# Lecture 1

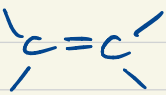
Most important fundamental observation about nature?

Matter is made of discrete & infinitesimal particles, in constant motion.

— Feynmann

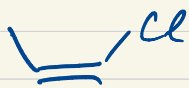
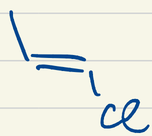
Concept anticipated by ancient Greek & Indian philosophers

Distinct chemical substances

$H_2O$ (l)  (g) $Fe_2O_3$(s)

often appearing in mixtures

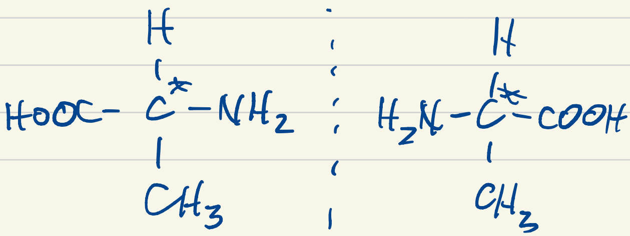
Distinct can depend on context

1-chloropropene  vs 

geometric isomers

alanine

stereoisomers



water — $H_2O$ vs $D_2O$
isotopomers

alumina — $\alpha$-$Al_2O_3$ vs $\theta$ vs $\gamma$
polymorphs

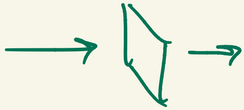
## Amounts

$$\begin{tikzcd}
 & \text{number } (n_j) \text{ (moles)} \arrow[dl, leftrightarrow, "MW"'] \arrow[dr, leftrightarrow, "MW/\rho"] & \\
\text{mass } (m_j) \text{ (g, kg)} \arrow[rr, leftrightarrow, "\rho"'] & & \text{volume } (V_j) \text{ (liters)}
\end{tikzcd}$$

$$\left.\begin{array}{l} \rho\text{, density} \\ + \\ MW/\rho\text{, molar volume} \end{array}\right\} \begin{array}{l} \text{s, l weak fn of } T, P \\ \text{g strong " " "} \end{array}$$

$$v = \frac{MW}{\rho} \approx \frac{RT}{P} \cdot Z$$

# Flows



$$\begin{tikzcd} & \frac{\text{number}}{\text{time}}\,(F_j) \arrow[dl, leftrightarrow, "MW"'] \arrow[dr, leftrightarrow, "MW/\rho"] & \\ \frac{\text{mass}}{\text{time}}\,(\dot{m}_j) \arrow[rr, leftrightarrow, "\rho"'] & & \frac{\text{volume}}{\text{time}}\,(\dot{v}_j) \end{tikzcd}$$

## Composition (activities)

key connection to equilibrium & to rates

Normalize amts/flow to any extensive quantity

$$N_{tot} = \sum_j N_j$$

$$m_{tot} = \sum_j m_j$$

$$V_{tot} = \sum_j \bar{V}_j$$ right? Oh no!

- mole fractions $x_j, y_j = \dfrac{N_j}{N_{tot}} = \dfrac{F_j}{F_{tot}}$

- concentrations

$$C_j = \frac{N_j}{V_{tot}} = \frac{F_j}{\dot{V}_{tot}}$$

- molality $\frac{n_j}{m_{tot}}$

- partial pressure

$$P_j = y_j \cdot P$$

## Example (trivial)

Air is 80% $N_2$/20% $O_2$ (what are these units?)

Mass flow controller delivers 1 g/s dry air to reactor.

$F_{N_2}$? $F_{O_2}$? $\dot{V}$? what would you need to know?

$\dot{m} = 1\,g/s$

$y_{O_2} = 0.2$

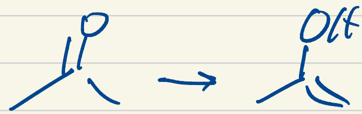
$y_{N_2} = 0.8$

# chemical reaction

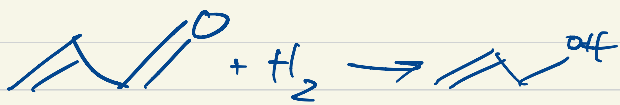
conversion of one substance to another

conserves mass & atoms

## isomerization

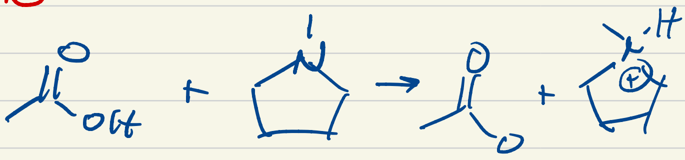
$A \rightarrow B$ 

## condensation



$A + B \rightarrow C$

## acid-base



$A + B \rightarrow C + D$

## combustion

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

## redox

$$MnO_4^- + SO_3^{2-} \rightarrow MnO_2 + SO_4^{2-}$$

you balance!

