

# Elementary Notions about Chemical Kinetics

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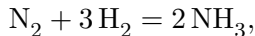
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Any chemical reaction can be written as  $0 = \sum_i \nu_i A_i$

Here

- ▶ The chemical formula of the  $i$ th species in the reaction is  $A_i$ .
- ▶  $\nu_i$  is the stoichiometric coefficient of the  $i$ th species.
- ▶  $\nu_i$ 's are positive for products and negative for reactants.

For example,



would be written in this notation as

$$0 = -\text{N}_2 - 3\text{H}_2 + 2\text{NH}_3.$$

## The extent of a chemical reaction is denoted as $\xi$

The number of moles of the  $i$ th species,  $n_i$ , is given by

$$n_i = n_i^0 + \nu_i \xi$$

where  $\xi$  is the extent/advancement of the reaction and  $n_i^0$  is the number of moles of the  $i$ th species initially, that is, when  $\xi = 0$ .

- ▶  $\xi$  is **positive** and has **units of moles**.
- ▶  $\xi$  is similar, but not identical, to the fractional dissociation used in equilibrium calculations.

Imagine performing the  $\text{N}_2$  and  $\text{H}_2$  reaction starting with 2 moles of  $\text{N}_2$  and 7 moles of  $\text{H}_2$ . For complete conversion to  $\text{NH}_3$  we have ( $\text{N}_2$  is the limiting reagent)

$$n_1 = 2 - 1 \times 2, \quad n_2 = 7 - 3 \times 2, \quad n_3 = 0 + 2 \times 2$$

$$\text{Rate of reaction} \equiv \frac{d\xi}{dt}$$

The rate of a reaction is the rate of the extent of the reaction with time

$$\frac{dn_i}{dt} = \nu_i \frac{d\xi}{dt}$$

$$\frac{d\xi}{dt} = \frac{1}{\nu_i} \frac{dn_i}{dt}$$

- ▶ Rate of a reaction is not defined until a balanced chemical equation is written.
- ▶ Rate of a reaction is positive, and generally decreases with time.

The rate of ammonia production from hydrogen and nitrogen may be written as

$$\frac{d\xi}{dt} = \frac{1}{-1} \frac{dN_2}{dt} = \frac{1}{-3} \frac{dH_2}{dt} = \frac{1}{2} \frac{dNH_3}{dt}$$

The rate of reaction is equal to the rate of disappearance of  $N_2$  or one-third the rate of disappearance of  $H_2$  or one-half the rate of formation of  $NH_3$ .

The relation of the rate of reaction to the rate of change of the mole numbers depends on the particular set of coefficients used in balancing the chemical equation.

There is no unique way to choose this set of coefficients

Rate of reaction is studied by following a measurable property

Select a property of the system,  $Z$ , with a known dependence on the mole numbers or concentrations.

$$Z = Z(n_1, n_2, n_3, \dots).$$

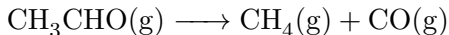
$$\frac{dZ}{dt} = \frac{\partial Z}{\partial n_1} \frac{dn_1}{dt} + \frac{\partial Z}{\partial n_2} \frac{dn_2}{dt} + \dots$$

$$\frac{dZ}{dt} = \left( \nu_1 \frac{\partial Z}{\partial n_1} + \nu_2 \frac{\partial Z}{\partial n_2} + \dots \right) \frac{d\xi}{dt}$$

$$\frac{d\xi}{dt} = \frac{\frac{dZ}{dt}}{\left( \nu_1 \frac{\partial Z}{\partial n_1} + \nu_2 \frac{\partial Z}{\partial n_2} + \dots \right)}$$

## Total pressure is a measurable quantity for gas phase reactions

Consider conducting the reaction



starting from only acetaldehyde in a constant volume vessel.

$$n_1 = n^0 - \xi; \quad n_2 = 0 + \xi; \quad n_3 = 0 + \xi.$$

Then

$$p = (n_1 + n_2 + n_3) \frac{RT}{V} = (n^0 - \xi + \xi + \xi) \frac{RT}{V} = (n^0 + \xi) \frac{RT}{V}$$

$$\frac{dp}{dt} = \frac{RT}{V} \frac{d\xi}{dt} \quad \text{or} \quad \frac{1}{V} \frac{d\xi}{dt} = \frac{1}{RT} \frac{dp}{dt}$$

Use the formula from the previous slide to arrive at the same result.

Reaction Rate is dependent on

- ▶ Temperature
- ▶ Pressure
- ▶ concentrations of various species involved in the reaction,  $c_i$
- ▶ concentrations of the catalysts or inhibitors that may not appear in the overall reaction,  $c_x$

Rate law for the reaction

$$\frac{d\xi}{dt} = V f(T, P, c_i, c_x) + AF(T, P, c_i, c_x).$$

is also proportional to the volume of the phase,  $V$ , for a homogeneous reaction, and to the area of the active surface,  $A$ , for a surface reaction. Here,  $f(T, P, c_i, c_x)$  and  $F(T, P, c_i, c_x)$  are functions to be determined experimentally.



For homogeneous reactions

$$\frac{d\xi}{dt} = V f(T, P, c_i, c_x)$$

The rate of the reaction per unit volume, the specific rate,  $d(\xi/V)/dt$

$$\frac{d\left(\frac{\xi}{V}\right)}{dt} = f(T, P, c_i, c_x).$$

If the volume does not change with time, this equation takes the form

$$\frac{d(\xi/V)}{dt} = \frac{1}{\nu_i} \frac{d(n_i/V)}{dt}$$
$$\frac{1}{V} \frac{d\xi}{dt} = \frac{1}{\nu_i} \frac{dc_i}{dt}$$

Rate laws often have a power law dependence on concentration

$$\frac{1}{V} \frac{d\xi}{dt} = k c_A^\alpha c_B^\beta c_C^\gamma \dots$$

Concentrations of the species are  $c_A$ ,  $c_B$ , and  $c_C$ , and  $k$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$  are constants.

The constant  $k$  is the **rate constant of the reaction**, or the **specific rate of the reaction**, since  $k$  is the rate if all the concentrations are unity. In general the **rate constant depends on temperature and pressure**.

The constant  $\alpha$  is the **reaction order** with respect to A,  $\beta$  is the reaction order with respect to B, and  $\dots$ . The **overall reaction order is  $\alpha + \beta + \gamma$** .