Answers

Ch. 14 Chemical Equilibrium

14.1 Characteristics of a System at Chemical Equilibrium

1. Not completely on product or reactant side – have some of each
   - "product favored" – mostly product
   - "reactant favored" – mostly reactant

2. "Dynamic Equilibrium"
   - forward rate = reverse rate
   - reactions happen, but cancel each other out, so that no overall change
     - "steady state"

3. Previous Examples
   1. Vapor Pressure (closed container) Liquid $\rightleftharpoons$ vapor
   2. Saturated solution solid $\rightleftharpoons$ dissolved
   3. Weak acid/weak electrolyte $HF \rightleftharpoons H^+ + F^{\ominus}$

3. In achieving an equilibrium it doesn't matter whether you start from left side or right side
   - Either way, you end up with the same balance between reactants and products once equilibrium has been established
   - Figure 14.1 Moore, Fig T-117, 118 Brown

5. Catalysts Don't Change The Equilibrium Situation
   - they just help you to achieve it faster

6. A Change in Temperature does change the equilibrium steady state

14.2 The Equilibrium "Constant"

A. Intro

~~K~~

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$

At equilibrium, rate$_{forward}$ = rate $_{reverse}$

⇓ ↓

Rate forward: $k_f[A]$

Rate reverse: $k_r[B]$

Equality: $k_f[A] = k_f[B]$

Rearrange: $\frac{k_f}{k_r} = \frac{[B]}{[A]}$ $\frac{k_f}{k_r} = \boxed{K = \frac{[B]}{[A]}}$

Constant

products top

reactants bottom

Notes
1. K_c is a constant
2. Each reaction has its own unique "K" constant
   - called the "EQUILIBRIUM CONSTANT"
3. Ratio of **product** **over reactant**
   - concentrations in "M" (Molarity) = mole/liter

Qualitative things the value of K tells us:

1. At equilibrium, is the product favored or the reactant?
   - K»1 → product favored (K»1)
   - K«1 → reactant favored (K»1)

Concept Problem: $A \rightleftharpoons B$ Find [B]/[A] ratios if:

a. $K_c=10^3$ $\frac{1000\ B}{1\ A}$

b. $K_c = 10^{-3}$ $\frac{1\ B}{1000\ A}$

2. If the actual initial ratio Q does not equal the equilibrium ratio K, in which direction will reaction go to achieve equilibrium? (In other words, if you start out not at equilibrium, how will the system respond to get to equilibrium?)
   - If actual ratio "Q" < K, the product/reactant ratio will need to increase in order to reach the target "K"
     - Practical: Convert some reactants to products. Reactants↓ Products↑
   - If actual ratio "Q" > K, the product/reactant ratio will need to decrease in order to reach the target "K"
     - Practical: Convert some products back to reactants Reactants↑ Products↓

Concept Problem: $A \rightleftharpoons B$ $K_c=0.20$

How will [A] and [B] change/respond to reach equilibrium (which will go up and which will got down?) if initial conditions are:

a. [A] = 0.10 M and [B] = 0.00 M Q=0 too low ⇒ [B] ≈ 0.017M [A] ≈ 0.083 M

adjust → [A]↓ [B]↑

b. [A] = 0.10 M and [B] = 0.40 M

Q=4, too low, so [A]↑ [B]↓ ⇒ [B] ≈ .083M [A] = 0.417 M

3. What will specific concentrations be at equilibrium?
   - If you know K and some other initial information, you can solve for all the equilibrium concentrations

Concept Problem: $A \rightleftharpoons B$ $K_c=0.20$

a. If the system is at equilibrium and [A] = 0.10 M, what must be [B]?

$K = 0.20 = \frac{[B]}{0.10}$ $\boxed{[B] = 0.020\ M}$

b. If the system is at equilibrium and [B] = 0.10 M, what must be [A]?

