Atom Economy

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It is a well-known fact that Percentage of yield of a chemical reaction is a very important matter for a chemist. It provides a means of comparison of the theoretical and actual quantity of product. It actually evaluates the reaction efficiency. But more recently, calculation of 'atom economy' has become a more important for comparing the efficiency of chemical reactions.

Chemists commonly calculate percentage yield to ascertain the efficiency of a particular reaction as follows:

$$\boxed{\%\ \text{yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100}$$

Using this strategy, a reaction is said to be perfectly efficient if it gives 100% yield of desired product. However, calculation of percentage yield provides no information about the extent to which unwanted products are formed in the reaction pathway. In the chemical industry there are many examples of highly 'efficient' reactions that generate waste far greater in mass and volume than the desired product

Professor Barry Trost of Stanford University developed the concept of 'atom economy' and derives from the principles of 'green chemistry'.

The main aim of Green chemistry to design the chemical products/processes in which there must have a target to eliminate or reduce the use or generation of hazardous substances.

During the synthesis of a particular chemical product, all the atoms of the reactant may not be always incorporated in the desired products. The atoms which are not incorporated in the desired product will involve to generate the by product and waste product may be environmentally hazardous. Professor Sheldon of Delft University, Netherlands Quantified the concept of atom economy . For calculating the amount of waste product for a particular reaction, he calculated percentage atom utilization by dividing the molecular weight of the desired product by the molecular weights of all the products generated in a reaction as follows:

$$\%\ Atom\ utilisation = \frac{\text{Formula weight of desired product}}{\text{Formula weght of (the desired product + the waste and by − product)}} X\ 100$$

But in Most cases, it becomes very difficult to identify the waste and bye products. Hence, the concept of % Atom economy has been introduced to avoid the circumstances. This concept also gives the measure of the unwanted product formed in a particular reaction.

$$\boxed{\%\text{ atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100}$$

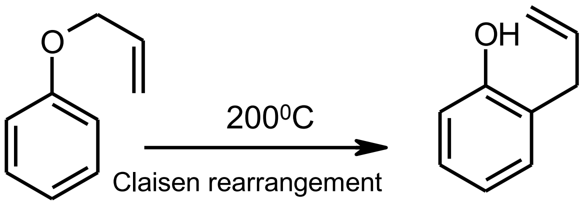
It has been reported that, since its introduction in the 1980s yearly 13,000 tonnes of the painkiller Ibuprofen have been produced. Initially, Boots used a six-step production process with an overall atom economy of just 40.1%. In the 1990s the Hoechst Celanese Corporation (in collaboration with Boots) developed a new, improved three-stage process to producing Ibuprofen with an atom economy of 77.4%. This improvement in atom economy resulted in a reduction in the quantity of unwanted by-products, and therefore in significant environmental and economic cost savings.

The atom economy of a reaction depends on the reagents used in the particular reaction and the type of chemical reaction involved. Most of common chemical reactions can be classified as rearrangement (e.g migration of an alkyl group), addition (Example 1),substitution (eg chlorination of methane) or elimination (eg dehydration). Rearrangement and addition reactions are atom economical by their very nature, since they simply involve repositioned of reactant atoms within the same molecule or incorporated within a second molecule. Substitution reactions, however, involve replacement of one group with another and therefore have intrinsically poor atom economy. Elimination reactions is also inherently atom uneconomical because of the fact that eliminated atoms are always lost as waste. In developing an atom economical reaction pathway, therefore, the industrial chemist may well prefer rearrangement and addition reactions over less environmental friendly substitution and elimination reactions.

Here. We are discussing these reactions with some examples as given below:

1. Rearrangement Reactions:

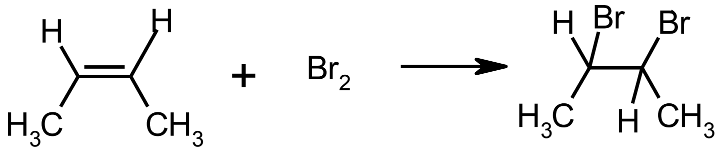
These reactions involves rearrangement of atoms that forms molecule. Hence, the atom economy of these reactions are 100%.



