

EQUILIBRIUM CONSTANT EXPRESSIONS AND CALCULATIONS

Special K traits:

1. K is a unitless constant
2. K is generated from equilibrium concentrations in MOLARITY units.
If other units are used, a special subscript is applied to K to note that change.
eg. if kPa units are used, the value would be K_p
3. K is a fixed constant for a given equilibrium system at a FIXED TEMP.

Only a change in temperature can change K.

Recall that entropy is favoured at high temp and enthalpy is favoured at low temp.

Changes in Conc, Pressure, Volume, etc. may alter the concentration of each individual species, **but this will not change K.**

$K_{RTP} \neq K_{STP}$ (not equal!)

4. Species in the solid or liquid states are included in K expressions only if the equilibrium system is HOMOGENEOUS.

In heterogeneous systems, they are excluded because their concentrations are invariable at a fixed temperature.

(i.e. density is constant at a fixed temperature)

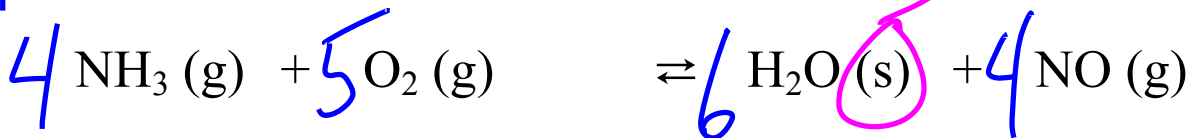
SEE GIVEN EXAMPLES.

#4. examples

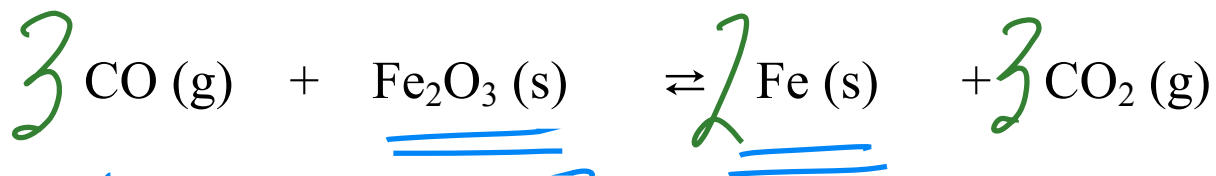
“Keq” expressions

Write the K expressions for the following.

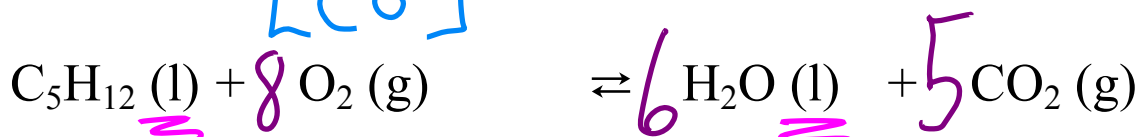
* BE SURE TO CHECK if the reaction is BALANCED, everytime!



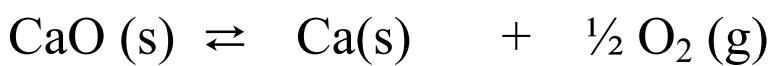
$$K_{eq} = \frac{[\text{NO}]^4}{[\text{NH}_3]^4 [\text{O}_2]^5}$$



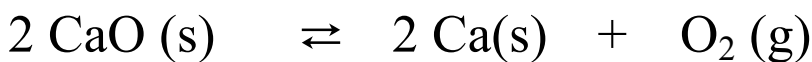
$$K_{eq} = \frac{[\text{CO}_2]^3}{[\text{CO}]^3}$$