$0.20 = \frac{.10}{[A]} =$ $\boxed{[A] = 0.50\ M}$

c. If the system is **not** at equilibrium, and the initial scenario has [B] = 0.50 M, what will be the concentrations after equilibrium is achieved?

	1A ⇌	1B
Initial	0	0.50
Change	+x	−x
Eq	x	.50−x

$K = 0.20 = \frac{[B]}{[A]} = \frac{0.50-x}{x}$

$0.20x = .50 - x$

$1.20x = 0.50$

$x = 0.417$

$\boxed{[A] = 0.417\ M \quad [B] = .50 - .417 = 0.083\ M}$

B. Writing K expressions: General

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

This simple, if all chemicals are gases or "solutes" (aq)

1. Products over reactants
2. To the "coefficient" power
3. Straight from the balanced equation
   - don't need mechanism, etc.
   - Not like a rate law where equation doesn't really tell you anything

Write K_c Expressions

a. $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$ $\qquad K=\frac{[NH]^2}{[N_2][H_2]^3}$

b. $A(g) + 2\,B(g) \rightleftharpoons 3\,C(g) + D(g)$ $\qquad K=\frac{[C]^3[D]}{[A][B]^2}$

C. Heterogeneous Equilibria: Do not include solids or liquids (solvents) in K expressions
- The concentrations of solids and liquids (solvents) are constant, so just wrap into K
- only gases and "aqueous things" (solutes) appear in K expressions
  - these are things whose concentrations are **not** constant
  - A(g), B(aq) Yes
  - C(l), D(s) No
- When water is involved as either a reactant or a product, it does **not** appear in the K expression (when the reaction takes place in aqueous solvent)

Ex. $CuOH(s) \rightleftharpoons Cu^+(aq) + OH^-(aq)$

$$K_1=\frac{[Cu^+][OH^-]}{[CuOH]} \quad \text{so} \quad \mathbf{K_2=[Cu^+][OH^-]}$$

Constant

↓ constant, $[K_1]\times[CuOH]$

Write K Expressions

a. $NaF(aq) + H_2O(l) \rightleftharpoons HF(aq) + NaOH(aq)$ $\qquad K=\frac{[HF][NaOH]}{[NaF]}$

b. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $\qquad K=[CO_2]$

c. $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$ $\qquad K=\frac{[H_3O^+][F^-]}{[HF]}$

D. K's for Related Reactions

- When a reaction is written in the reverse direction, the K value is inversed
  - $K_{reverse} = 1/K_{forward}$
- When the coefficients for a reaction are doubled or halved, the K value ends up being squared or "square rooted"

1. Suppose $A + B \rightleftharpoons C$ $K_c = 10^4$ $K = \frac{[C]}{[A][B]}$ forward

   What is K for $C \rightleftharpoons A + B$ (Draw both the expression and the actual K value) $K = \frac{[A][B]}{[C]}$ after reversal $= K_{reverse} = \frac{1}{K_{forward}}$

   $\boxed{K_{backwards} = \frac{1}{K_{forwards}}}$

2. Suppose $A + B \rightleftharpoons C$ $K_c = 10^4$ $K_1 = 10^4 = \frac{[C]}{[A][B]}$

   What is K for $2A + 2B \rightleftharpoons 2C$ (Draw both the expression and the actual K value)

   so $K_2 = \frac{[C]^2}{[A]^2[B]^2} = (10^4)^2 = \boxed{10^8} = (K_1)^2$

   $K_{new} = (K_{original})^2$

   $3A + 3B \rightleftharpoons 3C$

   $K = 10^{12}$ $K_{new} = (K_{original})^3$

14.3 Calculating K

- Key: You need all equilibrium concentrations. Then you can plug into K expression and solve.

Two ways to know all the equilibrium concentrations.

