KINETICS

RELATIVE REACTION RATES

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CHEMISTRY 165 // SPRING 2020

INTRODUCTION

What is chemical kinetics?

- Chemical kinetics: study of rates of reactions
- The reaction rate is a measure of the speed of a chemical reaction

Typically, the concentration is a convenient measure of the amount of reactant or product during the course of a reaction.

Consider a general chemical reaction

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$$

where A and B are reactants, C and D are products, and *a*, *b*, *c*, *d* are the mole coefficients. The rate of this reaction can be expressed as the change in the concentration of reactant A ($\Delta[A]$) over some amount of time (Δt)—in other words, how quickly we use up reactant A.

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t}$$

In principle, we could also measure the change in the concentration of reactant B or either of the products, C and D.

Q: *Does it matter what I measure though?*

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A: *No, because the balanced chemical equation tells us the stoichiometry of the chemical reaction, so we can always relate the rate at which we use up one reactant to the rate at which we use up another reactant, or to the rate at which we form one of the products, by using mole-mole ratios.*

GUIDED EXAMPLE

Consider the degradation of ammonia gas:

$$2\ NH_3\ (g) \rightarrow 1\ N_2\ (g) + 3\ H_2\ (g)$$

Write an expression that relates the rates of consumption of the reactants and the rates of the formation of the products.

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Let's start by defining the rate of the reaction in terms of the consumption of the reactant: NH_3

$$\text{Rate} = -\frac{\Delta[NH_3]}{\Delta t}$$

In most cases, we perform the reaction in a closed container such that the volume is constant throughout the reaction, so we are really only measuring the change in the number of moles. Now, let's use the balanced chemical equation to relate the rate of NH_3 consumption to the rate of H_2 formation:

By convention, we think of "rates" as positive values. So we put a negative sign since $\Delta[NH_3] < 0$ because reactants are consumed.

$$-\frac{\Delta[NH_3]}{\Delta t} \propto \frac{\Delta[N_2]}{\Delta t}$$

We do not put a negative sign since $\Delta[N_2] > 0$ because products are formed.

But how do we relate these rates together?

$$-\frac{\frac{\Delta n_{NH_3}}{V} \times \frac{1\ \text{mol}\ N_2}{2\ \text{mol}\ NH_3}}{\Delta t} = -\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = \frac{\Delta[N_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2]}{\Delta t}$$

This is how you can derive them.

These are the relative reaction rates!

PRACTICE PROBLEM 1

Consider the following unbalanced chemical equation:

$$PH_3\ (g) \rightarrow P_4\ (g) + H_2\ (g)$$

If, over a specific time period, 0.0081 mol PH_3 (g) are consumed in a 1.59 L container each second of the reaction, what is the rate of formation of P_4 (g)?

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Let's work in terms of concentration of the gas. Note that the concentration change is negative for reactants!

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From the balanced chemical equation, we know that for every 4 moles of PH_3 consumed, 1 mole of P_4 and 6 moles of H_2 are produced. Therefore, the relative rates are:

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Now we can solve for the rate of formation of P_4:

$$\frac{\Delta[\mathrm{P_4}]}{\Delta t} = -\frac{1}{4}\frac{\Delta[\mathrm{PH_3}]}{\Delta t} = -\frac{1}{4}\cdot\left[-0.0050_{94}\frac{\mathrm{M}}{\mathrm{s}}\right] = 0.0013\frac{\mathrm{M}}{\mathrm{s}}$$

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$$A + B \rightarrow C + D$$

After 25 seconds, you measure the rate of formation of C to be 2.97×10^{-6} M/s and the rate of formation of D to be 9.70×10^{-7} M/s. Based on this kinetic data, what is the mole-mole ratio between the two products: C and D?

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a A + *b* B → *c* C + *d* D

From this balanced equation, we can express the relative reaction rates as:

$$-\frac{1}{a}\frac{\Delta[\mathrm{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\mathrm{B}]}{\Delta t} = \frac{1}{c}\frac{\Delta[\mathrm{C}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\mathrm{D}]}{\Delta t}$$

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We are interested in the latter two terms, which deal with the two products formed:

$$\frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

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$$\frac{1}{c}\frac{\Delta[\mathrm{C}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\mathrm{D}]}{\Delta t}$$

We can rearrange this expression to find the mole-mole ratio between C and D, which is *c*/*d*:

$$\frac{c}{d} = \frac{\frac{\Delta[\mathrm{C}]}{\Delta t}}{\frac{\Delta[\mathrm{D}]}{\Delta t}} = \frac{2.97\times10^{-6}\,\frac{\mathrm{M}}{\mathrm{s}}}{9.70\times10^{-7}\,\frac{\mathrm{M}}{\mathrm{s}}} = 3.06 \approx 3$$