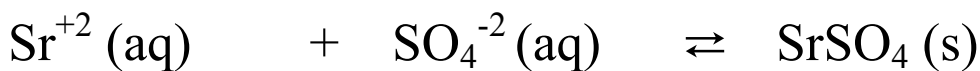
$$K_{eq} = \frac{[\text{CO}_2]^5}{[\text{O}_2]^8}$$



$$K_{eq} = [\text{O}_2]^{1/2}$$



$$K_{eq} = [\text{O}_2]$$



$$K_{eq} = \frac{1}{[\text{Sr}^{+2}][\text{SO}_4^{-2}]}$$

5. K values indicate whether REACTANTS OR PRODUCTS are favoured at a particular temperature.

Products are *favoured* when $K \gg 1$ and reactants are *favoured* when $K \ll 1$

more accurately $0 < K < 1$
i.e. decimal numbers
BUT NOT negative numbers!

6. K is independent of reaction mechanism, so catalysis does not change K. (Catalysts only alter how fast we arrive at equilibrium, or the pathway taken to "complete" the reaction).

Catalysts do not always speed up a reaction; often they just make the reaction

7. K assumes **IDEAL behaviour**.

- perfect elastic spheres (no energy loss)
- perfect spherical particles
- no intermolecular attraction
- particles occupy zero volume

POSSIBLE
(or easier)

K is a good approximation of the real behaviour in an equilibrium system.

HOW TO WRITE EQUILIBRIUM CONSTANT
EXPRESSIONS
AND
SOLVE FOR THE EQUILIBRIUM CONSTANT,
and/or solve for equilibrium molar concentrations

1. BALANCE THE EQUATION for the CHEMICAL REACTION.

2. DETERMINE:

- *The initial concentrations of each species,*
- *The concentration (moles per litre) of each species **that reacted***
 - **ACCORDING TO THE MOLAR RATIO**
- *The equilibrium concentration of each species.*

(you will not necessarily be able to determine these values in this particular order).

3. Write the **equilibrium constant expression** **EVERYTIME.**

THEN...show the numbers (and/or variables) that you are substituting into the K expression.

4. Solve for K and/or the variables in your K expression.

Use: (i) GRAPHICAL means

(ii) GUESSING - ***Trial and error***

- MOST USEFUL!

Will need to do (and show) "K trials"

(iii) QUADRATIC FORMULA

- if necessary / applicable

Quadratic Formula

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

Example Equation

$$\begin{array}{ccccccc} x^2 + 2x + 1 = 0 \\ \uparrow \quad \uparrow \quad \uparrow \\ a \quad b \quad c \end{array}$$

(iv) FACTORING

- a little cumbersome and sometimes not even achievable,
for our Chem 12 questions.



Be sure to **ALWAYS ESTABLISH AND STATE** your **LIMITS**



"Keq" calculations – Unit 2 Quiz Practice

1. Determine Keq at RTP for:

	C ₃ H ₈ (g)	+	5 O ₂ (g)	⇌	3 CO ₂ (g)	+	4 H ₂ O (l)
I	4.0 M		3.0 M		-----		-----
R	-0.50		-2.5		+1.5		
E	3.5		0.5		1.5 M		

2 SF
across
"R" line
1 dec
place
across
"E" line

pure liquid
so you can
NOT write
molarities
here!

$$\begin{aligned}K_{eq} &= \frac{[\text{CO}_2]^3}{[\text{C}_3\text{H}_8][\text{O}_2]^5} \\&= \frac{(1.5)^3}{(3.5)(0.5)^2} \\&= 30.8571\dots \\&= 3 \times 10^1 \text{ (1 SIG FIG)} \\&\text{OR } 30\end{aligned}$$

This reaction initially proceeds in the forward direction as products are being formed
At equilibrium the reaction favours products
(forward direction since $K > 1$)

2a. Determine K_{eq} at 300°C for.

