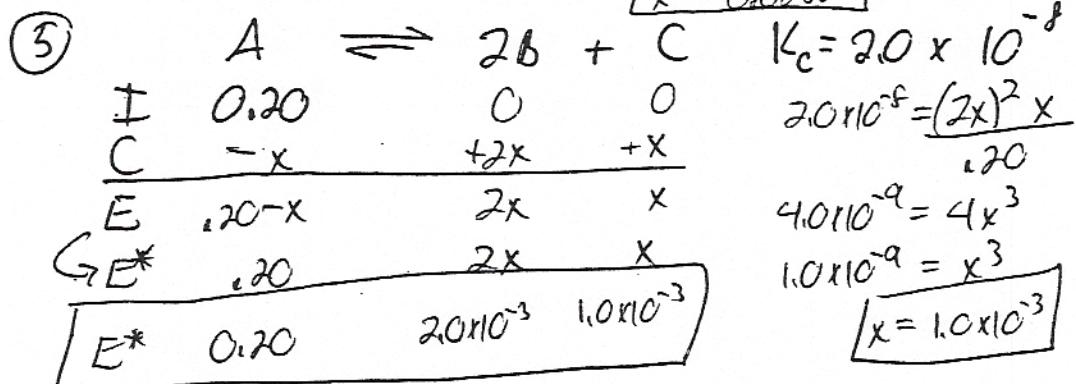
Need quadratic.

$$x = \frac{-0.018 \pm \sqrt{(0.018)^2 - 4(-5.4 \times 10^{-3})}}{2}$$

$$= \frac{-0.018 \pm \sqrt{0.005724}}{2}$$

$$= \frac{-0.018 \pm 0.0757}{2}$$

$$x = 0.0288$$



Solution With + Without Simplifying
Assumption

	$A \rightleftharpoons 2B + C$	$K_c = 2.0 \times 10^{-8}$
<u>With</u>	I 0.20	$0 \quad 0$
C $-x$	$2x \quad x$	
E $0.20-x$	$2x \quad x$	
E^* 0.20	$x \quad x$	

$$\text{so } K = 2.0 \times 10^{-8} = \frac{(2x)^2 x}{0.20} = \frac{4x^3}{0.20}$$

$$0.4 \times 10^{-8} = 4x^3$$

Easy

$$x^3 = 1.0 \times 10^{-9}$$

$$x = 1.0 \times 10^{-3}$$

Without (Using $0.20-x$ for EAS at eq)

$$K = 2.0 \times 10^{-8} = \frac{(2x)^2 x}{0.20-x}$$

$$\text{so } 2.0 \times 10^{-8} (0.20-x) = 4x^3$$

$$\text{so } 4.0 \times 10^{-9} - 2.0 \times 10^{-8} x = 4x^3$$

$$\text{so } 4x^3 + 2.0 \times 10^{-8} x - 4.0 \times 10^{-9} = 0$$

Not Easy !!

14.6 Response when an Eq. is Disturbed

"Steady state at equilibrium. But what if something does change? If we want a conc. to change, can we cause that?"
 (acid rain, lake acidity ...)

Le Chatelier's Principle: when system is disturbed from eq, it responds so as to ① reach a new eq. (usually same K, but different concs) and ② partially counteract the change

Qual: if something added, react to remove
 " " removed, " " replace

3 Factors

① Concentrations

Goals

② Temp

① restore $Q = K$

③ Volume

② offset change

A. Concentration

- if you add (or remove) chem, at that moment $Q \neq K$
- system (and concs) will shift forward or backward to adjust Q so $Q = K$
- Note: K value does not change
- many chemical ways to remove a chem (precipitation, acid-base, etc.)

