

# Topics in Chemistry

Many aspects of chemistry are not amenable to OOM estimation. For example, estimating the net energy change associated with a chemical reaction requires taking the difference between two numbers. If these two numbers are similar, the OOM result is indistinguishable from zero, which is not very helpful. As always, we'll try to focus on understanding fundamental processes in chemistry and make OOM estimations of relevant quantities.

## Definitions

**Elementary reaction:** A reaction that describes an actual event in nature as opposed to being the net result of a number of elementary reactions. In other words, an elementary reaction describes the components of an actual collision event (and subsequent reaction). Almost all elementary reactions involve one or two reactants (with one class of exceptions) since it is typically very difficult to get more than two molecules to collide simultaneously. Therefore, we'll consider a generic elementary reaction  $A + B \rightleftharpoons C + D$ , where A and B are reactants, and C and D are products, but the reaction can be reversed.

**Equilibrium constant:** Describes the equilibrium state of a reversible reaction, i.e. the relative amounts of reactants and products. For our elementary reaction, the equilibrium constant  $K$  is defined as:

$$K = \frac{\prod \text{products}}{\prod \text{reactants}} = \frac{[C][D]}{[A][B]} \quad (1)$$

where  $\prod$  represents "the product of" and the square brackets  $[ ]$  denote concentration in units such as mol/L.

**Reaction rate constant:** The constant of proportionality in a reaction rate equation. For example, for the generic bimolecular elementary reaction  $A + B \rightarrow C + D$ , the reaction rate equation would be  $\frac{d[A]}{dt} = -k[A][B]$  where the reaction rate constant  $k$  must be empirically determined. The negative sign tells you that A is being consumed by the reaction.

**Enthalpy:** Enthalpy  $H$  is most easily thought of as heat energy, although strictly speaking it's only heat energy in a system that is at constant pressure.

**Entropy:** Entropy  $S$  has many definitions, many of which are applicable under specific circumstances. We'll think of S as a measure of disorder, i.e. higher values of S are systems with greater disorder. A similar but slightly different view is that S represents the number of possible states for a system. This latter view explains why my bedroom is rarely neat. There are very few ways in which my bedroom, with all the clothes, books, etc. can be considered tidy. There are many configurations in which it would be

considered messy. A spontaneous change is unlikely to result in a more orderly room (it's uncommon for a thrown t-shirt to end up folded and in the right drawer of my dresser), thus over time things get messy.

**Gibbs Free Energy  $G$ :**  $G = H - TS$ , or equivalently,  $\Delta G = \Delta H - T\Delta S$  where it has been assumed that  $T$  is approximately constant for the reaction of interest (reasonable since  $S$  can vary by orders of magnitude, whereas  $T$  tends to vary over a much smaller range).  $G$  can be thought of as the energy relevant to chemical reactions, and thus involves both enthalpy and entropy. A reaction is *spontaneous* if  $\Delta G < 0$  for a reaction, i.e. it can occur without the input of energy. To satisfy this requirement, a reaction can either stabilize molecules (leading to  $\Delta H < 0$ ) or it can create greater disorder ( $\Delta S > 0$ ), or both.

**Unimolecular reaction:** A chemical reaction where there is only one reactant.

**Bimolecular reaction:** A chemical reaction where two molecules interact.

## Enthalpies

Chemical bonds have a typical strength of, say,  $5 \text{ eV} = (5 \text{ eV}) (2 \cdot 10^{-19} \text{ J/eV}) (6 \cdot 10^{23} \text{ mol}^{-1}) = 6 \cdot 10^4 \text{ J/mol}$  or  $60 \text{ kJ/mol}$ . Since molecules possess a number of bonds, this yields enthalpies of formation (energy required to tear separate all constituent atoms of a molecule from each other) with typical values of a few hundred  $\text{kJ/mol}$ . The enthalpy of *reaction* is a *difference* in the enthalpies of formation, and therefore also have a typical magnitude of  $100 \text{ kJ/mol}$  (either positive or negative).