	4 NH ₃ (g)	+	5 O ₂ (g)	\rightleftharpoons	6 H ₂ O (g)	+	4 NO (g)
I	6.00 M		8.00 M		-----		-----
R	-1.60		-2.00 $\times \frac{5}{4}$		+2.40 $\times \frac{6}{4}$		+1.60
E	4.40		6.00		2.40		1.60 M

$$K_{eq} = \frac{[\text{H}_2\text{O}]^6 [\text{NO}]^4}{[\text{NH}_3]^4 [\text{O}_2]^5} = \frac{(2.40)^6 (1.60)^4}{(4.40)^4 (6.00)^5} = 4.30 \times 10^{-4}$$

Since $K < 1$ this reaction favours reactants (reverse direction) at equilibrium

2b. Find $[\text{NH}_3]_{eq}$ at 300°C if $[\text{O}_2]_{eq} = 2.00 \text{ M}$ and $[\text{H}_2\text{O}]_{eq} = 1.00 \text{ M} = [\text{NO}]_{eq}$

	4 NH ₃ (g)	+	5 O ₂ (g)	\rightleftharpoons	6 H ₂ O (g)	+	4 NO (g)
E			2.00 M		1.00 M		1.00 M

$$K_{eq} = \frac{[\text{H}_2\text{O}]^6 [\text{NO}]^4}{[\text{NH}_3]^4 [\text{O}_2]^5}$$

$$4.30 \times 10^{-4} = \frac{(1)^6 (1)^4}{[\text{NH}_3]^4 (2)^5}$$

$$[\text{NH}_3] = 2.92 \text{ M}$$

same temp means same K value as 2a.

In #3 the reaction initially proceeds to the right to make products, however at equilibrium the reaction favours the reverse direction (at this temperature), since $K < 1$

3. Determine K_{eq} at 150 K for:

	$2 \text{NH}_3 (\text{g})$	\rightleftharpoons	$3 \text{H}_2 (\text{g})$	+	$\text{N}_2 (\text{g})$
I	0.200 M		-----		0.080 M
R	-0.044	$\times \frac{3}{2}$	+0.066	$\div 3$	+0.022
E	0.156 M		.066		0.080 TYP0 .102

3 dec. places \rightarrow

2 SIG FIGS

$$K_{eq} = \frac{[\text{H}_2]^3 [\text{N}_2]}{[\text{NH}_3]^2} = \frac{(0.066)^3 (0.102)}{(0.156)^2} = 1.2 \times 10^{-3}$$

4a.

	$\text{H}_2 (\text{g})$	+	$\text{I}_2 (\text{g})$	\rightleftharpoons	$2\text{HI} (\text{g})$
I	2.00 M		2.00 M		-----
R	-x		-x		+2x
E	2.00-x		2.00-x		2x

$K_{eq} = 5.00 \times 10^1$ at 110°C . How much of the hydrogen gas reacted?

$$K_{eq} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$50 = \frac{(2x)^2}{(2.00-x)^2}$$

LIMITS! $0 < x < 2.0$

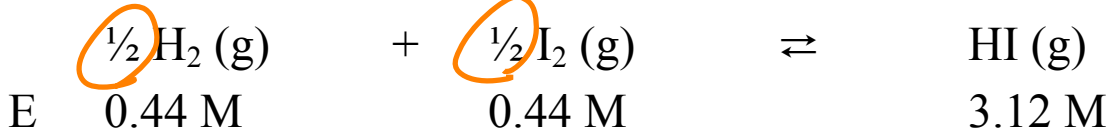
$$x = 1.56 \text{ OR } 2.79$$

4b. Calculate the equilibrium concentrations of all reactants and products.