1. You are simply given all of the equilibrium concentrations. (easy)
2. You are given all of the **initial** concentrations, and **at least one final concentration**, but then must use the "ICE" (**I**nitial-**C**hange-**E**quilibrium) method to figure out what they would all be at equilibrium (harder)

A. Given all of the Equilibrium concentrations, solve for K (easy)

Solution steps:

a. Based on the balanced reaction, write out the correct K expression
b. Enter the known concentrations values and solve for K

1. For $A \rightleftharpoons B + C$, find K_c if [A] = 0.26 M, [B] = 0.26 M, [C] = 0.93 M.

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

2. For $A + 2B \rightleftharpoons 2C + D$, find K_c if [A] = 0.15, [B] = 0.18, [C] = 2.0×10^{-4}, [D] = 3.0×10^{-6}

$$K = \frac{[C]^2[D]}{[A][B]^2} = \frac{(2 \times 10^{-4})^2 (3.0 \times 10^{-6})}{(0.15)(0.18)^2} = \frac{1.2 \times 10^{-13}}{4.86 \times 10^{-3}} = \boxed{2.5 \times 10^{-11}}$$

B. Given all of the all of the **initial** concentrations, and **at least one final concentration**, solve for K (harder).

Solution steps:

a. Based on the balanced reaction, write out the correct K expression
b. Use the "ICE" (Initial-Change-Equilibrium) method to figure out the equilibrium concentrations
c. Enter the equilibrium concentration values and solve for K

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] Use Molarity
   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.

Use the ICE method to find the equilibrium concentrations and the K values for the following:

3.	2A +	2B ⇌	C +	2D
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

$$K_c = \frac{[C][D]^2}{[A]^2[B]^2} = \frac{(0.05)(0.20)^2}{(0.10)^2(0.20)^2} = 5$$

$\boxed{K_c = 5}$

4.	1A +	2B ⇌	C +	D
I	0.20	0.20	0	0
C	−0.05	−0.10	+0.05	+.05
E	0.15	0.10	.05	.05

$$K_c = \frac{[C][D]}{[A][B]^2} = \frac{(.05)(.05)}{(.15)(.10)^2} = 1.7$$

$\boxed{K_c = 1.7}$

14.4 Chemical Meaning of K

1. $K_c \gg 1$ Product Favored
2. $K_c \ll 1$ Reactant Favored
3. $K_c \approx 1$ Significant quantities of both products and reactants---calculations required

- There are many cases where $K_c \ll 1$, but small amount of product are still very important.

14.5 Using K_c

A. Predicting the direction of a reaction, given information about actual situation

K=equilibrium Q=actual rations(same format)

- If Q=K, you're at equilibrium. The situation won't change
- If Q<K, you're not at equilibrium. You are short on product, so reactions will go to products to achieve equilibrium. Shift from left to right.
- If Q>K, you're not at equilibrium. You have excess product, so products will go to reactants to achieve equilibrium. Shift from right to left.

1. $A + B \rightleftharpoons C$ $K_c = 72$

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

a. What is Q? $Q = \frac{[C]}{[A][B]} = \frac{0.33}{(0.33)(0.33)} = \boxed{3}$ Too low, not at equilibrium.

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

Shift to the right, increase [C], decrease [A] and [B]

c. What will happen to the concentrations of: (will they go up or down?)

[A] ↓ [B] ↓ [C] ↑

B. Calculating Equilibrium Concentrations, Given K and Some Other Information

1. If all but one equilibrium concentration is given: (easy, plug and chug…)

Solution steps:

a. Based on the balanced reaction, write out the correct K expression
b. Enter the known K and the known concentrations values and solve for the unknown concentration

Example. $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$ $K_c = 6.8 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]}$

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

$$\underset{K_c}{6.8 \times 10^{-4}} = \frac{[H^+](0.10)}{(0.10)} \qquad \boxed{[H^+] = 6.8 \times 10^{-4}}$$