## Reactions Rates

Truly *unimolecular* reaction rates (versus ones where there is a implicit second reactant such as sunlight) are governed by a decay constant in exactly the same way as radioactive decay, so we won't discuss this any further. The **maximum bimolecular** reaction rate is governed by the rate of collision between the molecules. The description of this collision rate depends on whether we are discussing a liquid or a gas. We'll do both of these.

### Maximum Gas Phase Reaction Rates

For simplicity, we assume that each molecule can be described as a sphere, and that inter-molecular potentials are negligible, i.e. molecules are completely non-interacting, like billiard balls. The collision rate between two gases labelled 1 and 2,  $z_{12}$ , in units of collisions per unit volume per unit time is:

$$z_{12} \sim \pi d_{12}^2 v_{12} n_1 n_2 \quad (2)$$

where  $d$  is diameter,  $v$  is velocity, and  $n$  is concentration in units of number per volume. The appropriate diameter for the problem is  $d_{12} = d_1 + d_2$ , and the characteristic velocity is given by  $v_{12}^2 = v_1^2 + v_2^2$ , which implicitly assumes that the mean angle of collision is 90 degrees. Recall from earlier in the class that gas velocities are typically on the order of the sound speed, and scales as  $M^{-1/2}$ , so lighter gases have higher sound speeds at the same temperature. Thus, the reaction rate constant in this scenario is given by:

$$k_{12} = \pi d_{12}^2 v_{12} \quad (3)$$

as determined by comparison of Eq. 2 and the definition of the reaction rate constant. Now we OOM estimate these values. We choose a typical value of  $d_{12}$  to be 2 Å, and a typical sound speed is 500 m/s (but can be somewhat higher if very light gases are involved, such as hydrogen or helium). This then yields a **characteristic maximum bimolecular gas reaction rate constant** of  $10^{-16} \text{ m}^3 \text{ s}^{-1}$ , which can be attained if *every* collision yields a reaction.

Example: lifetime of O(<sup>1</sup>D) in atmosphere; Lysol spray can

## Maximum Liquid Phase Reaction Rates

In liquids, the diffusivity of a molecule is a useful way to think about reaction rates. One way to think of diffusivity of a molecule is:

$$D \sim \frac{d\langle r^2 \rangle}{dt} \quad (4)$$

where  $\langle r^2 \rangle$  is the mean square displacement, the mean being the average of many realizations of the same Brownian experiment (why didn't we use  $\langle r \rangle$  instead?). Thus, a molecule with a higher diffusivity will tend to experience more collisions due to its greater range of motion, i.e. it is the equivalent to velocity in Eq. 2. Using dimensional analysis, then, we'll determine the analogous equation for liquids as Eq. 3 is to gases. The rate constant  $k_{12}$  has units of  $\text{m}^3 \text{ s}^{-1}$ , and we already have a diffusivity with units of  $\text{m}^2 \text{ s}^{-1}$ , so all we have left is to determine a length scale. Since we're talking about collision of molecules, the obvious length scale is  $d_{12}$ . So this leaves us with the OOM estimate of:

$$k_{12} \sim d_{12} D_{12} \quad (5)$$

where the appropriate diffusivity  $D_{12} = D_1 + D_2$  just as for  $d_{12}$ . It turns out that the constant of proportionality is actually  $2\pi$ , a factor we can choose to ignore or not since it's somewhere on the border of being important in an OOM sense. We'll ignore it for now. There is another factor that's unknown, and is known as the electrostatic factor  $f$ . If both colliding molecules have a net charge, then we have to increase (decrease) the collision rate if the molecules have opposite (same) signed charges. This factor depends on a number of factors, such as the qualities of the solvent medium in which the reaction is occurring, the magnitude of the charges, and temperature. Typical values are between a factor of 3 and 10 faster or slower.