$$[\text{H}_2] = [\text{I}_2] = 2.00 - 1.56 = 0.44 \text{ M (2 dec pl)}$$

$$[\text{HI}] = 2(1.56) = 3.12 \text{ M (3 SF)}$$

4c. Consider:



balanced with $\frac{1}{2}$
 $\therefore \sqrt{K}!$

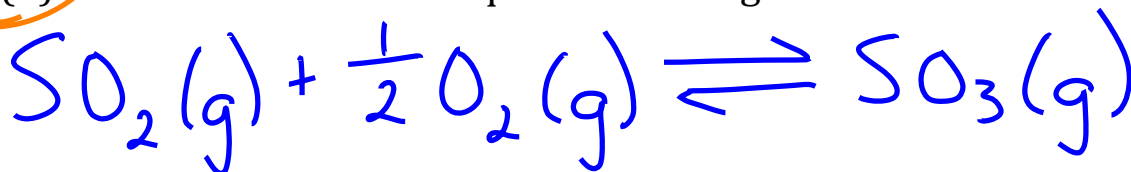
Find the relationship between this K_{eq} and your answer from 4a.

$$K_{eq} = \frac{[\text{HI}]}{[\text{H}_2]^{1/2} [\text{I}_2]^{1/2}} = \frac{3.12}{(.44)^{1/2} (.44)^{1/2}} = 7.09$$

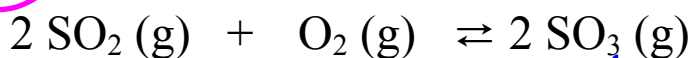
$\sqrt{50} = 7.1!$

4d. Given $K_{eq} = 6.6 = \frac{[\text{SO}_3]}{[\text{SO}_2] [\text{O}_2]^{1/2}}$

(1) write a balanced equation for all gases involved



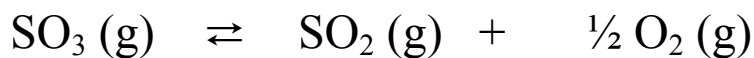
(2) what is the numerical value of K_{eq} for:



$$K_2 = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = (K_1)^2 = 6.6^2 = 44$$

balanced "x2"
so K^2

(3) what is the numerical value of K_{eq} for:



The reverse of reaction (1)

$$K_{eq} = \frac{[\text{SO}_2] [\text{O}_2]^{1/2}}{[\text{SO}_3]} = \frac{1}{6.6} = 0.15$$

so K is the RECIPROCAL!

5.

	H ₂ (g)	+	I ₂ (g)	⇌	2HI (g)
I	4.00 M		2.00 M		-----
R	-x		-x		+2x
E	4-x		2-x		2x

If $K_{eq} = 5.00 \times 10^1$ at 110°C , find equilibrium concentrations of hydrogen and iodine gas.

$$K = 50 = \frac{(2x)^2}{(4-x)(2-x)}$$

LIMITS: $0 < x < 2$

$$x = 1.869$$

$$[H_2]_E = 2.13 \text{ M}$$

$$[I_2]_E = .13 \text{ M}$$

6. At a certain temperature, 0.040 M of phosphorus pentachloride was placed in a flask and allowed to come to equilibrium in a closed system. The concentration of each of the products at equilibrium was 0.025 M. Calculate K_{eq} .

	PCl ₅ (g)	⇌	PCl ₃ (g)	+	Cl ₂ (g)
I	0.040 M		-----		-----
R	-.025		+.025		+.025
E	.015		0.025 M		0.025 M

$$K_{eq} = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.025)^2}{0.015}$$

$$= 4.2 \times 10^{-2}$$

same K value

7. The same reaction was carried out at the same temperature (as in question # 6), but a different starting concentration of reactants was used. Calculate $[PCl_5]_I$ and $[PCl_5]_{eq}$.

	$PCl_5(g)$	\rightleftharpoons	$PCl_3(g)$	+	$Cl_2(g)$
I	x		-----		-----
R	- .10		+ .10		+ .10
E	x - .10		0.10 M		.10

SET LIMITS!

$4.2 \times 10^{-2} = \frac{(.10)^2}{x - .10}$

$x > .10$

$[PCl_5]_I = x$
 $x = .34 M$
 $[PCl_5]_E = .24 M$

8. The reaction: $2XY(g) \rightleftharpoons X_2(g) + Y_2(g)$ has a $K_{eq} = 35$ at $25^\circ C$. If 3.0 moles of XY are injected into a 1.0 L container at $25^\circ C$, find the equilibrium $[X_2]$ and $[Y_2]$.