In this rearrangement reaction, % Atom economy = (134.175/134.175) x 100 = 100%

2. Addition reaction: – halogenation of an alkene

a)



(Z)-but-2-ene	Bromine Br_2	2,3-dibromobutane
C_4H_8		$C_4H_8Br_2$
1mol	1mol	1mol
(12 x 4) + (8 x 1)	2 x 79.9	(12 x 4) + (8 x 1) + (79.9 x 2)
= 56g	= 159.8g	= 215.8g

Total mass of reactants = 56 g + 159.8 g = 215.8 g (Note: Product mass is also 215.8 g)

Mass of desired product (2,3-dibromobutane) = 215.8 g

$$\boxed{\%\text{ atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100}$$

$$\%\text{ atom economy} = \frac{215.8}{215.8} \times 100 = \mathbf{100\%}$$

This process is 100% atom efficient, with all the reactant atoms included within the desired product.

b)

% Atom Economy = (44.096/44.096) x 100 = 100 %

3. **Substitution reaction:** One or more atoms substituted by another atom or group of atoms.

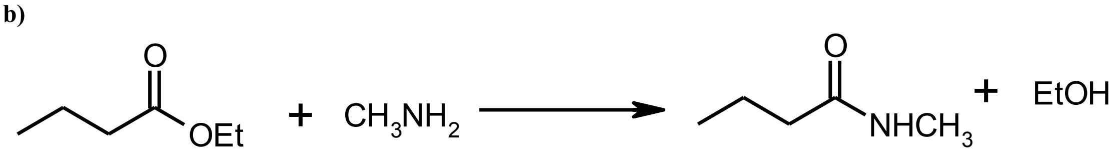
a) CH_3 CH_2 CH_2CH_2OH + NaBr + H_2SO_4 → CH_3 CH_2 CH_2CH_2 Br + $NaHSO_4$+ H2O

Here, -OH group substituted by a - Br group

$$\% \, \boldsymbol{Atom\ Economy} = \frac{\textbf{Mass Of } (\mathbf{4H + 9H + 1Br})\boldsymbol{atoms}}{\textbf{Mass of } (\mathbf{4C + 12H + 5O + 1Br + 1Na + 1S})\textbf{atoms}} \boldsymbol{X}\ \mathbf{100}$$

$$= \frac{\mathbf{137amu}}{\mathbf{275\ amu}} \boldsymbol{X}\ \mathbf{100} = \mathbf{50\%}$$

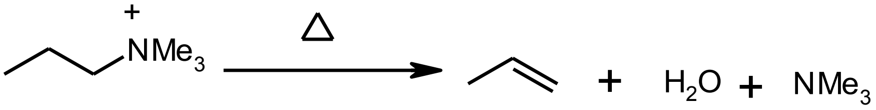
b)



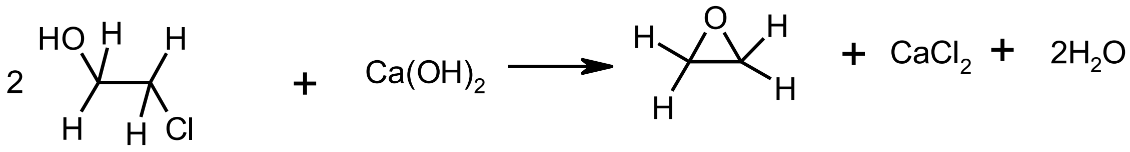
% Atom Economy = (87.120 / 133.189) x 100 = 65.41 %

4. **Elimination reaction:**

A)



% atom economy= (42.080 / 119.205) x 100 = 35.30 %



2[(12 x 2) + (5 x 1) + 16 + 35.5]	40 + 2(16 +1)	2[(12 x 2) + (4 x 1) + 16]	40 + (2 x 35.5)	2X18
= 161 g	=74g	= 88g	=111 g	=36g

Total mass of reactants = 161 g + 74 g = 235 g

(Note: Total product mass = 235 g)

Mass of desired product ethylene oxide = 88 g

% Atom economy = 88/235 x100 = 37.4%

This above elimination reaction is therefore only 37.4% atom efficient, with the remaining 62.6% in the form of unwanted waste products (calcium chloride and water).

It has been observed that, Catalysts have a crucial role in improving the atom economy of chemical reactions. They allow the development of more effective synthetic reaction Routes, which produce fewer waste products, and can be recovered and reused.

Some more examples of atom economy calculations:

1. $Fe_2O_{3(s)} + 3CO_{(g)}$ ===> $2Fe_{(l)} + 3CO_{2(g)}$

We can calculate the atom economy for extracting iron in Blast furnace using the atomic masses of Fe = 56, C = 12, O = 16.

The reaction equation can be expressed in terms of theoretical reacting mass units

[(2 x 56) + (3 x 16)] + [3 x (12 + 16)] ===> [2 x 56] + [3 x (12 + 16 + 16)]

[160 of Fe_2O_3] + [84 of CO] ===> [112 of Fe] + [132 of CO_2]

so there are a total of 112 mass units of the useful/desired product iron, Fe,

out of a total mass of reactants **or** products of 160 + 84 = 112 + 132 = 244.