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

$$6.8 \times 10^{-4} = \frac{(1 \times 10^{-3})[F^-]}{0.20} \qquad \boxed{[F^-] = 0.136\ M}$$

and K number

2. If only initial concentrations are given, use ICE

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

   Molarities
3. Use "x" to define the change of one substance.
4. Use stoichiometric relationships to determine the changes in the concentrations for the others, in terms of "x".
5. Calculate the equilibrium concentrations of all chemicals in terms of initial concentrations and "x", and enter them in the table.
    - Ex: $0.30 - x$, or $0.30 - 2x$, or $0.00 + x$, or $0.00 + 2x$ …..
    - **If K is small** so that "x" is likely to be small, **use the simplifying assumption** that $[A]_{initial} - \text{"x"} = [A]_{initial}$
        - This is often justified, and can greatly simplify the math.
        - Ex: $0.20 - x = 0.20$ if x is smaller than 0.01
6. Solve for "x" (This is the hard part!)
7. **Once "x" is known, use it to solve for the actual equilibrium concentrations**
8. Check: Does Answer Make Any Sense?
9. Check: If you made the "simplifying assumption", was it justified? (Was "x" < 5% of $[A]_{initial}$?)

Note: Some hard math!! Quadratics are tedious!

- If possible, being able to avoid needing to solve quadratics saves a lot of time (and mistakes)

***Great simplifying assumption (avoids a lot of quadratics):**

1. changes "x" are often small
    - For something with nonzero original concentration, the change "x" in concentration is often so small that it doesn't significantly change the original concentration
    - [original concentration] – "x" (change in concentration) = [original concentration]

2. Useful strategy:
    a. Make the simplifying assumption
    b. Check at end whether "x" > 5% of the original concentration
        - If not, the simplifying assumption is pretty good
        - If yes, the simplifying assumption is not valid and leads to some nontrivial error. In which case you need to go back and solve completely (often involving quadratic or perhaps even worse).

Concept Example: Why is the Simplifying Assumption Often Justifiable? 0.20-x = ???

If "x" =	Then 0.20-x =	Rounded	Is simplifying assumption valid?
2×10^{-7}	0.20 – 0.0000002 = .1999998	= 0.20	Yes
2×10^{-6}	0.20 – 0.000002 = 0.199998	= 0.20	Yes
2×10^{-5}	0.20 – 0.00002 = 0.19998	= 0.20	Yes
2×10^{-4}	0.20 – 0.0002 = 0.1998	= 0.20	Yes
2×10^{-3}	0.20 – 0.002 = 0.198	= 0.20	Yes
2×10^{-2}	**0.20 – 0.02 =** 0.18	≠ 0.20	$\boxed{\text{No}}$

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

Problems

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

$\boxed{\text{Quadratic Required}}$

K is too large to justify simp. assump.

	$N_2O_4 \rightleftharpoons$	$2NO_2$
Initial	0.10	0
Change	– x	+2x
Equilibrium	.1 – x	2x
~~Equilibrium with Simplifying Assumption~~	(.1 – .0509)	2 x .0509
Equilibrium:	.0491 M	.102

$[N_2O_4]$	.049 M
~~$[N_2O_4]$~~ $[NO_2]$	.102 M

$$K = 0.211 = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(2x)^2}{.1-x}$$

$$.0211 - .211x = 4x^2$$

$$4x^2 + .211x - .0211 = 0$$

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

$$x = \frac{-.211 \pm \sqrt{(.211)^2 - 4(4)(-.0211)}}{2 \times 4}$$

$$= \frac{-.211 \pm \sqrt{0.382}}{8} = \frac{-.211 \pm .618}{8} = \boxed{.0509}$$

2. Find final concentrations:

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

	$HA \rightleftharpoons$	H^+ +	A^-
Initial Concentrations	0.20	0	0
Change	–x	+x	+x
Equilibrium	.20 – x	x	x
Equilibrium with Simplifying Assumption	.20	x	x
Equilibrium:	.20M	1.79×10^{-4}	1.79×10^{-4}

