

A Chemistry Toolkit

Barry Linkletter

University of Prince Edward Island

Abstract

This short document contains a brief and incomplete list of mathematical statements and formula that may be useful to students in the chemistry 112 course. This is not a review of the course. It is simply an overview of the math involved with the core concepts of the course. Many definitions and important ideas have been left out. If you have anything that you wish to add, please write it up and send it to me.

Contents

1	The Ideal Gas Law	2
2	Concentration	2
3	Reaction rates	2
4	Equilibrium	5
5	Acid Equilibrium	7

1 The Ideal Gas Law

A gas that has ideal behavior (most small gas molecules will be nearly ideal in behavior at reasonable pressures and temperatures) can be described by the ideal gas law.

$$PV = nRT$$

The gas constant, R , that is generally used has units of pressure and volume. Typically, $R = 0.0821 \frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}$ is used most often in this course.

2 Concentration

The most common forms of concentration used in this course are units of moles/L (**Molarity**) to describe concentrations of molecules in the volume of a solution or of gas molecules in the volume of their container. Another way to describe concentration of gas molecules in the volume of a container is to use the pressure of the gas (**Partial Pressure**).

2.1 Molarity

$$c = \frac{n}{V}$$

2.2 Partial Pressure

$$P = \frac{n}{V} \cdot RT$$

We see here that partial pressure is the molarity of the gas in the container, modified by the gas constant and temperature.

3 Reaction rates

For a simple reaction, rate is the change in concentration of a reactant or product with time. This change is often expressed as the first derivative of concentration w.r.t. time.

$$v = \frac{-d[\text{reactant}]}{dt} = \frac{d[\text{product}]}{dt}$$

3.1 Defining Reaction Rate

The reactant is disappearing so its rate of change is negative, the product is appearing so its rate of change is positive. If there is higher order stoichiometry in the reaction then this will be taken into account in the rate definition.

Tab. 1: Definitions Of Rate In Some Example Reactions

	Reaction	Rate, v
1	$A \rightarrow B$	$-\frac{d[A]}{dt}, \frac{d[B]}{dt}$
2	$A \rightarrow 2B$	$-\frac{d[A]}{dt}, \frac{1}{2} \cdot \frac{d[B]}{dt}$
3	$2A \rightarrow B$	$-\frac{1}{2} \cdot \frac{d[A]}{dt}, \frac{d[B]}{dt}$
4	$A + B \rightarrow C$	$-\frac{d[A]}{dt}, -\frac{d[B]}{dt}, \frac{d[C]}{dt}$
5	$A + B \rightarrow 2C$	$-\frac{d[A]}{dt}, -\frac{d[B]}{dt}, \frac{1}{2} \cdot \frac{d[C]}{dt}$
6	$A + 2B \rightarrow C$	$-\frac{d[A]}{dt}, -\frac{1}{2} \cdot \frac{d[B]}{dt}, \frac{d[C]}{dt}$

3.2 Rate Laws

The rate of a reaction is proportional to the concentration of the reactants. The rate law defines the relationship between reactant concentrations and rate. The rate law does not necessarily correlate to the overall reaction equation in multi step reactions.

Tab. 2: Example Rate Laws for Some Reaction Schemes

	Reaction	Example Rate Law
1	$A \rightarrow B$	$v = k \cdot [A]$
2	$A \rightarrow 2B$	$v = k \cdot [A]$
3	$2A \rightarrow B$	$v = k \cdot [A]^2$
4	$A + B \rightarrow C$	$v = k \cdot [A] \cdot [B]$
5	$A + B + C \rightarrow D + E$	$v = k \cdot [A] \cdot [B]^2$
6	$A + 2B \rightarrow C$	$v = k \cdot [A] \cdot [B]$

Observe that in the case of the last two reaction equations in Table 2 do not correspond exactly to the reaction equation. I also used different expression to describe the rate. Using the rate laws we can determine the rate of a reaction or we can determine the **rate constant**, k , for a reaction under the given conditions.

3.3 Integrated Rate Laws

If we wish to determine the concentration of a reactant or product over time we must integrate the rate law (recall that the rate is the first derivative of concentration w.r.t. time, the antiderivative of rate would be an expression for concentration at a given time.) In our course we only considered the two simplest cases: a simple first order reaction and a simple second order reaction wherein both reactants were identical in concentration.

