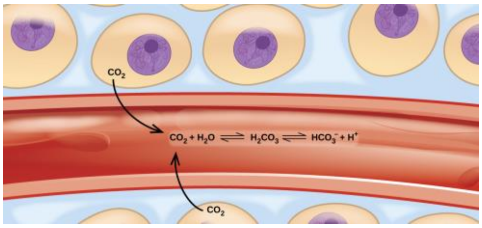
Ch. 13: Fundamental Equilibrium Concepts



Movement of carbon dioxide through tissues and blood cells involves several equilibrium reactions.

OpenStax: Chemistry

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The Equilibrium State

- **Not all chemical reactions go to completion — there are many that are reversible and they attain a state of equilibrium in which a mixture of reactants and products is present.**
- **Equilibrium defined**:
  - **Rate of the forward reaction equals the rate of the reverse reaction.**
  - **Reactant and product concentrations remain constant and no longer change.**
  - **It DOES NOT mean reactant and product concentrations are equal!**

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$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

- Note: a double arrow is used for an equilibrium reaction to show it is a reversible reaction.
- In the forward reaction each molecule of N_2O_4 breaks down to form two molecules of NO_2.
- In the reverse reaction two molecules of NO_2 combine to form N_2O_4.
- Equilibrium occurs when the rate at which an N_2O_4 molecule breaks apart in the forward reaction is equal to the rate at which it is formed by the reverse reaction.

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Equilibrium is Dynamic!

The conversions of reactants to products and products to reactants are still going on, although there is no net change in the number of reactant and product molecules.

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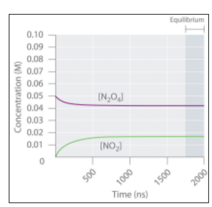
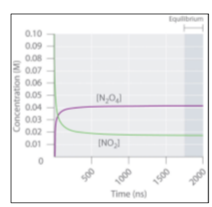
Chemical Equilibrium

$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

$\text{rate}_f = k_f[N_2O_4]$ and $\text{rate}_r = k_r[NO_2]^2$



Starting with N_2O_4



Starting with NO_2

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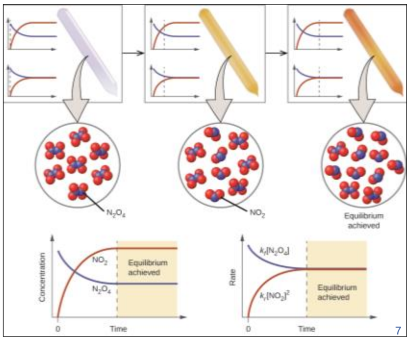
Concentration and rate vs. time

Figure 13.2

$N_2O_4 \rightleftharpoons 2NO_2$

N_2O_4 = colorless

NO_2 = orange



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Relationship Between Rate Constants and Equilibrium Constants

$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

At equilibrium: rate forward = rate reverse

$k_f[N_2O_4] = k_r[NO_2]^2$

equilibrium expression

$$\frac{k_f}{k_r} = K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

equilibrium constant

⇒K_c is the equilibrium constant, a numerical value.

⇒The ratio is the equilibrium constant expression.

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The Equilibrium Constant

For a reaction: **aA + bB ⇌ cC + dD**

Equilibrium Constant: $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ ← products / ← reactants

K_c is the ratio of the equilibrium concentrations of products over the equilibrium concentrations of reactants each raised to the power of their stoichiometric coefficients.

K_c is a constant at a given temperature for a reaction at equilibrium (law of mass action).

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The Equilibrium Constant, K_c

Write the equilibrium constant expressions (K_c) for the following equations.

a) $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

b) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

a) b)

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Equilibrium Constant

The equilibrium concentrations of reactants and products may be different, but the value for K_c remains the same.