Therefore, the % ***atom economy*** = 100 x 112 / 244 = **45.9%**

Important Note: It doesn't matter whether you use the total mass of reactants or the total mass products in the calculations, they are the same due to the **law of conservation of mass**

2. The fermentation of sugar to make ethanol ('alcohol') and (b) converting ethanol to ethane:

(a) glucose (sugar) == enzyme ==> **ethanol + carbon dioxide**

$C_6H_{12}O_{6(aq)}$ ==> **$2C_2H_5OH_{(aq)} + 2CO_{2(g)}$**

atomic masses: **C = 12**, **H = 1** and **O = 16**

formula mass of glucose reactant = **180** (6x12 + 12x1 + 6x16)

formula mass of ethanol product = **46** (2x12 + 5x1 + 1x16 + 1x1)

relative mass of desired useful product in the equation = 2 x 46 = **92**

% Atom economy = 100 x 92/180 = **51.1%**

(b) ethanol === heat/catalyst ===> ethene + water

It possible to use ethanol from fermentation to produce ethene for plastics (polymers) manufacture instead of relying on the cracking of crude oil fractions (e.g. a country like Brazil with a huge agriculture system but no oil deposits.

CH_3CH_2OH ===> CH_2=CH_2 + H_2O

formula masses: ethanol = 46, ethene = 28, water = 18

% atom economy = 100 x 28/46 = 60.9%

3. All about making hydrogen

In these three examples, Reactions A to C : Relative atomic masses are used: C = 12.0, H = 1.0, O = 16.0

Hydrogen is used in synthesizing ammonia and making margarine, and is made on a large scale from reacting methane with water

Methane + water ==> hydrogen + carbon monoxide

Reaction equation A.: **$CH_4(g) + H_2O(g)$ ==> $3H_2(g)$ + $CO(g)$**

Using formula masses gives the ratios gives

16 + 18 ==> (**3 x 2**) + 28

34 mass units of reactants ==> **6** mass units of useful product

% Atom economy = 100 x 6 / 34 = **17.6%**

BUT, the 82.4% of waste toxic carbon monoxide must be dealt with in some way!

It seems a very inefficient process BUT ...

(i) Hydrogen has very small molecular mass and 75% of the molecules are the desired product.

(ii) You can actually burn the carbon monoxide as a fuel to provide energy for power generation.

(iii) Methane is readily available from the petrochemical industry and is much cleaner to work with than impure coal (see reactions 2. and 3.), which must be converted to coke first - an extra process.

So, a low atom economy doesn't always mean the process is not economically viable or necessarily produces undue waste.

Hydrogen can be made from reacting water with coke (a form of carbon made by roasting coal)

A second reaction used to manufacture hydrogen

carbon + water ===> hydrogen + carbon monoxide

Reaction equation B.: **$C(s)$ + $H_2O(g)$ ===> $H_2(g)$ + $CO(g)$**

formula masses: 12 + 18 (= 30) ==> 28 + 2 (= 30)

% atom economy = 100 x 2 / 30 = **6.67 %**

This is a much lower atom economy than reaction, and only 50% of the molecules are useful product.

However, the carbon monoxide can be made to react further with water to form more hydrogen carbon monoxide + water ===> hydrogen + carbon dioxide

Reaction equation C.: **$CO(g) + H_2O(g) \Longrightarrow H_2(g) + CO_2(g)$**

formula masses: 28 + 18 (= 46) ===> 2 + 44 (= 46)

% atom economy = 100 x 2 / 46 = **4.35 %**

This is an even lower atom economy than reaction, and again, only 50% of the molecules are useful product.

However: (a) it does take care of poisonous carbon monoxide, but there is also something else you can do ...

(b) You can combine these process, so combining equations 2. and 3. we get ...

$C(s) + H_2O(g) \Longrightarrow H_2(g) + CO(g)$ plus

$CO(g) + H_2O(g) \Longrightarrow H_2(g) + CO_2(g)$ gives

$C(s) + 2H_2O(l) \Longrightarrow 2H_2(g) + CO_2(g)$

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formula masses: 12 + 2x18 (= 48) ===> 4 + 44 (= 48)

% atom economy = 100 x 4 / 48 = **8.33 %**

This is a higher atom economy than reactions B or C, **and** 67% of the molecules are useful product.

Only 50% of the molecular products are the desired product in reactions B. and C.

Therefore employing a secondary process improves the efficiency of this particular process for making hydrogen.

It should be noted that **carbon monoxide is a water insoluble toxic gas** and not easy to deal with.

