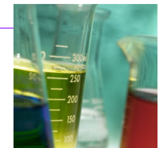
Strategy to Finish Ch. 4



Mon (today) – 4.6
  Chemical Reaction Terminology

Wed (9/22) – 4.7
  Balances on Process with Reactions, including DOF

Fri (9/24) – 4.7
  Practice balances w/reactions

Mon (9/27) – 4.8
  Combustion

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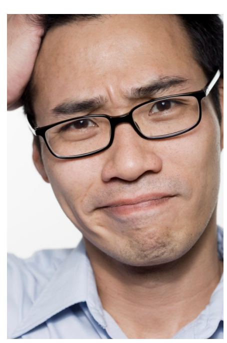
Word to the Wise

- Balances with chemical reaction are:
  - Easy!
  - Most missed competency on the L3 exam!



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Stoichiometric

(I shouldn't have to review this)

$$N_2 + 3H_2 \rightarrow 2NH_3$$

- **Stoichiometric coefficients** (ν_i)
  - Found in stoichiometric equation (numbers in front of species that balance the equation)
  - Negative for reactants, positive for products
  - $\nu_{N2} = -1$, $\nu_{H2} = -3$, $\nu_{NH3} = 2$
- **Stoichiometric ratio**
  - Molar ratio in stoichiometric equation
    - The stoichiometric ratio here is N_2/H_2 = 1:3
  - If we actually have a system that has a 1:3 proportion, then we say it is in **stoichiometric proportion**

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Non-Stoichiometric

$$N_2 + 3H_2 \rightarrow 2NH_3$$

- Occurs quite a bit!
- **Limiting reactant** – whichever reactant will be consumed first!
  - If we start with 1 mole N_2, 2 moles H_2, then H_2 is the limiting reactant
    - If the 2 moles of H_2 are consumed, there will still be N_2 left!
- **Excess reactant** – whichever reactant would be left over after consuming the limiting reactant
  - In the example above, N_2 is the excess reactant

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More Terms

($N_2 + 3H_2 \rightarrow 2NH_3$)

- **Stoichiometric Requirement**
  - Given x number of moles of one reactant, how many moles of the other reactant(s) are needed in stoichiometric proportion?
    - Given 2 moles of N_2, what is the stoichiometric requirement of H_2 to form NH_3? (6 moles)
- **Percent Excess** Suppose we have 2 moles N_2 and 7 moles H_2
    - There will be 1 mole of H_2 left after complete reaction
    - % excess = $(n_{i,0} - n_{i,\ stoich})/n_{i,\ stoich}$
    - = (7-6)/6 in this case = 1/6, or 16.7% excess H_2

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Fractional Conversion

- f_i in our text, X_i in most others
  - Relative amount of reactant converted

    = $n_{reacted}/n_{fed}$

  - f_i (or X_i) = $\frac{n_{i,0}-n_i}{n_{i,0}} = 1 - \frac{n_i}{n_{i,0}}$

    also $n_i = n_{i0}(1 - X_i)$
- Start with 3 moles H_2, end with 0.3 moles H_2, then

  $f_{H2} = (3 - 0.3)/3 = 0.9$, or 90% conversion

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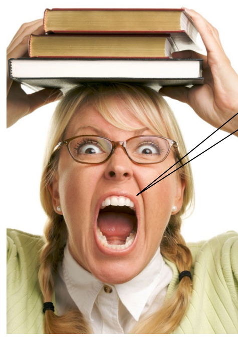
Extent of Reaction
(ξ, pronounced ksee, but spelled xi)

- Moles reacted, normalized to stoichiometric equation (this is the definition if there is only one reaction)

$$n_i = n_{i0} + \xi\nu_i \quad \text{or} \quad \xi = (n_i - n_{i0})/\nu_i$$



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Extent of Reaction
(ξ, pronounced ksee)

- Moles reacted, normalized to stoichiometric equation

$$n_i = n_{i0} + \xi\nu_i \quad \text{or} \quad \xi = (n_i - n_{i0})/\nu_i$$

- note that ν_i is negative for a reactant, positive for a product
- ξ has units of moles (or moles/time for $\dot{\xi}$)*
- One value of ξ for each reaction (not one per species)

*The author changed his mind on the units for ξ in the 4th Edition!! He gave units of moles to ν_i in the 4th edition so ξ would be unitless. This makes no sense! In my class, ξ has units of moles.