Trial	$[N_2O_4]_i$, M	$[NO_2]_i$, M	$[N_2O_4]_{eq}$, M	$[NO_2]_{eq}$, M	K_c
1	0.0400	0.0000	0.0337	0.0125	4.64×10^{-3}
2	0.0000	0.0800	0.0337	0.0125	4.64×10^{-3}
3	0.0600	0.0000	0.0522	0.0156	4.66×10^{-3}
4	0.0000	0.0600	0.0246	0.0107	4.65×10^{-3}
5	0.0200	0.0600	0.0429	0.0141	4.63×10^{-3}

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

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

For Trial 1

K_c =

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K_c Characteristics:

1) **Equilibrium can be attained starting with only reactants or products (or can start with a mixture of reactants and products).**
2) **K_c does not depend on the initial concentrations of reactants and products.**
3) **K_c does depend on temperature.**
4) **K_c values are listed without units.**

⇒ **don't include units when calculating K_c.**

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Calculating K_c

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

At 500 K, the following concentrations were measured: $[N_2] = 3.0 \times 10^{-2}$ M, $[H_2] = 3.7 \times 10^{-2}$ M, $[NH_3] = 1.6 \times 10^{-2}$ M. What is K_c?

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K_c tells us extent of reaction

- **Large K_c: If $K_c > 10^2$, the reaction is nearly complete; products are favored.**
  Eq lies to right (more products)
- **Small K_c: If $K_c < 10^{-2}$, the reaction hardly proceeds at all; reactants are favored.**
  Eq lies to left (more reactants)
- **If K_c is in the range 10^{-2} - 10^2, appreciable amounts of reactants and products are present.**
  Eq lies close to middle

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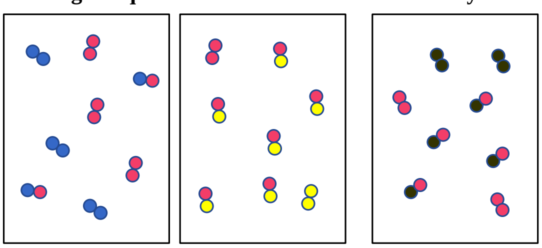
Interpreting Equilibrium Constants

- **Which system below (all at equilibrium) has the largest equilibrium constant? Smallest? Why?**



$A_2 + B_2 \rightleftharpoons 2\,AB$ $A_2 + C_2 \rightleftharpoons 2\,AC$ $A_2 + D_2 \rightleftharpoons 2\,AD$

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Heterogenous Equilibria

Homogeneous equilibria: all substances are in one phase (all gas, all solid, etc.)

Heterogeneous equilibria: substances in 2 or more different phases.

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

- Pure solids and liquids have constant concentrations so they are not included in the K expressions.
- **Omit solids and liquids from K expressions**
  --only include gases and aqueous substances which have variable concentrations!

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Heterogeneous Equilibria

K_c – use [ ] terms to represent concentrations of (aq) and (g) substances.

K_p – use P terms to represent the partial pressure of (g) substances.

Write K_c **and** K_p expressions for the following equations :

a) $2Cu_2S(s) + 3O_2(g) \rightleftharpoons 2Cu_2O(s) + 2SO_2(g)$

b) $Hg(l) + Hg^{2+}(aq) \rightleftharpoons Hg_2^{2+}(aq)$

DON'T include solids and liquids in K expressions!

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Answers K_c & K_p Expressions

a) $2Cu_2S(s) + 3O_2(g) \rightleftharpoons 2Cu_2O(s) + 2SO_2(g)$

b) $Hg(l) + Hg^{2+}(aq) \rightleftharpoons Hg_2^{2+}(aq)$

Always include charges for ions!

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Example K_p

$CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)}$

- At 1000 K, the equilibrium pressure are: CH_4 = 0.20 atm, H_2S = 0.25 atm, CS_2 = 0.52 atm, and H_2 = 0.10 atm.
- What is K_p?

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Relationship between K_c and K_p

Pressure is directly proportional to concentration.

- PV = nRT → P = (n/V) RT → P = MRT where n/V = M

$$K_p = K_c(RT)^{\Delta n}$$

Δn = # product gas molecules - # reactant gas molecules

R = 0.08206 L·atm / mol·K

T = temperature in Kelvin

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When does $K_c = K_p$?

They are equal when there are the same # of gas molecules on both sides of equation.