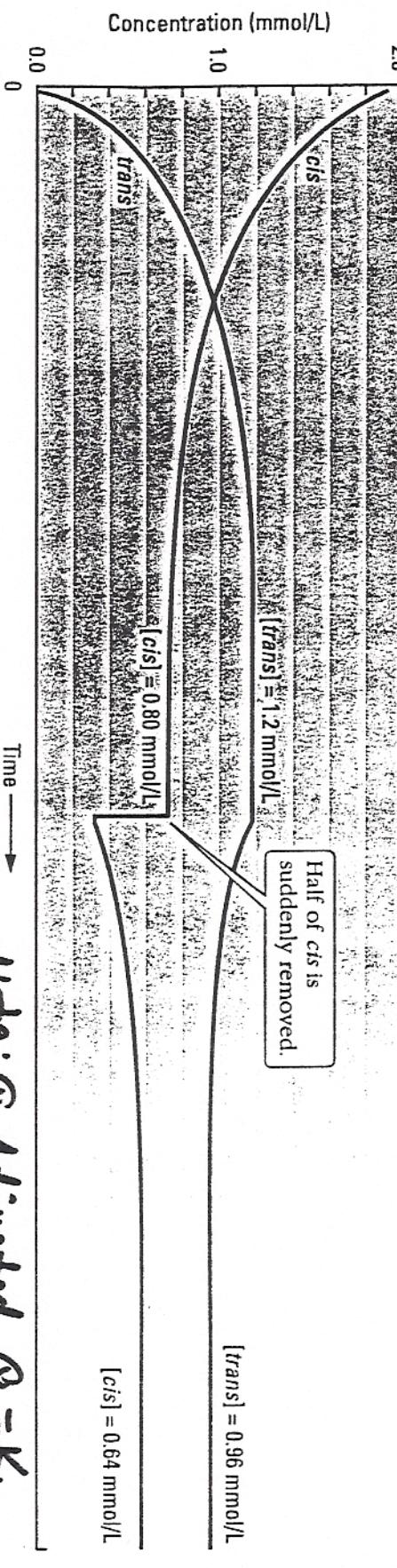
$$Q = 1.5 \quad K = 1.5$$

$Q < K$. The system is reacting to establish the first equilibrium:
 Rate_{forward} > Rate_{reverse}

$Q = K$. The system is at the first equilibrium:
 Rate_{forward} = Rate_{reverse}

$Q > K$. The reaction shifts backward to establish a second equilibrium:
 Rate_{forward} < Rate_{reverse}

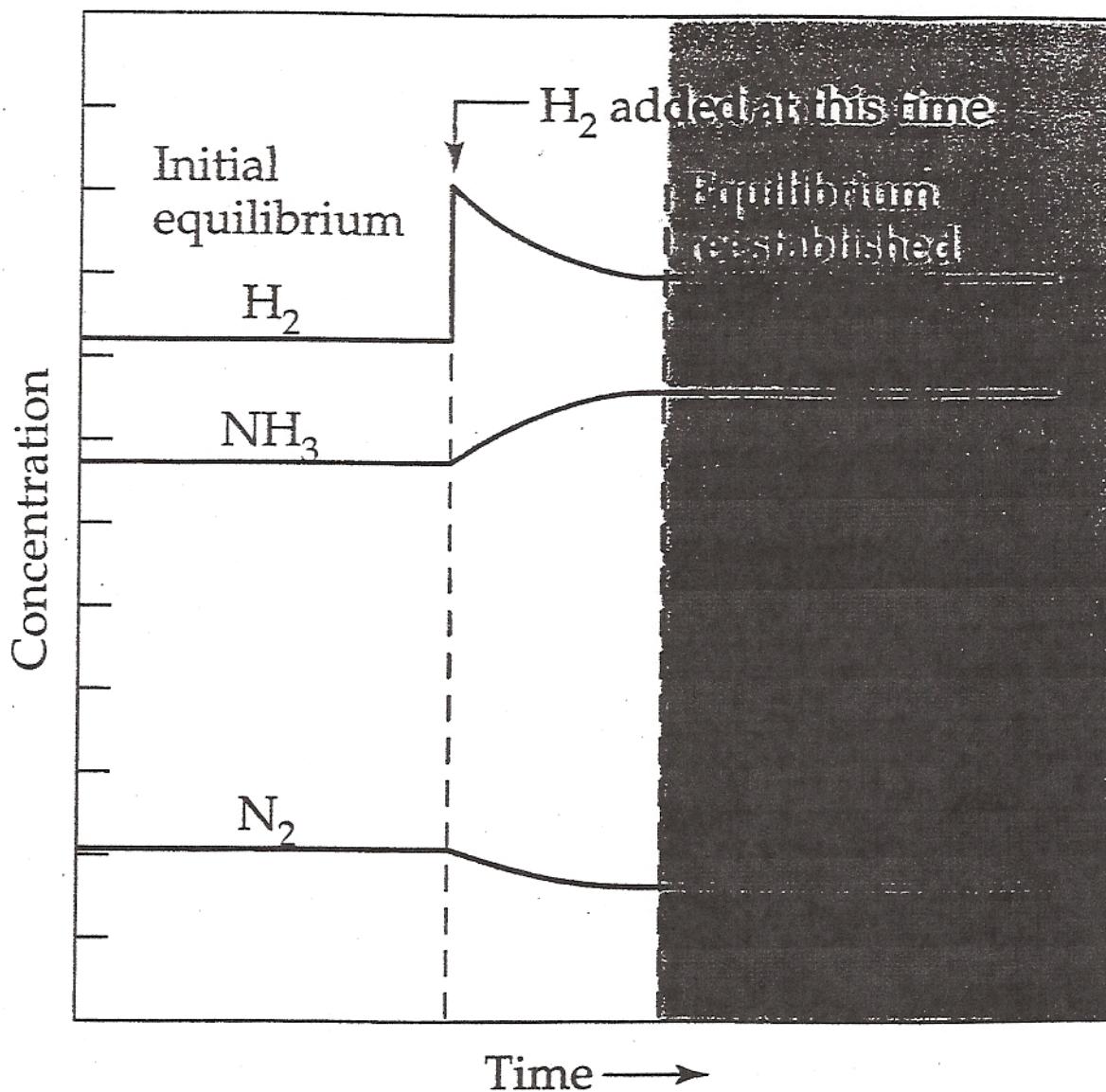
$Q = K$. The system is at the second equilibrium
 Rate_{forward} = Rate_{reverse}



