

Relating Stoichiometry via Limiting Reagents:

Let's say we're reacting 5.00 grams of methane with 16.0 grams of oxygen AND we want to find moles of $\text{CO}_2(\text{g})$ produced:

	$\text{CH}_4(\text{g})$ +	$2 \text{O}_2(\text{g})$	$\rightarrow \text{CO}_2(\text{g})$	$+2 \text{H}_2\text{O}(\text{g})$
Molecular Weight (g/mol)	16.05	32.00		
grams	5.00	16.0		
moles	0.312	0.500		

We find the moles of the limiting reagent and then proceed as usual to find the quantity of our product, $\text{CO}_2(\text{g})$:

$$5 \text{ grams of } \text{CH}_4(\text{g}) \times \frac{1 \text{ mol}}{16.05 \text{ g}} = 0.312 \text{ moles of } \text{CH}_4(\text{g}) \times \frac{1 \text{ CO}_2(\text{g})}{1 \text{ CH}_4(\text{g})} = 0.312 \text{ mol CO}_2(\text{g})$$

$$16 \text{ grams of } \text{O}_2(\text{g}) \times \frac{1 \text{ mol}}{32.00 \text{ g}} = 0.500 \text{ moles of } \text{O}_2(\text{g}) \times \frac{1 \text{ CO}_2(\text{g})}{2 \text{ O}_2(\text{g})} = 0.250 \text{ mol CO}_2(\text{g})$$

We find out that oxygen is limiting. Sounds legitimate – but what if we wanted to find the quantity of excess reagent ($\text{CH}_4(\text{g})$) left over? Well, we'd do another calculation with the limiting reagent, because the limiting reagent USES up the excess. Strange – everything seems tied together by the limiting reagent:

$$0.500 \text{ moles of } \text{O}_2(\text{g}) \times \frac{1 \text{ CH}_4(\text{g})}{2 \text{ O}_2(\text{g})} = 0.250 \text{ mol CH}_4(\text{g}) \text{ used}$$

$$0.312 \text{ moles of } \text{CH}_4(\text{g}) - 0.250 \text{ mol CH}_4(\text{g}) \text{ used} = 0.062 \text{ mol CH}_4(\text{g}) \text{ left}$$

Perhaps there's an easier way – if everything is dependent on the limiting reagent and the coefficients we can relate the two together:

All quantities in moles	$\text{CH}_4(\text{g})$ +	$2 \text{O}_2(\text{g})$	$\rightarrow \text{CO}_2(\text{g})$	$+2 \text{H}_2\text{O}(\text{g})$
Initial (mol)	1.00	0.500	0	0
Change (mol)	-x	-2x	+x	+2x
Final (mol)		0		

Notice that the only column we know is for the limiting reagent – we know $0.500 - 2x = 0$. Therefore we can say $x = 0.250$:

All quantities in moles	$\text{CH}_4(\text{g})$ +	$2 \text{O}_2(\text{g})$	$\rightarrow \text{CO}_2(\text{g})$	$+2 \text{H}_2\text{O}(\text{g})$
Initial (mol)	0.312	0.500	0	0
Change (mol)	-0.250	$-2 \cdot 0.250$	+0.250	$+2 \cdot 0.250$
Final (mol)	0.062	0	0.250	0.500

Applications to Equilibrium:

In the example on the previous page, we saw all of the reagents are linked together by their stoichiometric coefficients!

(the numbers in front of the formulas e.g. $1 \text{ CH}_4(\text{g})$, $2 \text{ O}_2(\text{g})$, $1 \text{ CO}_2(\text{g})$, $2 \text{ H}_2\text{O}(\text{g})$)

The simple explanation is that it takes two wheels to make a bicycle – anything else and it doesn't work. Similarly, chemical reactions happen in stoichiometric ratios and this is ALWAYS TRUE – because atoms are indivisible (unless we go into nuclear chemistry).