Example. Does $K_c = K_p$?

a) $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$

b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

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Example: Converting from K_c to K_p

$N_2(g) + 3H_2(g) \rightleftharpoons 2\ NH_3(g)$ At 375 °C, $K_c = 2.79\text{x}10^{-5}$

What is K_p?

$$\boxed{K_p = K_c(RT)^{\Delta n}}$$

Note: while K_c and K_p don't have units we must plug in values that have correct units or K values wouldn't be a constant!

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Manipulating Reactions & K values

A. Reversing a Reaction

1) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ $\quad \mathbf{K_1} = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$

2) $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ $\quad \mathbf{K_2} = \dfrac{[NO]^2[O_2]}{[NO_2]^2}$

K_2 is reciprocal of K_1:

If $K_1 = 6.8\text{x}10^5$, then K_2 =

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B. Adding Reactions:

1. $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ $\quad K_1 = \dfrac{[NO]^2[O_2]}{[NO_2]^2}$

2. $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$ $\quad K_2 = \dfrac{[H_2O]^2}{[H_2]^2[O_2]}$

3. $2NO_2 + 2H_2 \rightleftharpoons 2NO + 2H_2O$ $\quad K_3 = \dfrac{[NO]^2[H_2O]^2}{[NO_2]^2[H_2]^2}$

Thus $K_3 = K_1 * K_2$

If $K_1 = 1.5\text{x}10^{-6}$ and $K_2 = 2.4\text{x}10^{47}$

Then K_3 =

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Reaction Quotient, Q

Q is set up like K, but we plug in initial concentrations and compare Q to K to tell which direction (if any) a reaction must go to reach equilibrium.

- If $Q_c < K_c$, reaction shifts right (small Q means not enough products so shifts right to make more products).
- If $Q_c > K_c$, reaction shifts left (big Q means too many products so shifts left to convert products into reactants).
- If $Q_c = K_c$, reaction is at equilibrium (no shift).

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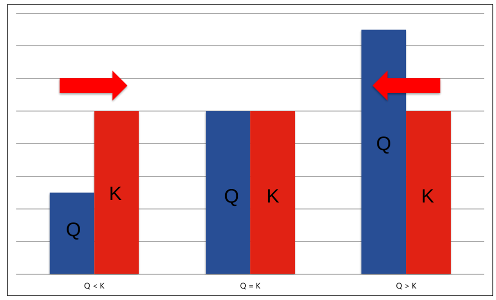
Q (blue) versus K (red)



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Finding Q & Direction of Shift

Example. For the reaction, B ⇌ 2A, K_c = 3. Suppose 3.0 moles of A and 3.0 moles of B are introduced into a 2.00 L flask.

a) **Is this system at equilibrium?**
b) **In which direction will the reaction proceed to reach equilibrium?**
c) **Does the concentration of B increase, decrease or remain the same as the system moves towards equilibrium?**

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Calculating Q for B ⇌ 2A

[A] =

[B] =

- Q =

- Compare Q to K_c =3
- What direction does equilibria shift?
- Does [B] increase or decrease?

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Le Chatelier's Principle

Le Châtelier's principle: **When a *stress* is applied to a system at equilibrium, it will respond by *shifting* in the direction that counteracts the effect of the stress.**

Types of Stresses

- **A change in concentration (addition or removal of a reactant or product).**
- **A change in pressure or volume (only important for gas phase reactions).**
- **A change in temperature.**

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Concentration Changes

- Adding a reactant or product, the equilibria shifts away from the increase in order to consume part of the added substance.
- Removing a reactant or product, the equilibria shifts toward the decrease to replace part of the removed species.

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Effect of Concentration Changes

Addition of a reactant or removal of a product will cause equilibrium to shift to the right.

Removal of a reactant or addition of a product or will cause equilibrium to shift to the left.