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Extent of Reaction

Example

$N_2 + 3H_2 \rightarrow 2NH_3$

- Example
  - Start with 3 moles H_2 and 1.5 moles N_2
  - 0.3 moles of H_2 are left after rxn (measured)
  - $\xi = (n_i - n_{i0})/\nu_i =$ (0.3 – 3) /(-3) = 2.7/3 = 0.9 moles
  - So $n_{NH3} = n_{i0} + \xi\nu_i$ = 0 + (0.9) · (2) = 1.8 moles
  - Also, n_{N2} = 1.5 + (0.9) · (-1) = 0.6 moles

- Note that ξ does not change with species, but there is one ξ for each reaction

$$\xi = \frac{n_{H_2} - n_{H_2,0}}{\nu_{H_2}} = \frac{n_{N_2} - n_{N_2,0}}{\nu_{N_2}} = \frac{n_{NH_3} - n_{NH_3,0}}{\nu_{NH_3}}$$

- In other words, the extent of reaction is a normalized amount of stuff reacting with units of moles

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Another Way to Look at ξ

Accum = In – Out + Gen – Cons

- The ξ is the normalized generation term
  - i.e., $(0 = n_{i,in} - n_{i,out} + \xi * \nu_i)$, at least for a product
  - Units of mols or mols/time ($\dot{\xi}$)
  - If accum = 0, then

$$0 = n_{i,in} - n_{i,out} + \xi * \nu_i$$

$$\xi = \frac{n_{i,out} - n_{i,in}}{\nu_i}, \text{ or}$$

$$n_{i,out} = n_{i,in} + \xi * \nu_i$$

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Practice

$C_3H_8 + 7/2\ O_2 \rightarrow 3\ CO + 4\ H_2O$

- Start with 2 moles propane, 10 moles O_2
- Limiting reactant: propane
- %Excess of excess reactant:

  (10 – 7)/7 = 3/7 = 42.8%

If 1.5 moles of propane react,

- Fractional conversion (f_{C3H8}) = (2 – 0.5)/2 = 75%
- Extent of reaction (ξ) = (0.5 – 2)/(-1) = 1.5 moles
- n_{O2} = 10 + (1.5) · (-7/2) = 4.75 moles
- n_{CO} = 0 + 1.5 · 3 = 4.5 moles
- n_{H2O} = 0 + 1.5 · 4 = 6.0 moles

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Multiple Reactions

Use ξ's in mole balance for each species

$C_2H_6 + 5/2\ O_2 \rightarrow 2CO + 3H_2O$

$CO + ½\ O_2 \rightarrow CO_2$

- There must be a different extent of reaction for each reaction!
  - ξ_1 for reaction 1
  - ξ_2 for reaction 2
- In general, for *j* reactions (*i is for species)*

$$n_i = n_{i,0} + \sum_j \nu_{ij}\xi_j$$

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Multiple Reactions

Use ξ in mole balance for each species

$$C_2H_6 + 5/2\ O_2 \rightarrow 2CO + 3H_2O$$
$$CO + \frac{1}{2}\ O_2 \rightarrow CO_2$$

Mole balances

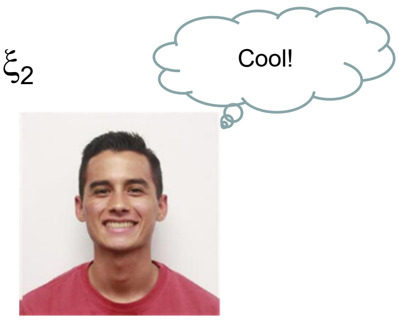
$n_{C2H6} = n_{C2H6,0} - \xi_1$

$n_{O2} = n_{O2,0} - 5/2\ \xi_1 - \frac{1}{2}\ \xi_2$

$n_{CO} = n_{CO,0} + 2\xi_1 - \xi_2$

$n_{H2O} = n_{H2O,0} + 3\ \xi_1$

$n_{CO2} = n_{CO2,0} + \xi_2$



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Yield & Selectivity

- These both have to do with multiple products, only one of which is most desired
- **Yield** = (moles of desired product)/
  (max possible moles at complete conversion)
- **Selectivity** = (moles desired product)/
  (sum of undesired products)
  - There are lots of ways to define selectivity
  - Often it is where the carbon goes, and we ignore H_2 as a product when calculating selectivity

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Practice

$$C_2H_6 \rightarrow C_2H_4 + H_2$$
$$C_2H_6 + H_2 \rightarrow 2\ CH_4$$
$$C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$$

Start with 100 moles of C_2H_6

After reaction, we have:

- 65 mols C_2H_4
- 15 mols C_2H_6
- 60 mols H_2
- 25 mols CH_4
- 5 mols C_3H_6

- Find yield and selectivity if C_2H_4 is the desired product
- Find ξ_1, ξ_2, and ξ_3

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Answers (fill-in)

- $Yield_{C2H4}$ = 65/100 = 65%
- Selectivity = 65/(25 + 5) = 2.2
- Set up each mole balance

n_{C2H6} = 15 moles = $n_{C2H6,0} - \xi_1 - \xi_2 - \xi_3$

n_{C2H4} = 65 moles =

n_{H2} = 60 moles =

n_{C3H6} = 5 mols =

So….