Distinct stoichiometry

$NH_3$ combustion

$$4\,NH_3 + 3\,O_2 \longrightarrow 2\,N_2 + 6\,H_2O$$

$$4\,A_1 + 3\,A_2 \longrightarrow 2\,A_3 + 6\,A_4$$

Define stoichiometric coefficient

$$\nu_j = \begin{cases} < 0 & \text{reactant} \\ > 0 & \text{product} \end{cases}$$

$$\sum_j \nu_j A_j = 0 \quad \Big\}\cdot c \quad \text{can always scale}$$

$\nu_1 = -4 \quad \nu_2 = -3 \quad \nu_3 = 2 \quad \nu_4 = 6$

Define advancement / extent $\xi$

| | | | |
|---|---|---|---|
| $n_{10}$ | $n_{20}$ | $n_{30}$ | $n_{40}$ |
| $-4\xi$ | $-3\xi$ | $2\xi$ | $6\xi$ |
| $n_{10}-4\xi$ | $n_{20}-3\xi$ | $n_{30}+2\xi$ | $n_{40}+6\xi$ |

$$\boxed{N_j = N_{j0} + \nu_j \xi}$$

$$\boxed{F_j = F_{j0} + \nu_j \xi}$$

$\xi$ extensive (moles), can be $\gtrless 0$
moles/time

$\leftarrow \xi < 0 \quad \xi > 0 \rightarrow$

bounded $N_j = N_{j0} + \nu_j \xi \geq 0 \quad \forall j$

reactants, $\nu_j < 0$

$$\xi \leq -\frac{N_{j0}}{\nu_j}$$

products, $\nu_j > 0$

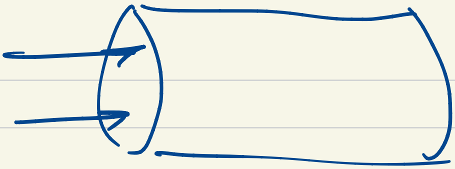
$$\xi \geq -\frac{N_{j0}}{\nu_j}$$

$$\xi_{max} = \min_{\text{reactants}} \left[ -\frac{N_{j0}}{\nu_j} \right] \qquad \xi_{min} = \max_{\text{products}} \left[ -\frac{N_{j0}}{\nu_j} \right]$$

$$\xi_{min} \leq \xi \leq \xi_{max}$$

ex $NH_3$

$O_2$



$$F_{NH_3,0} = 0.006 \text{ mol/s}$$

$$F_{O_2,0} = 0.012 \text{ mol/s}$$

Limiting agent?

$$NH_3: \quad \frac{-0.006}{-4} = 0.00125 \quad * \text{ limiting}$$

$$O_2: \quad \frac{-0.012}{-3} = 0.004$$

$$\xi_{max} = 0.00125 \text{ mol/s}$$

Max $O_2$ consumption?

$$F_{O_2} = 0.012 - 3(0.00125)$$
$$\approx 0.008 \text{ mol/s}$$

Fractional consumption?

$$\frac{F_{O_2,0} - F_{O_2}}{F_{O_2,0}} = \frac{0.012 - 0.008}{0.012} =$$

"conversion"

$\xi$ is extensive. Common to normalize to $\xi_{max}$

$$X = \xi / \xi_{max} = -\left(\frac{\nu_{lim}}{N_{lim,0}}\right)\xi$$

intensive conversion

Same notation extensible to multiple reactions:

$$4\,NH_3 + 3\,O_2 \longrightarrow 2\,N_2 + 6\,H_2O$$

$$4\,NH_3 + 5\,O_2 \longrightarrow 4\,NO + 6\,H_2O$$

$$-4A_1 - 3A_2 + 2A_3 + 6A_4 = 0$$

$$-4A_1 - 5A_2 + 4A_5 + 6A_4 = 0$$

$$\underbrace{\begin{pmatrix} -4 & -3 & 2 & 6 & 0 \\ -4 & -5 & 0 & 6 & 4 \end{pmatrix}}_{\underline{\nu}\ \text{stoichiometric matrix}} \underbrace{\begin{pmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \end{pmatrix}}_{\text{species vector}} = 0$$

$$\underline{\nu}\,\vec{A} = 0 \qquad \sum_j \nu_{ij} A_j = 0 \quad \forall i \text{ rxns}$$

Each rxn gets its own advancement $\xi_i$:

$$n_j = n_{j0} + \sum_i \nu_{ij} \xi_i$$

$$\vec{n} = \vec{n}_0 + \underline{\nu} \, \vec{\xi}$$

-or- $$F_j = F_{j0} + \sum_i \nu_{ij} \xi_i$$

Given all flows, can solve for advancements.

"Conversion" ambiguous when multiple rxns are possible.
Avoid, or define carefully.

extent-dependent compositions:

mole fraction

$$x_j, y_j = \frac{n_j}{\sum_j n_j} = \frac{n_{j0} + \nu_j \xi}{\underbrace{\sum_j (n_{j0} + \nu_j \xi)}_{n_{tot}}}$$

concentration

If reactor volume / volumetric flow rate is constant, easy:

$$c_j = n_j / V$$

Often deal w/ constant pressure:

$$V = \sum_j \bar{v}_j(T,P) \cdot n_j$$

$$= \sum_j \bar{v}_j (n_{j0} + \nu_j \xi)$$

If ideal gases, $\bar{v}_j \approx \frac{RT}{P} \quad \forall j$

$$V = \left(\frac{RT}{P}\right) \sum_j (n_{j0} + \nu_j \xi)$$

$$c_j = \frac{n_j}{V} = \left(\frac{RT}{P}\right) y_j$$

Often deal with cases in which there is a diluent in excess

$$n_{tot} = \sum_i n_i \text{ must include diluent}$$

$$\approx \text{constant}$$