Note: ① Adjusted $Q = K$,

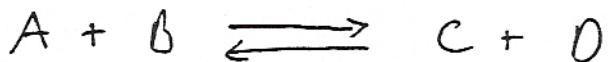
but specific concentrations have changed

② Final $[cis]$ is $\frac{4}{5}$ as low as right after disruption, but change only partially.



- ① Note: Adjusted $Q = K$, but final concs different from original
- ② Disruption of $[H_2]$ is counteracted, partially

(14-14)



<u>Disruption</u>	<u>Immediate Impact on Q</u>	<u>Direction to Restore Eq</u>	<u>Response of [A]</u>	<u>Response of [B]</u>	<u>Response of [C]</u>	<u>Response of [D]</u>
Add A	$Q < K$	forward	↓	↓	↑	↑

Add B

Add C

Add D

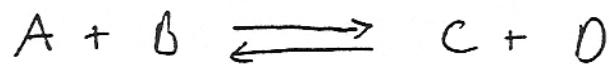
Remove A

Remove B

Remove C

Remove D

(14-14)



<u>Disruption</u>	<u>Impact on Q</u>	<u>Direction to Restore Eq</u>	<u>Response of [A]</u>	<u>[B]</u>	<u>[C]</u>	<u>[D]</u>
Add A	$Q < K$	forward	\downarrow	\downarrow	\uparrow	\uparrow

Add B	$Q < K$	\rightarrow	\downarrow	\downarrow	\uparrow	\uparrow
-------	---------	---------------	--------------	--------------	------------	------------

Add C	$Q > K$	\leftarrow	\uparrow	\uparrow	\downarrow	\downarrow
-------	---------	--------------	------------	------------	--------------	--------------

Add D	$Q > K$	\leftarrow	\uparrow	\uparrow	\downarrow	\downarrow
-------	---------	--------------	------------	------------	--------------	--------------

Remove A	$Q > K$	\leftarrow	\uparrow	\uparrow	\downarrow	\downarrow
----------	---------	--------------	------------	------------	--------------	--------------

Remove B	$Q > K$	\leftarrow	\uparrow	\uparrow	\downarrow	\downarrow
----------	---------	--------------	------------	------------	--------------	--------------

Remove C	$Q < K$	\rightarrow	\downarrow	\downarrow	\uparrow	\uparrow
----------	---------	---------------	--------------	--------------	------------	------------

Remove D	$Q < K$	\rightarrow	\downarrow	\downarrow	\uparrow	\uparrow
----------	---------	---------------	--------------	--------------	------------	------------

B. Volume (when gases involved)

- volume changes change concs, at instant of change $Q \neq K$

Qual: when volume expands, want more gas to fill it
 when volume shrinks, want to get rid of gas

<u>Disruption</u>	<u>Response</u>
Volume Increase	Shift toward side with more gas
Volume Decrease	" less

- if moles of gas equal, no impact
- note: K unchanged

C. Temp

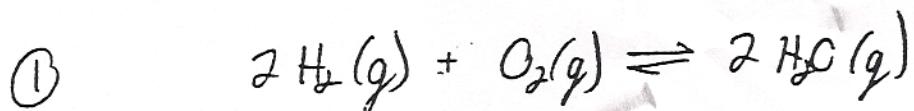
- heat viewed as reactant (endo, $\text{O}H > 0$) or product (exo, $\text{O}H < 0$)

offset } - with temp change, system responds to
 change } remove heat (after temp increase) or
 } replace heat (after temp decreased)
 } K changes!!