Increase Increase Decrease

$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$

Decrease Decrease Increase

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Changes in P and V

- **Increase in volume: more space = more gases allowed. Shift to side with more moles of gas.**
- **Increase in pressure (same as decrease in volume): less volume = less gas allowed. Shift to side with fewer moles of gas.**
- **If same number of moles on both sides, P and V don't affect equilibrium.**
- **Adding an inert gas (e.g. a noble gas) also doesn't cause an equilibrium shift or affect K_c.**

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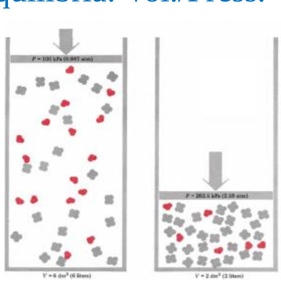
Shifting Equilibria: Vol./Press.

When volume is **decreased**, pressure is increased. Equilibrium is driven toward the side with fewer **moles of gas**. What happens when volume is increased?



$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$
gray red

Image from UC Davis: http://chemwiki.ucdavis.edu/Textbook_Maps/General_Chemistry_Textbook_Maps/Map%3A_Chem PRIME_(Moore_et_al.)/13Chemical_Equilibrium/13.09%3A_The_Effect_of_a_Change_in_Pressure, 33

Changes in P and V

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

1 + 3 = 4 moles (left) **2 moles (right)**

What will happen if we increase pressure?

What will happen if we increase volume?

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Changes in Temperature

$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$ $\Delta H^o = +57.2$ kJ

Endothermic, heat is a reactant, so adding heat helps the reaction proceed forward.

Heat + reactants $\rightleftharpoons$ products

$\uparrow$heat, eq shifts $\rightarrow$

$\downarrow$heat, eq shifts $\leftarrow$

Endo likes it hot!

Low T High T

https://en.wikipedia.org/wiki/Le_Chatelier%27s_principle 35

How T alters K_c

Changes in Conc., P, and V just shift equilibrium position to maintain a constant K.
Both the equilibrium position and K_c will vary with temperature:
$\Rightarrow$ K_c is larger when the reaction shifts right (more products).
$\Rightarrow$ K_c is smaller when the reaction shifts left (more reactants).

Example. The temperature is decreased for the reaction: $2CO_2 \rightleftharpoons 2CO + O_2$, $\Delta H = 566$ kJ.
a) Will the equilibrium shift left or right? b) Does K_c become larger or smaller?

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Effect of Temperature Changes

For an endothermic reaction, heat is a reactant:

heat + reactants ⇌ products $\Delta H^\circ > 0$ kJ/mol

- **Adding heat shifts the reaction →, K_c ↑**
- **Removing heat shifts the reaction ←, K_c ↓**

Endo likes it hot!

For an exothermic reaction, heat is a product:

reactants ⇌ products + heat $\Delta H^\circ < 0$ kJ/mol

- **Adding heat shifts the reaction ←, K_c ↓**
- **Removing heat shifts the reaction →, K_c ↑**

Opposite of endo!

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Endotheric or Exothermic Reaction?

$CoCl_4^{2-} + 6H_2O \rightleftharpoons Co(H_2O)_6^{2+} + 4Cl^-$

blue **pink**

Room Temperature | Bunsen burner | Ice water bath

http://www.rsc.org/learn-chemistry/resource/res00000001/the-equilibrium-between-two-coloured-cobalt-species?cmpid=CMP00005957

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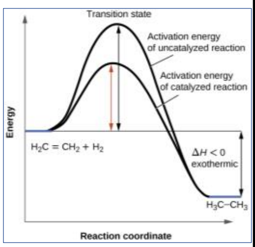
Effect of Catalysts & Inert Gases

Catalysts – adding a catalyst reduces E_a which occurs to the same extent for both the forward and reverse reactions.

- It reduces the time required to reach equilibrium but has **no effect** on K_c or the position of equilibrium.
- Adding an **inert gas** also has no effect on position of Equilibrium.