	$2XY(g)$	\rightleftharpoons	$X_2(g)$	+	$Y_2(g)$
I	3.0 moles L		-----		-----
R	- 2x		+ x		+ x
E	3.0 - 2x		x		x

$K_{eq} = \frac{[X_2][Y_2]}{[XY]^2}$

$35 = \frac{x^2}{(3 - 2x)^2}$

$\sqrt{35} = \frac{x}{(3 - 2x)^2}$

$5.916(3 - 2x) = x$
 $x = 1.383 M$
 $[X_2]_E = [Y_2]_E = 1.4 M$

9. Given the equilibrium equation: $3A(g) + B(g) \rightleftharpoons 2C(g)$
 If 2.50 moles of A and 0.500 moles of B are added to a 2.00 L container, an equilibrium is established in which the [C] is found to be 0.250 M.

a) Find [A] and [B] at equilibrium.

	3A(g)	+	B(g)	\rightleftharpoons	2C(g)
I	$\frac{2.50 \text{ moles}}{2.00 \text{ L}}$ $= 1.25 \text{ M}$		$\frac{0.500 \text{ moles}}{2.00 \text{ L}}$ 0.250 M		-----
R	$- 0.375$		$- 0.125$		$+ 0.250$
E	0.875 0.88		0.125		0.250 M

3 SF

3 SF

$$K_{eq} = \frac{[C]^2}{[A]^3[B]} = \frac{(0.250)^2}{(0.88)^3(0.125)} = 0.73$$

2 dec places 3 dec places

b) Calculate the value of the equilibrium constant K_{eq} .

$K = 0.75$ if you wait until the end to round off to 2 SF (if you use $(0.875)^3$)

$$\frac{1.00 \text{ mol}}{100.0 \text{ L}} = 0.0100 \text{ M}$$

10. At a certain temperature the reaction:



has a $K_{\text{eq}} = 0.400$. Exactly 1.00 mol of each gas was placed in a 100.0 L vessel and the mixture was allowed to react in a closed system.

Find the **equilibrium concentration** of each gas.

	CO(g)	+	H ₂ O(g)	⇌	CO ₂ (g)	+	H ₂ (g)
I	0.0100 M		0.0100 M		0.0100 M		0.0100 M
R	+x		+x		-x		-x
E	.01+x		.01+x		.01-x		.01-x

We know $K = 0.400$
so using "I" data

$$K_{\text{TRIAL}} = \frac{(0.01)^2}{(0.01)^2}$$

see next page

∴ has to go LEFT

SINCE RATIO $\frac{\text{products}}{\text{reactants}}$ too large

11. At 800°C, for the reaction: $\text{CO}_2\text{(g)} + \text{H}_2\text{(g)} \rightleftharpoons \text{CO(g)} + \text{H}_2\text{O(g)}$
the equilibrium constant K_{eq} is 0.279. If 1.50 moles of CO₂ and 1.50 moles of H₂ are added to a 1.00 L container, find the [CO] at equilibrium?

	CO ₂ (g)	+	H ₂ (g)	⇌	CO(g)	+	H ₂ O(g)
I	1.50 M		1.50 M		0		0
R	-x		-x		+x		+x
E	1.50-x		1.50-x		x		x