Temp Increase	$\text{O}H > 0$	forward	K increases
	$\text{O}H < 0$	reverse	K decreases

D. Catalyst: get to eq. faster, but otherwise no impact

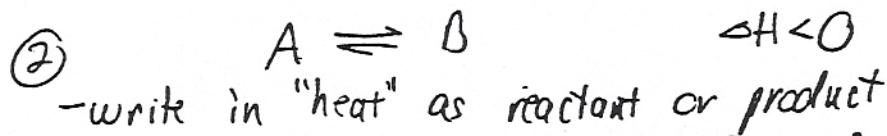
14.7 Slim: Eq. favors more stable chems



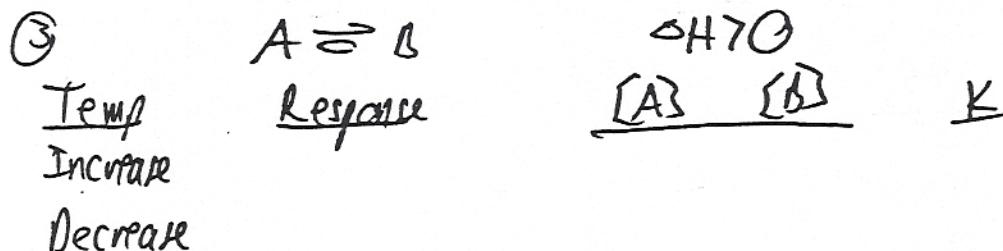
<u>Volume Change</u>	<u>Direction to Restore Eq</u>	<u>Response of</u> [H ₂] [O ₂] [H ₂ O]
----------------------	--------------------------------	--

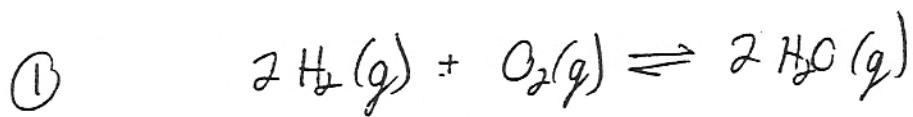
Increase

Decrease

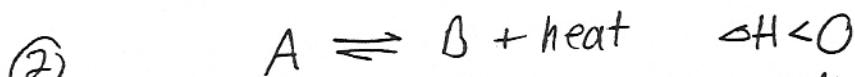


<u>Temp Change</u>	<u>Direction to Restore Eq</u>	<u>Response of</u> [A] [B]	<u>K</u>
Increase			
Decrease			



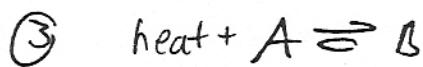


<u>Volume Change</u>	<u>Direction to Restore Eq</u>	<u>Response of</u>	$[\text{H}_2]$	$[\text{O}_2]$	$[\text{H}_2\text{O}]$
Increase	←		↑	↑	↓
Decrease	→		↓	↓	↑

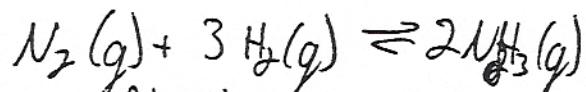


- write in "heat" as reactant or product

<u>Temp Change</u>	<u>Direction to Restore Eq</u>	<u>Response of</u>	$\frac{[A]}{[B]}$	K
Increase	←		↑	↓
Decrease	→		↓	↑



<u>Temp</u>	<u>Response</u>	$\frac{[A]}{[B]}$	K
Increase	→	↓	↑
Decrease	←	↑	↓



$$\Delta H = -Q$$

Disruption

Direction to
Restore Eq

Response of
 $[N_2]$ $[H_2]$ $[NH_3]$ K

1. Raise temp

2. Increase volume

3. Add N_2

4. Remove NH_3

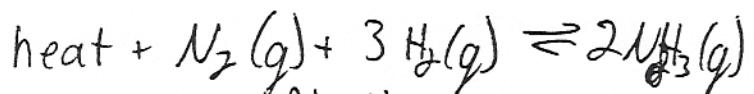
5. Lower temp

6. Add NH_3

7. Remove N_2

8. Reduce Volume

14-17



$$\Delta H = ?$$

<u>Disruption</u>	<u>Direction to Restore Eq</u>	<u>Response of</u> $\{\text{N}_2\}$ $\{\text{H}_2\}$ $\{\text{NH}_3\}$	K
1. Raise temp	→	↓ ↓ ↑	↑
2. Increase volume	←	↑ ↑ ↓	-
3. Add N_2	→	↓ ↓ ↑	-
4. Remove NH_3	→	↓ ↓ ↑	-
5. Lower temp	←	↑ ↑ ↓	↓
6. Add NH_3	←	↑ ↑ ↓	-
7. Remove N_2	←	↑ ↑ ↓	-
8. Reduce Volume	→	↓ ↓ ↑	-