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

$$1.6 \times 10^{-7} = \frac{x^2}{.20}$$

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

$$x = 1.79 \times 10^{-4}$$

$\boxed{\text{Simplifying Assumption is Good}}$

3. Find final concentrations given: $K_c = 2.4 \times 10^{-6}$

$\boxed{\text{Simplifying Assumption}}$

	A	⇌	B	+	C
Initial	0.30		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$.3-x$		x		x
Equilibrium with Simplifying Assumption	$.3$		x		x

$\boxed{\text{K small, simplifying assumption good}}$

$0.30 > 100\ K_c$

$$K = \frac{[B][C]}{[A]}$$

$$2.4 \times 10^{-6} = \frac{x^2}{.3}$$

$$x^2 = 7.2 \times 10^{-7}$$

$$\boxed{x = 8.49 \times 10^{-4}}$$

Equilibrium:

$[A] = 0.30$

$[B]_{eq} = 8.49 \times 10^{-4}\ M$

$[C]_{eq} = 8.49 \times 10^{-4}\ M$

4. Find final concentrations given: $K_c = 0.018$

$\boxed{\text{Quadratic}}$

	A	⇌	B	+	C
Initial	0.30		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$.3-x$		x		x
	0.235		0.065		0.065

$\boxed{\text{K too large for simplifying assumption}}$

$$0.018 = \frac{x^2}{.3-x}$$

$$.0054 - .018x = x^2$$

$$x^2 + 0.018x - .0054 = 0$$

$$x = \frac{-0.018 \pm \sqrt{(0.018)^2 - 4(-.0054)}}{2}$$

$$= \frac{-.018 \pm \sqrt{0.0216}}{2} = \frac{-.018 \pm .147}{2}$$

$$x = 0.0646$$

Equilibrium: $x = 0.065$

$[A]_{eq} = .3 - .065 = 0.235\ M$

$[B]_{eq} = 0.065\ M$

$[C]_{eq} = 0.065\ M$

5. Find final concentrations given: **A "Square Root" Simplification** $K_c = 0.060$

~~Simplifying Assumption~~

$\boxed{\text{Square Root Simplification}}$

	A	+	B	⇌	C	+	D
Initial	0.30		0.30				
Change	$-x$		$-x$		$+x$		$+x$
Equilibrium	$.3-x$		$.3-x$		x		x

$\boxed{\text{K too large for simplifying assumption}}$

$$K = \frac{[C][D]}{[A][B]} = \frac{x^2}{(.3-x)^2}$$

$$\sqrt{0.060} = \sqrt{\frac{x^2}{(.3-x)^2}} \xrightarrow[\text{root both sides}]{\text{square}} 0.245 = \frac{x}{.3-x}$$

$$.0735 - .245x = x$$

$$0.0735 = 1.245x$$

$$x = 0.059$$

$[A_{eq}] = 0.241$

$[B]_{eq} = 0.241$

$[C]_{eq} = [D]_{eq} = 0.059$

6. Find final concentrations given: Solution with and Without Simplifying Assumption

$A \rightleftharpoons 2B + C$ $K_c = 2.0 \times 10^{-8} = \frac{[B]^2[C]}{[A]}$

⇓ small, so simplifying ok

	A	2B	C
Initial	0.20	0	0
Change	$-x$	$+2x$	$+x$
Equilibrium	$.2-x$	$2x$	x
Equilibrium with Simplifying Assumption	$.2$	$2x$	x

With Simplifying Assumption

$$2\times10^{-8} = \frac{(2x)^2x}{.2} = \frac{4x^3}{.2}$$

$$4.0\times10^{-9} = 4x^3$$

$$1\times10^{-9} = x^3$$

$$x = (1\times10^{-9})^{1/3}$$

$$x = 1.0\times10^{-3}$$

$$\boxed{\begin{aligned}[A] &= 0.2\\ [B] &= 2.0\times10^{-3}\\ [C] &= 1.0\times10^{-3}\end{aligned}}$$