$$K_{\text{eq}} = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]}$$

$$\sqrt{0.279} = \sqrt{\frac{x^2}{(1.50-x)^2}}$$

$$x = 0.518 \checkmark$$

LIMITS $0 < x < 1.50$

$$[\text{CO}]_E = x = 0.518 \text{ M}$$

3 SF

#10 continued

$$K_{eq} = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

$$.0400 = \frac{(.0100 - x)^2}{(.0100 + x)^2}$$

$$\sqrt{.0400} = \frac{.0100 - x}{.0100 + x}$$

$$x = \underline{.00225145}$$

3 SF

$$[CO]_E = [H_2O]_E = .0100 + x$$
$$= .0123 \text{ M (4 dec places)}$$

$$[CO_2]_E = [H_2]_E = .0100 - x$$
$$= .0077 \text{ M (4 d.p.)}$$

12. Given this equilibrium reaction: $\text{COCl}_2 \rightleftharpoons \text{CO} + \text{Cl}_2$

Calculate all three equilibrium concentrations when $K_{\text{eq}} = 0.680$ with $[\text{CO}]_i = 0.500$ and $[\text{Cl}_2]_i = 1.00$ M.

	COCl_2 (g)	\rightleftharpoons	CO (g)	+	Cl_2 (g)
I	0		0.500 M		1.00 M
R	+x		-x		-x
E	x		0.500 - x		1.00 - x

$$K_{\text{eq}} = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]}$$

$$0.680 = \frac{(0.500 - x)(1.00 - x)}{x}$$

$$0.680x = 0.5 - 1.5x + x^2$$

$$x^2 - 2.18x + 0.500 = 0$$

LIMITS! $0 < x < 0.500$

$$\therefore x = 0.26$$

Both roots yield positive values, so how do we pick the correct one?

The answer lies in the fact that x is not the final answer, whereas $(0.5 - x)$ is.

It is the term $(0.5 - x)$ which must be positive. So the root of 1.92 is rejected in favor of the 0.26 value to achieve a positive value for concentration.

$$[\text{CO}]_E = 0.500 - 0.260 = 0.240 \text{ M (3 SF AND 3 dec pl)}$$

$$[\text{Cl}_2]_E = 1.00 - 0.260 = 0.76 \text{ M (2 dec places)}$$

$$[\text{COCl}_2]_E = x = 0.260 \text{ M (3 SF)}$$

13. The same reaction (as in question # 6) was carried out (at the same temperature) and the following information was noted:

$$K = 4.2 \times 10^{-2}$$



Is this given data at equilibrium?

$$K_{\text{TRIAL}} = \frac{(0.60)(0.60)}{(0.25)} = 1.44$$

How do you know?

NOT at equil because K_{TRIAL} RATIO is too large

If the answer is no:

$$\underline{\text{True } K_{\text{EQ}}} < \underline{K_{\text{TRIAL}}}$$

1) what must happen for this system to reach equilibrium?

The system must proceed to the LEFT to reduce the RATIO and achieve $K = .042$

2) calculate the new equilibrium concentrations and show numerical proof that these concentrations do in fact reflect a system at equilibrium.

$$.042 = \frac{(0.60 - x)^2}{(0.25 + x)}$$

LIMITS $0 < x < 0.60$

$$x = .8098$$

$$x = .4322$$

$$\begin{aligned}\text{CHECK} &= \frac{(.60 - .4322)^2}{(.25 + .4322)} \\ &= .04127\dots \\ &\quad \text{close enough} \checkmark\end{aligned}$$

$$\begin{aligned}[\text{PCl}_3]_E &= .60 - x \\ &= .60 - .43 \\ &= .17 \text{ M}\end{aligned}$$

$$[\text{Cl}_2]_E = .17 \text{ M}$$

$$\begin{aligned}[\text{PCl}_5]_E &= .25 + x \\ &= .25 + .43 \\ &= .68 \text{ M}\end{aligned}$$

With these 2 SF #s,

$$\frac{(.17)^2}{.68} = .042$$

check \checkmark

~~#12 answer:~~

~~Both roots yield positive values, so how do we pick the correct one?~~

~~The answer lies in the fact that x is not the final answer, whereas $(0.5 - x)$ is.~~

~~It is the term $(0.5 - x)$ which must be positive.~~

~~So the root of 1.92 is rejected in favor of the 0.26 value to achieve a positive value for concentration.~~