ξ_3 =

ξ_1 =

ξ_2 =

65 mols C_2H_4
15 mols C_2H_6
60 mols H_2
25 mols CH_4
5 mols C_3H_6

Note:
- Lots of ways to define yield and selectivity
- Usually we use carbon and ignore hydrogen

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Answers

$C_2H_6 \rightarrow C_2H_4 + H_2$
$C_2H_6 + H_2 \rightarrow 2\ CH_4$
$C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$

- $Yield_{C2H4}$ = 65/100 = 65%
- Selectivity = 65/(25 + 5) = 2.2
- Set up each mole balance

n_{C2H6} = 15 moles = $n_{C2H6,0} - \xi_1 - \xi_2 - \xi_3$
n_{C2H4} = 65 moles = $0 + \xi_1 - \xi_3$
n_{H2} = 60 moles = $0 + \xi_1 - \xi_2$
n_{C3H6} = 5 mols = $0 + \xi_3$

Now find ξ's

65 mols C_2H_4
15 mols C_2H_6
60 mols H_2
25 mols CH_4
5 mols C_3H_6

So….

ξ_3 = 5 mols
ξ_1 = 65 + 5 = 70 mols (from C_2H_4 balance)
ξ_2 = 70 – 60 = 10 mols (from H_2 balance)

Note:
- Lots of ways to define yield and selectivity
- Usually we use carbon and ignore hydrogen

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Example: $CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$

Suppose you had 100 mol of CO_2 and 250 mol of H_2, find limiting reactant and % excess of other reactant

- Limiting reactant = H_2
- % Excess CO_2 = (100-250/3)/(250/3) = 20%

Suppose 80 mol of CH_3OH was formed, find ξ and f_{H2}.

- $\xi = (n_{CH3OH} – 0)/1$ = 80 mol (also = n_{H2O})
- n_{CO2} = 100 mol + (-1)*(ξ) = 20 mol
- n_{H2} = 250 mol + (-3)*(ξ) = 10 mol
- $f_{H2} = X_{H2}$ = (250 – 10)/250 = 1 – 10/250 = 0.96 (i.e., 96%)

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Equilibrium Example
(page 122 in book)

$CO + H_2O = CO_2 + H_2$,
start with 1 mol CO, 2 mol H_2O

$$\frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}} = K_{eq} = 1.0$$

$n_{CO} = 1.0 - \xi$
$n_{H2O} = 2.0 - \xi$
$n_{CO2} = \xi$
$n_{H2} = \xi$
$n_{total} = 3.0$

$y_{CO} = (1.0 - \xi) / 3.0$
$y_{H2O} = (2.0 - \xi) / 3.0$
$y_{CO2} = \xi / 3.0$
$y_{H2} = \xi / 3.0$

$$K_{eq} = 1.0 = \frac{(\xi)(\xi)}{(1-\xi)(2-\xi)}$$

Strategy:
- Plug expressions for y_i into equilibrium expression
- Solve for ξ (quadratic eqn. or use solver)
- Calculate final moles of each species from ξ
- Calculate f_{CO}

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Chemical Reaction Terms

Term	Definition	Units	Example
Stoichiometric Equation	Balanced Eqn		$N_2 + 3H_2$ ==> $2NH_3$
Stoichiometric Coefficient (ν_i)	Coefficients of stoich eqn that balance eqn, negative for reactants		$\nu_{N2} = -1$, $\nu_{H2} = -3$, $\nu_{NH3} = 2$
Stoichiometric Ratio (S.R.)	Molar ratio in stoichiometric eqn		1 N_2 / 3 H_2 in example above
Stoichiometric Proportion	If actual molar ratio in system equals the S.R.		If you really have a 1:3 N_2/H_2 molar ratio
Limiting Reactant	Whichever reactant has less than stoichiometric proportion		If 1 mole N_2 and 2 moles H_2, H_2 is the limiting reactant
Excess Reactant(s)	Reactant(s) with more than stoichiometric proportion		N_2 in box above
Stoichiometric Requirement	Stoichiometric amount needed	Moles	If you have 1 mole N_2, the stoichiometric requirement is 3 moles H_2
Percent Excess	% above stoich. proportion $(n_i - n_{i,stoich})/n_{stoich} \times 100\%$	%	If you have 4 moles H_2, 1 mole N_2 (4-3)/3 = 1/3 = 33% excess H_2
Fractional Conversion (f_i or X_i)	Relative amount of feed reactant converted $\frac{n_{i,0} - n_i}{n_{i,0}}$	fraction (or %)	Start with 3 moles H_2, end with -.3 moles H_2 F = (3 – 0.3)/3 = 0.9, or 90% conversion
Extent of Reaction (ξ)	Amount reacted, normalized to the stoichiometric equation $\xi = \frac{n_i - n_{i,0}}{\nu_i}$	Moles	In box above, $\xi = (0.3 - 3.0)/(-3) = 0.9$ moles
Yield	$\frac{\text{mole of desired product}}{\max \text{ possible moles at complete conversion}}$	fraction	See worksheet
Selectivity	$\frac{\text{moles of desired product}}{\sum \text{moles undesired products}}$	fraction	

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