As already mentioned you can burn it as a fuel for power generation or heating a reactor vessel.

BUT, carbon dioxide is not toxic (as long as plenty of air is around!) and importantly, it readily dissolves in sodium hydroxide solution in gas flow 'scrubbers' to leave hydrogen as the only remaining gas.

This greatly reduces the cost of purifying the hydrogen to use e.g. in the Haber Synthesis of ammonia and the hydrogenation of unsaturated plant fats to make spreadable margarine.

Also, the reaction between steam and carbon monoxide is exothermic, this reduces the energy needs of the overall process.

4. Making hydrogen using electrolysis

Relative atomic masses: Na = 23.0, Cl = 35.5, H = 1.0, O = 16.0

Process A. **Electrolysis of aqueous sodium chloride solution** (brine)

Overall change: $2NaCl(aq) + 2H_2O(l)$ ====> $2NaOH(aq) + Cl_2(g) + H_2(g)$

total masses for reactants or products = (2 x 58.5) + (2 x 18) =

mass of desired product 2

% atom economy = 100 x 2 / = 153 = **1.31%**

Very low atom economy and waste to deal with, BUT, sodium hydroxide and chlorine are useful saleable chemicals.

Process B. **Electrolysis of acidified water**

Overall change: $2H_2O(l)$ ===> $2H_2(g) + O_2(g)$

total masses for reactants or products = (2 x 18) = (4 + 32) = 36

mass of desired product 2

% atom economy = 100 x 4 / = 36 = **11.1% .** This has a much greater atom economy than process B and no waste products, no pollution.

This is an ideal process, especially if you can use green energy e.g. from wind turbine, solar cell or hydroelectric sources of electricity.

BUT, both processes have their place in the chemical industry - from Process A we do need sodium hydroxide and chlorine to manufacture other products e.g. soap from NaOH + plant oil and PVC from ethane and chlorine.

5. The following reactions contrast with the 100% atom economy of ammonia production (for which much of the hydrogen is made), because it's an **addition reaction** with no extra waste products

$N_2 + 3H_2$ ==> $2NH_3$

mass of reactants = mass of useful products = 100% atom economy

6. In organic chemistry, these three types of reaction can never have a 100% atom economy because there are always at least two products - desired useful product and often a waste product e.g. (i) **Condensation** reaction - a small molecule formed in joining two molecules to make a larger molecule

e.g. **n HOOC-[][][][]-COOH + n H_2N-[][][][]-NH_2 ==> -(-OC[][][][]-CONH-][][][]-NH-$)_n$-+ 2n H_2O**

a schematic example of condensation polymerisation

(ii) **Elimination** reaction - a group of atoms eliminated from a molecule

e.g. $\mathbf{CH_3CH_2OH \implies CH_2{=}CH_2 + H_2O}$

water eliminated from ethanol to form ethene

(iii) **Substitution** reaction - one or more atoms substituted by another atom or group of atoms

e.g. $\mathbf{CH_3CH_2Br + NaOH \implies CH_3CH_2OH + NaBr}$

-Br group substituted by an -OH group

7. You can use either (a) hydrogen or (b) a hydrocarbon gas like methane to reduce the oxides of metals of low reactivity to obtain the metal itself.

Here. Cu can be obtained the reduction of copper(II) oxide, Using the atomic masses: Cu = 63.5, H = 1, O =16, C = 12

a) $\mathbf{CuO + H_2 \implies Cu + H_2O}$

How we can calculate the atom economy of the reaction ?

Formula masses: $CuO = 79.5$, $H_2 = 2$, $Cu = 63.5$, $H_2O = 18$

Total mass of reactants = total mass of products 79.5 + 2 = 63.5 + 18 = 81.5

% atom economy of desired product Cu = 100 x 63.5/81.5 = **<u>77.9%</u>**

(b) $\mathbf{4CuO + CH_4 \implies 4Cu + 2H_2O + CO_2}$

Calculate the atom economy of the reaction.

Formula masses: $CuO = 79.5$, $CH_4 = 16$, $Cu = 63.5$, $H_2O = 18$, $CO_2 = 44$

Total mass of reactants = total mass of products

(4 x 79.5) + 16 = (4 x 63.5) + (2 x 18) + 44 = 334

% atom economy of desired product Cu = 100 x (4 x 63.5)/334 = **<u>76.0%</u>**

(c) **Which reaction has the higher atom economy? BUT, would this be the preferential method used?**

Reaction (a) has the higher atom economy, BUT, hydrogen is probably more costly to produce than cheap methane gas from crude oil. Therefore method (b) is probably more economic.