What if the reaction doesn't go to completion? This is the case in equilibrium:

All quantities in moles/L	$2 \text{ HI}(\text{g})$	\rightleftharpoons	$\text{H}_2(\text{g}) +$	$\text{I}_2(\text{g})$
Initial	0.500		0	0
Change	-2x		+x	+x
Equilibrium	0.300			

Equilibria never go to completion (at least not in a closed system!). We see that the final amount of $\text{HI}(\text{g})$ is 0.300 moles, $0.500 - 2x = 0.300$ implies then that $x = 0.100 \text{ mol/L}$:

All quantities in moles/L	$2 \text{ HI}(\text{g})$	\rightleftharpoons	$\text{H}_2(\text{g}) +$	$\text{I}_2(\text{g})$
Equilibrium	0.300		0.100	0.100

In an equilibrium, the 'final' or equilibrium concentrations NEVER go to zero! Instead, the reaction proceeds until it reaches the equilibrium constant, K:

$$K_{\text{eq}} = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}{[\text{HI}(\text{g})]^2} = \frac{[0.100 \text{ mol/L}][0.100 \text{ mol/L}]}{[0.300 \text{ mol/L}]^2} = 0.111$$

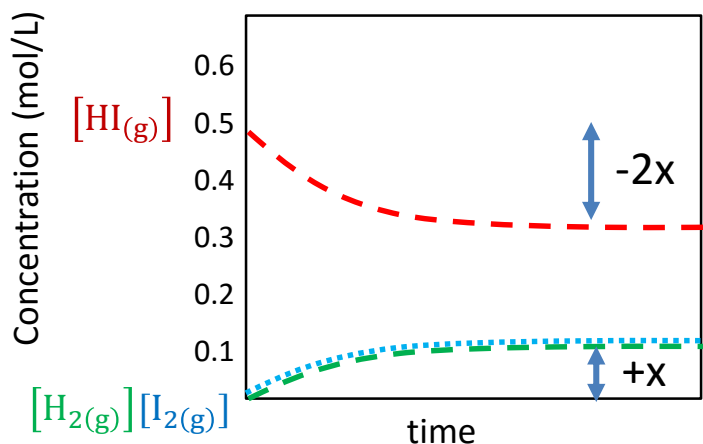
Note that K is a **constant** that is **specific to a reaction at a specified temperature**. K is also ALWAYS unit less (its multiplied by the reciprocal of its units e.g. $\frac{\text{mol}}{\text{L}} \times \frac{\text{L}}{\text{mol}} = 1$). A key takeaway of ice tables is that each of the columns is actually just a sideways equation:

Reagent/Equation	Initial	+ Change	= Equilibrium
$\text{HI}(\text{g})$	0.500	-2x	=0.300
$\text{H}_2(\text{g})$	0	+x	= ?
$\text{I}_2(\text{g})$	0	+x	= ?

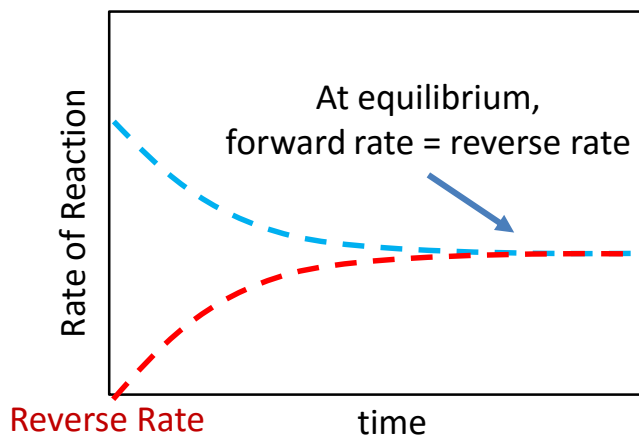
In fact, we literally solved the above ice table as a system of equations. You used equation 1 to find x and then plug it into the other two equations.

What happens in an Equilibrium?

All quantities in <u>moles/L</u>	$2 \text{ HI}_{(g)}$	\rightleftharpoons	$\text{H}_{2(g)} +$	$\text{I}_{2(g)}$
Initial	0.500		0	0
Change	-2x		+x	+x
Equilibrium	0.300		0.100	0.100

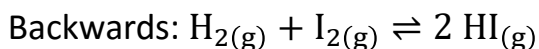
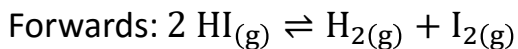


Forward Rate



Notice that the amount of change in the concentration/time diagrams is directly proportional to the x value. ICE tables reflect what is going on with a chemical system.