Tab. 3: Integrated Rate Laws

	Rate Law	Integrated Rate Law
1	$v = k \cdot [A]$	$[A] = [A]_0 - k \cdot t$
2	$v = k \cdot [A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + k \cdot t$

3.4 Activation Energy and Rate

The rate of a reaction is controlled by the energy barrier that must be overcome between initial and final states. A simple way to model this system is the Arrhenius equation.

$$k = Ae^{-\left(\frac{E_a}{R \cdot T}\right)}$$

A linear version of the Arrhenius equation can be constructed by applying a log function. A plot of $\ln k$ vs. $1/T$ will be able to find E_a from the slope of the line.

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}$$

4 Equilibrium

Concentrations of reactants and products in a reaction will change until the rate at which reactants are converted to products equals the rate at which products are converted to reactants. In systems where the reverse reaction has a significant rate constant we will reach an equilibrium state where measurable concentrations of both reactants and products are present. At equilibrium, concentrations are no longer changing.

The concentrations observed at equilibrium are defined by an equilibrium constant for the reaction under the given conditions. The **equilibrium constant**, K_{eq} , is the product of the concentration of products divided by the product of the concentrations of reactants.

$$K_{eq} = \frac{[products]}{[reactants]}$$

When defining the K_{eq} we only consider reactants and products whose concentrations are changing significantly. Solids always have a constant concentration and are not included in the equilibrium expression. Solvent is also considered to be constant in concentration if it is involved in the chemical reaction.

Table 4 on the following page shows examples of equilibrium equations.

Tab. 4: Example Equilibrium Constants For Some Reaction Schemes

	Reaction	Example Equilibrium
1	$A \rightleftharpoons B$	$K_{eq} = \frac{[B]}{[A]}$
2	$A \rightleftharpoons 2B$	$K_{eq} = \frac{[B]^2}{[A]}$
3	$2A \rightleftharpoons B + C$	$K_{eq} = \frac{[B] \cdot [C]}{[A]^2}$
4	$A + B \rightleftharpoons C$	$K_{eq} = \frac{[C]}{[A] \cdot [B]}$
5	$A_{(s)} + B \rightleftharpoons C$	$K_{eq} = \frac{[C]}{[B]}$
6	$A + B \rightleftharpoons C_{(s)} + D$	$K_{eq} = \frac{[D]}{[A] \cdot [B]}$
7	$A_{(s)} \rightleftharpoons B + C$	$K_{eq} = [B] \cdot [C]$
8	$A \rightleftharpoons B + C$	$K_{eq} = \frac{[B] \cdot [C]}{[A]}$
9	$A_{(l)} \rightleftharpoons A_{(g)}$	$K_{eq} = [A]_{(g)}$

Reaction 7 in Table 4 is the equilibrium for solubility of a typical salt like NaCl. The **solubility product**, K_{sp} , is just the equilibrium constant between the ions being solvated in solution and being in a crystalline solid.

Reaction 8 in Table 4 is the kind of equilibrium that we see in acid-base equilibria. Read on...

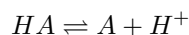
Reaction 9 in Table 4 is the equilibrium for vapour pressure over a liquid. The liquid does not change in concentration as it evaporates. Since the gas can expand to take up the volume of the container, it can change in volume.

5 Acid Equilibrium

This is no different than the equilibrium systems described above. An acid dissociates by donating its proton to the solvent, water. We usually ignore the water (but remember it is there) in the acid dissociation reaction and equilibrium definition.

5.1 Acid Dissociation

We usually refer to the **equilibrium constant for acid dissociation** as K_a . for



we know that

$$K_a = \frac{[A] \cdot [H]}{[HA]}$$

This is just an equilibrium as we have seen before. It is no different. We can use this to calculate the dissociation of weak acids in water. We can calculate the amount of acid concentration, $[H]$, needed to achieve a given ratio of $[A]/[HA]$. We can use an observed ratio of $[A]/[HA]$ at a given value of $[H]$.

5.2 pH

We often deal with concentrations of hydronium ion from $10^{-2} M$ to $10^{-12} M$. This is a huge range. It is more convenient to discuss hydronium concentration in terms of powers of 10. A \log_{10} scale is used — it is the pH scale.

$$pH = -\log [H_3O^+]$$

can also be described as

$$pH = -\log [H^+]$$

5.3 pKa

K_a values also have a very, very large range — from 10^{-50} to 10^7 . Such a large range is best expressed on a logarithmic scale so we use the p function.

$$pK_a = -\log [K_a]$$

5.4 The Hendersson-Hasselbach Equation

A simple rearrangement of the K_a expression and the application of the p function gives a very convenient form of the acid equilibrium. . .

$$pH = pK_a + \log \frac{[A]}{[HA]}$$