Without Simplifying Assumption

$$2\times10^{-8} = \frac{(2x)^2x}{.2-x}$$

$$4\times10^{-9} - (2\times10^{-8})x = 4x^3$$

Solution With and Without Simplifying Assumption: $A \rightleftharpoons 2B + C$ $K_c = 2.0 \times 10^{-8}$

$A \rightleftharpoons 2B + C$

With

	A	2B	C
I	0.20	0	0
C	-x	2x	x
E	.20-x	2x	x
E^*	0.20	x	x

So $K = 2.0 \times 10^{-8} = \frac{(2x)^2x}{0.20} = \frac{4x^3}{.20}$

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

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

Easy

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

Without (using .20 – x for [A] at eq)

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

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

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

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

Not Easy!!!

14.6 How Systems Respond When an Equilibrium is Disturbed. LeChatelier's Principle.

1. At Equilibrium, there is a steady state of concentrations.
2. How does a system respond when an equilibrium is disturbed?

Le Chatelier's Principle: when a system is disturbed from equilibrium, it responds so as to reduce or counteract the effect of the change.

1. A revised equilibrium gets reestablished
    a. Usually the same K value must still apply
        - unless the temperature is changed
    b. But different actual concentrations result
        - whether you added or subtracted a reactant, a product, some solvent, or the volume
2. The reaction can move in the forward direction (more reactants go to product side) or the reverse direction (more products go back to starting materials) as needed to offset a change

Qual: If something extra is added, react from that side toward the other to remove some of it
If something is removed, react from the other side to replace it

LeChateliers's Principle: Summary

A change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner as to reduce or counteract the effect of the change.

Factor that Changes	Direction of the Change	Direction to Restore Equilibrium
1. Concentration	↑ Reactant	Forward
	↑ Product	Reverse
2. Temperature	↑ T, when $\Delta H > 0$	Forward – K increases
	↑ T, when $\Delta H < 0$	Reverse – K decreases
3. Volume	↑ V, when $\Delta n_{gas} > 0$	Forward
	↑ V, when $\Delta n_{gas} = 0$	No effect
A change in volume impacts gas pressure. An increase in volume reduces pressure.	↑ V, when $\Delta n_{gas} < 0$	Reverse

If you reverse any of the Changes above, the **Direction to reach Equilibrium** reverses

3 Factors That can Be Changed	Goals
1) Concentrations 2) Temperature 3) Volume (which impacts gas pressure)	1) restore Q = K 2) offset change

↳ when gases are involved

A. Concentration Change: Addition or Removal of Either a Reactant or a Product

1. If you add (or remove) a chem, at that moment $Q \neq K$
2. The system (and concentrations) will shift forward or backward to adjust Q so $Q = K$
   - **NOTE: K value does not change**
   - many chemical ways to remove a chem (precipitations, acid-base, etc.)

Example

$$A + B \rightleftharpoons C + D$$

following the original disruption

Disruption	Immediate Impact on Q	Direction to Restore Eq	Response of: [A]	[B]	[C]	[D]
Add A	$Q < K$	Forward →	↓	↓	↑	↑
Add B	$Q < K$	→	↓	↓	↑	↑
Add C	$Q > K$	←	↑	↑	↓	↓
Add D	$Q > K$	←	↑	↑	↓	↓
Remove A	$Q > K$	←	↑	↑	↓	↓
Remove B	$Q > K$	←	↑	↑	↓	↓
Remove C	$Q < K$	→	↓	↓	↑	↑
Remove D	$Q < K$	→	↓	↓	↑	↑

B. Volume Change: Only Relevant When Gases are Involved

1. When the volume changes, it causes a change in concentrations
   - at the instant of change $Q \neq K$
   - note: the actual K value is unchanged
2. Qualitative sense:
   a. **When the volume expands, you want to generate more gas molecules to fill it**
   b. **When the volume shrinks, you want to get rid of gas molecules so it isn't too full**
3. Volume changes will only matter if one side of the equation has more gas on it than the other
   - if moles of gas are equal on both sides, volume changes have no impact