An equilibrium has a reverse reaction that is occurring at the same time as the forward:

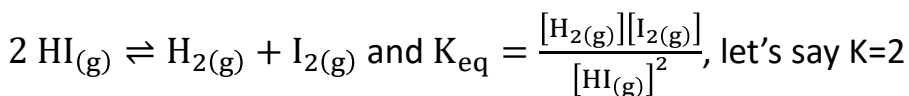


Equilibrium is dynamic and the reaction is always going on. The system **appears** static however both reactions are still going on! At equilibrium the concentrations are constant and this makes color and pressure constant.

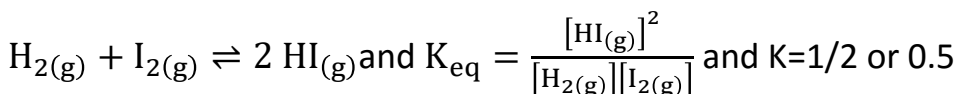
Mass is always constant (you can't create matter – you just exchange atoms in a reaction).

Pressure is constant for systems where the change in moles of gas is zero throughout the whole process. For instance the system above uses 2 moles of gas to make 2 moles of gas, so, $\Delta n_{gas}=0$.

Whenever we talk about equilibrium constants we should treat the equation as written:



If we write the equation backwards we get



Manipulating Equilibrium Constants

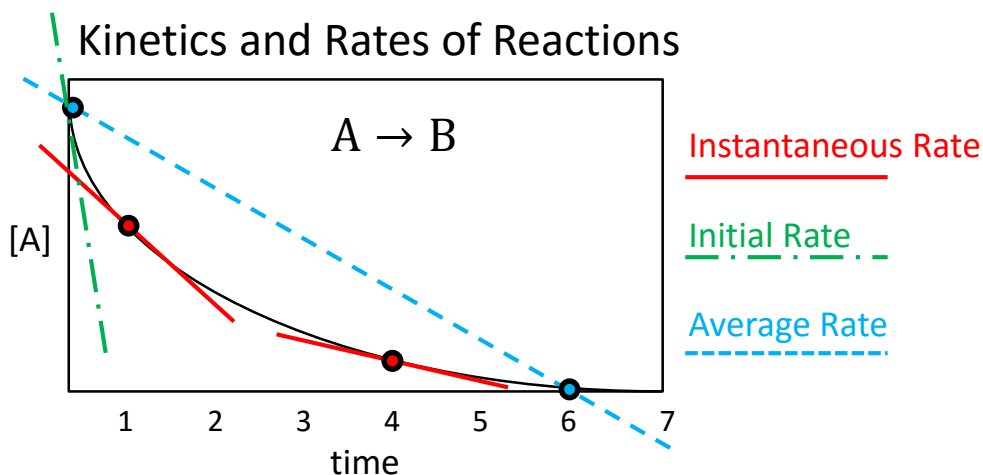
Whatever you do to the reaction, you raise the equilibrium constant to that same power, for instance:

Manipulation of Equation	Effect on K
$\times 1 = A + B \rightleftharpoons C$	K^1
$\times 2 = 2A + 2B \rightleftharpoons 2C$	K^2
$\times 3 = 3A + 3B \rightleftharpoons 3C$	K^3
$\times -1 = C \rightleftharpoons A + B$	$K^{-1} = \frac{1}{K}$
$\times -\frac{1}{2} = \frac{1}{2}C \rightleftharpoons \frac{1}{2}A + \frac{1}{2}B$	$K^{-\frac{1}{2}} = \frac{1}{K^{1/2}} = \frac{1}{\sqrt{K}}$

Manipulating equilibrium constants is different from manipulating ΔH because whatever you do to the reaction, K is raised to that same power

The full course goes through equilibrium and ice tables in detail and also has some great ways at looking at Le Chatelier's Principle and Qualitative Shifts in Equilibrium

Kinetics and Rates of Reactions

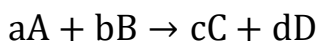


The graph above shows the change in concentration over time for A. As A is used up, its concentration is lower and so it reacts slower. The graph is labelled with the average rate from 0 to 6 seconds and also the instantaneous rates at 0, 1 and 4 seconds. The instantaneous rate at 0 seconds is known as the initial rate. The rate of this graph is its slope because the slope of this graph is $\frac{\text{Change in Concentration}}{\text{Change in Time}} = \frac{\Delta[A]}{\Delta t}$.