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Applying Le Chatelier's Principle

- Determine how the equilibrium will shift if the following changes are made:
- $2Cl_{2(g)} + 2H_2O_{(g)} \rightleftharpoons 4HCl_{(g)} + O_{2(g)}$ $\Delta H^o = +113$ kJ
  - a) Temperature is increased
  - b) Volume is increased
  - c) Pressure is decreased
  - d) HCl is added
  - e) Ne (g) is added
  - f) Cl_2 is added
  - g) H_2O is removed

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ICE method – use to find eq [ ]'s, given K_c and initial [ ] 's

1. **I = initial concentration**: Initial concentration of reactants are usually given; initial [Product]'s are assumed to be 0 unless otherwise specified.
2. **C = change in concentration**: Assign change as the variable x; use the stoichiometry of the reaction to assign changes for all species.
3. **E = equilibrium concentration:** E = I + C

Note, values in ICE tables can be in terms of moles or Molarity (or atm for K_p), but values used in the K_c expression must be in terms of Molarity (or atm for K_p).

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Solving for Equil. Conc.

- 3 methods for finding equilibrium concentrations:
  - Use perfect squares (e.g. $H_2 + I_2 \rightleftharpoons 2HI$)
    - $50.5 = \frac{(2x)^2}{(1.00-x)^2}$
  - Assume x is much smaller than initial concentration; **General** rule: if K < 10^{-3}, assume x is small
    - Omit –x terms
  - Use quadratic if K_c is too big to make assumption.
    - get two values of x; one will give negative eq concentration(s)

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

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Equil. Conc. - Perfect Squares

Calculate the equilibrium concentrations of all species.

H_2 (g) + I_2 (g) ⇌ 2HI (g) K_c = 50.5

Given the initial concentrations of H_2 and I_2 are both 1.00 M.

Set up ICE

	H_2 (g) +	I_2 (g) ⇌	2HI (g)
I	1.00	1.00	0
C	-x	-x	+2x
E	1.00 - x	1.00 - x	+2x

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

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Perfect Square Cont

$K_c = \frac{[HI]^2}{[H_2][I_2]}$ Plug in eq terms from ICE:

Solve for x:

Plug x into eq [ ]'s:

•plug eq concs. back into K_c to doublecheck!

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Using Q to find Eq Concentrations

A 5.00 L reaction vessel is filled with 2.50 moles of H_2, 2.50 moles of I_2, and 25.0 moles of HI. K_c = 81.0 at 670 K.

H_2(g) + I_2(g) ⇌ 2HI (g),

I (M)

Is it at equilibrium? Use Q to tell direction it proceeds!

Q =

compare Q to K

What are the equilibrium concentrations?

	H_2 (g) +	I_2 (g) ⇌	2HI (g)
I			
C			
E			

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Approximation Method- Assume small x

Calculate the equilibrium concentrations for

N_2(g) + O_2(g) ⇌ 2 NO(g) K_c = 1.0 x 10^{-5}

Initial: 0.80 M   0.20 M

- Set up K_c:
- Set up ICE and plug eq concs into K_c:
- Assume x is small (its much smaller than 0.80 or 0.20) because K_c is small (less than 10^{-3})

x =

[N_2] = , [O_2] = , [NO] =

- Check assumption: (x /initial concentration) * 100% < 5%

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Quadratic Method

Assumption that x is small isn't always valid!

What to do?

Quadratic formula!!!

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

•**Gives two values of x:**
- **If obtain +x and –x, pick +x!**
- **If both x's are +, pick smaller x!**

Can eq concentrations (M) be – values?

Note: only one x should give you all + eq concs!

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Quadratic Example

H_2*(g)* + F_2*(g)* ⇌ 2HF*(g)*, K_c = 1.15x10^2

3.000 moles of H_2 and 6.000 moles of F_2 are placed in a 3.000 L container

Calculate the equilibrium concentrations of all species.

x =

[H_2] =

[F_2] =

[HF] =

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Solving for x and K_c

In an experiment, 3.00 moles of CO and 5.00 moles of H_2O were placed in a 2.00 L flask at 350 K.

$CO (g) + H_2O (g) \rightleftharpoons CO_2 (g) + H_2 (g)$

At equilibrium, there were 2.00 mol of CO remaining. What is the value of the equilibrium constant for this reaction?

	CO (g) +	H_2O (g) $\rightleftharpoons$	CO_2 (g) +	H_2 (g)
Initial	1.50 M	2.50 M	0	0
Change	- x	- x	+ x	+ x
Equilibrium	1.00 M	2.00 M	0.500 M	0.500 M

x = K =

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