Disruption	**Response**
Volume Increase	**Shift toward side with more gas**
Volume Decrease	**Shift toward side with less gas**

4. Volume and Pressure: A different qualitative way to understand why a system will respond
   - When the volume expands, pressure ~~increases~~ decreases
   a. When the volume expands and the pressure drops, you want to generate more gas molecules to fill the container and restore pressure
   b. When the volume shrinks, you want to get rid of gas molecules to unclutter the container and to restore the original pressure

Volume Example $\overset{\text{3 gases}}{2H_2(g) + O_2(g)} \rightleftharpoons \overset{\text{2 gases}}{2H_2O(g)}$

Volume Change	Direction to Restore Eq	Response of moles of: $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O$
Increase fill it up	←	↑ ↑ ↓
Decrease	→	↓ ↓ ↑

volume is only a factor with gases, and when one side has more gas than other

C. Temperature Change

1. View heat as either a reactant or a product
   - $\Delta H > 0$ Endothermic Heat is required, on Reactant Side
   - $\Delta H < 0$ Exothermic Heat is produced, on Product Side
2. When the temperature rises, the system responds so as to remove extra heat
3. When the temperature drops, the system responds so as to replace missing heat
4. When the system shifts to the right or to the left in response to a temperature change, this means that chemical concentrations change, too
5. A Temperature Changes Causes a Changes in the K Value
   - Because the Product/Reactant Ratio Changes
     - $\Delta H > 0$ Rise in temp → shift to right → K rises
     - $\Delta H > 0$ Drop in temp → shift to left → K drops
     - $\Delta H < 0$ Rise in temp → shift to left → K drops
     - $\Delta H < 0$ Drop in temp → shift to right → K rises

1. Write in "heat" as reactant or product, and predict the responses when temperature changes:

$A \rightleftharpoons B + \text{heat}$ $\Delta H < 0$ $\boxed{\text{exo}}$

Temperature Change	Direction to Restore Eq	Response of moles of: $A \rightleftharpoons B$	Response of K Value
Increase	←	↑ ↓	↓
Decrease	→	↓ ↑	↑

2. Write in "heat" as reactant or product, and predict the responses when temperature changes:

$\text{heat} \; A \rightleftharpoons B$ $\Delta H > 0$ $\boxed{\text{endo}}$

Temperature Change	Direction to Restore Eq	Response of moles of: $A \rightleftharpoons B$	Response of K Value
Increase	→	↓ ↑	↑
Decrease	←	↑ ↓	↓

3. Write in "heat" as reactant or product, and predict the responses to the changes:

$$\text{heat} + \overset{4\ \text{gas}}{N_2(g) + 3H_2(g)} \rightleftharpoons \overset{2\ \text{gas}}{2NH_3(g)} \qquad \Delta H > O \qquad K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Disruption	Direction to Restore Eq	Response of moles of:			Response of K Value
		$N_2(g)$ +	$3H_2(g)$	$\rightleftharpoons 2NH_3(g)$	
1. Temperature Increase	→	↓	↓	↑	↑
2. Volume Increase	←	↑	↑	↓	no change
3. Added N_2	→	↓	↓	↑	—
4. Removal of NH_3	→	↓	↓	↑	—
5. Reduced temperature	←	↑	↑	↓	↓
6. Added NH_3	←	↑	↑	↓	—
7. Removal of N_2	←	↑	↑	↓	—
8. Volume reduction	→	↓	↓	↑	—

D. Addition Catalyst: Equilibrium is reached faster, but the actual K value or equilibrium product/reactant ratios are unchanged.

14.7 LeChatelier's Principle on the Nanoscale. Skim. Equilibria favor more stable chemicals