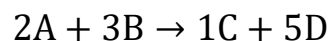
Every instantaneous rate is a tangent. A tangent is just a mathematical line that touches a curve only once. It tells you the slope of that curve at any point. There are infinite tangents to a rate curve because there are infinite points and the rate is always changing.

Kinetics

For a hypothetical reaction:



OR



Reaction rate is given as:

$$\text{rate} = -\frac{\Delta A}{a\Delta t} = -\frac{\Delta B}{b\Delta t} = +\frac{\Delta C}{c\Delta t} = +\frac{\Delta D}{d\Delta t} \quad \text{OR} \quad \text{rate} = -\frac{\Delta A}{2\Delta t} = -\frac{\Delta B}{3\Delta t} = +\frac{\Delta C}{\Delta t} = +\frac{\Delta D}{5\Delta t}$$

Where the coefficients 2, 3, 1, 5 were chosen arbitrarily.

Notice that every reagents' rate is divided by the coefficient – this is because, like Hess's Law, rate is for 1 mole of reaction! For instance, let's say that the rate of consumption of A is $3 \text{ mol L}^{-1} \text{ s}^{-1}$, what is the rate of consumption or production for all the other reagents?

$$-\frac{3 \text{ mol/L}}{\text{s}} A \times \frac{-3 B}{-2 A} = -\frac{4.5 \text{ mol/L}}{\text{s}} B \quad \leftarrow \text{notice that the sign is negative because reactants get consumed! (this is like having a negative 'change')}$$

$$-\frac{3 \text{ mol/L}}{\text{s}} A \times \frac{+1 C}{-2 A} = +\frac{1.5 \text{ mol/L}}{\text{s}} C \quad \leftarrow \text{notice that I flipped the sign because C is a product}$$

$$-\frac{3 \text{ mol/L}}{\text{s}} A \times \frac{+5 D}{-2 A} = +\frac{7.5 \text{ mol/L}}{\text{s}} D$$

If we use any other reagent to do these conversions, we should get the same numbers:

$$+\frac{1.5 \text{ mol/L}}{\text{s}} C \times \frac{+5 D}{+1 C} = +\frac{7.5 \text{ mol/L}}{\text{s}} D$$

This is because all of the reagents are related by their coefficients. But how does this work into the rate law given at the very beginning of the page?

$$\frac{\Delta A}{\Delta t} = -\frac{3 \text{ mol/L}}{\text{s}} \quad \frac{\Delta B}{\Delta t} = -\frac{4.5 \text{ mol/L}}{\text{s}} \quad \frac{\Delta C}{\Delta t} = +\frac{1.5 \text{ mol/L}}{\text{s}} \quad \frac{\Delta D}{\Delta t} = +\frac{7.5 \text{ mol/L}}{\text{s}}$$

And then, Rate =

$$= -\frac{\Delta A}{a\Delta t} = -\frac{\Delta B}{b\Delta t} = +\frac{\Delta C}{c\Delta t} = +\frac{\Delta D}{d\Delta t} = -\frac{3 \text{ mol L}^{-1}\text{s}^{-1}}{2} = -\frac{4.5 \text{ mol L}^{-1}\text{s}^{-1}}{3} = +\frac{1.5 \text{ mol L}^{-1}\text{s}^{-1}}{1} = +\frac{7.5 \text{ mol L}^{-1}\text{s}^{-1}}{5}$$

Notice when we use the rate as above, we always get $\text{Rate} = +\frac{1.5 \text{ mol/L}}{\text{s}}$, this is because rate is always positive (a reaction is always happening or not – it's never negative or anti happening). And, additionally, this is the rate for 1 mole of any reagent (much like in Hess's Law, we had a ΔH in kJ for the whole reaction that could be used to find kJ/mol for any reagent).

We're going to go a lot more in detail into these ideas in the full course, this Friday, March 18th from 3:30 to 9:30 pm – please sign up online at

<https://www.prep101.com/course.php?school=5&id=550>

I look forward to seeing you there!

To your success!