**Kinetics - Part 1**

**Why?**

Chemical kinetics is the study of the rates of chemical reactions; i.e., how fast reactants are converted into products. Experimentally determined rate law expressions show how the rate of a reaction depends upon the concentrations of the reactants and sometimes the products, too. This knowledge can be used to gain insight into the detailed molecular pathway (the mechanism) by which the reaction occurs. Understanding the mechanism allows chemists to devise ways of improving or modifying a chemical reaction for useful purposes.

**Learning Objectives**

•Understand how reaction rate is defined and measured

•Understand the meaning of experimentally determined rate law expressions

•Be able to define the rate of any reaction on the basis of the stoichiometry

•Given a rate law expression, predict how reaction rate changes with changes

 in reactant concentrations

•Be able to determine the form of the differential rate law expression for a

 reaction from kinetic data

•Be able to calculate a rate constant value, with the proper units, from kinetic data

**Defining Rate of a Reaction**

Rate is a change in some value over a period of time. The rate of a reaction is generally expressed in terms of the change in concentration (or pressure for a gas) of reactants or products with time. The rate of a chemical reaction is not a constant. Rather, in most cases, it changes continuously. Generally, a reaction starts with a fast rate and becomes slower as it progresses. Moreover, the rates of chemical reactions are influenced by temperature, being faster at higher temperature.

We can define the **rate of a reaction** on the basis of the **disappearance of any reactant** or **appearance of any product**. But regardless of the species we choose to follow, for any point in the course of the reaction, ***rate*** *should be defined so as to give the same number, regardless of the particular reactant or product on which it is based.* To accomplish this, we must define rate on the basis of the stoichiometry of the reaction. Also, we will conventionally define rate as a positive number, regardless of whether we are following the disappearance of a reactants or the appearance of products over time.

Suppose we want to define the rate of the reaction:

**Cl2(g) + 2NO(g) 🡪 2NOCl(g)** over time at 2300K.

Starting with 1.00 M Cl2, 2.00 M NO, and no NOCl in a vessel of fixed volume. *(Note that the initial concentrations need not be in the stoichiometric ratio.)*

As the reaction proceeds, the concentrations of reactants, Cl2(g) and NO(g), will decline, and the concentration of the product, NOCl(g), will increase, as shown in the following plot.



If we follow the change in concentration of Cl2 over some small period of time,

**t = t2 – t1**, say from **t1**, = 5 x 10-5 s to **t2** = 10 x 10-5 s.

The rate of change in concentration of chlorine gas will be

Rate = -[Cl2] = -([Cl2] 2 – [Cl2]1)

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The bracket notation, such as [Cl2], means “concentration of” in mol/L units. Since Cl2 is being consumed in the reaction, [Cl2] will be negative. We add a negative sign in front of [Cl2] so that rate will always be defined as a positive number.

If we follow the change in NO concentration instead, we could write

 -[NO] = -([NO] 2 – [NO]1)

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However, since two moles of NO are used for every one mole of Cl2, this change would be two times as great as the change in chlorine concentration over the same period of time. To avoid ambiguity and to make ratebe numerically the same, regardless of which species we follow, we divide the change in NO concentration with time by two. Thus,

Rate = -1/2[NO] = -1/2([NO] 2 – [NO]1)

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If we followed the build-up of NOCl instead, we would define rateon this basis as

Rate = +1/2[NOCl] = +1/2([NOCl] 2 – [NOCl]1)

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Note that we have a positive factor of 1/2, because [NOCl] is increasing at

twice the rate of decline in [Cl2] over any time period.

**We define *Rate of Reaction* in terms of the stoichiometry of the reaction.**

For a general reaction of the for ***a*A + *b*B 🡪 *c*C + *d*D**

Rate of Reaction = - 1[A] = - 1[B] = + 1[C] = + 1[D]

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Any of these definitions is equivalent to the others and gives the same numerical value for a particular interval of time. *Rate* will start out high at the beginning of the reaction and get smaller as the reaction continues.

**Key Questions**

1. Answer the following questions using the reaction below:

2 N2O5(*g*) 🡪 4 NO2(*g*) + O2(*g*)

At a particular point in the course of the reaction above, the rate of disappearance of N2O5(*g*) was found to be -1.16 x 10–4 mol/L.s

1. What is the rate of appearance of NO2(*g*) at this point?
2. What is the rate of appearance of O2(*g*)?
3. What is the rateof the reaction at this point?