Chemists prefer units of moles to units of number, so we can throw in Avogadro's constant  $N_A$  to convert the rate constant to chemistry-happy units. This leaves us with the full equation:

$$k_{12} = 2\pi f d_{12} D_{12} \sim N_A d_{12} D_{12} \quad (6)$$

where we'll just stick to the second estimate in Eq. 6 for simplicity. Note that the units for  $k_{12}$  are  $\text{m}^3 \text{s}^{-1} \text{mol}^{-1}$ , and therefore the appropriate concentrations units for  $n_1$  and  $n_2$  are  $\text{mol m}^{-3}$ . If we use a typical diffusivity in liquids of  $10^{-9} \text{ m}^2 \text{s}^{-1}$ , and again  $d_{12}$  to be  $2 \text{ \AA}$ , we get **a characteristic maximum bimolecular liquid reaction rate constant** of  $10^{-19} \text{ m}^3 \text{s}^{-1}$  or in chemistry units,  $10^5 \text{ m}^3 \text{s}^{-1} \text{mol}^{-1}$ . This value can be higher for smaller molecules (higher diffusivity). Note that this is roughly 3 orders of magnitude smaller than the reaction rate in gases, although absolute reaction rates also must factor in the reactant concentrations, which can be much higher in liquids than in gases.

We'll continue our OOM tour of rate constants after a brief detour into equilibrium.

## Equilibrium Constants

Now let us revisit the idea of an equilibrium constant. Consider the reaction:



where the forward reaction  $A + B \rightarrow C + D$  has characteristic reaction rate  $k_{AB}$  as defined by:

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k_{AB} [A] [B] \quad (8)$$

and the backward reaction  $C + D \rightarrow A + B$  has a characteristic reaction rate  $k_{CD}$  defined similarly. At equilibrium, the rates of the forward and backward reactions must be the same. This implies that:

$$k_{AB} [A] [B] = k_{CD} [C] [D]$$

which can be rearranged to give:

$$\frac{k_{AB}}{k_{CD}} = K = \frac{[C][D]}{[A][B]} \quad (9)$$

If you compare Eqs. 1 and 9, you'll see that the equilibrium constant  $K$  can be written as a ratio of rate constants! Thus, equilibrium constants are at heart derived from combinations of rate constants. The relationship between  $K$  and  $\Delta G$  for a reaction can be shown to be (I'm not going to derive it here):

$$\Delta G_{rxn} = -RT \ln K \quad (10)$$

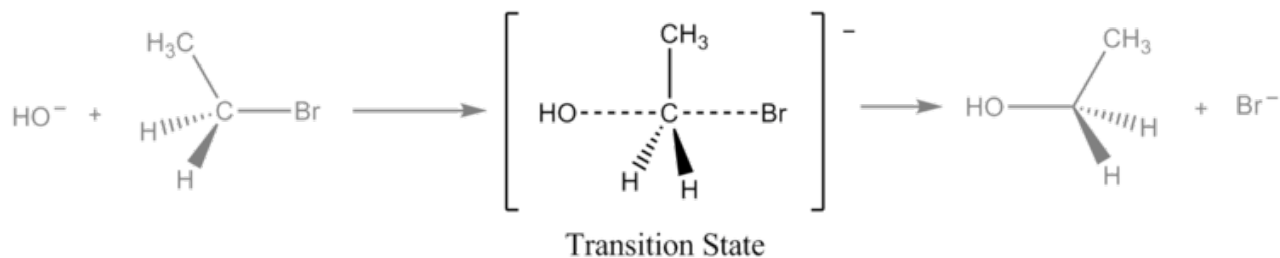


Figure 1: Simple example of transition state theory.

From this equation, we can infer that equilibrium favors the products (i.e.  $K \ll 1$ ) if  $\Delta G_{rxn}$  is *large* and *negative*. Physically, this can be interpreted as the *products* having a *lower energy state*, and therefore *more stable*, and thus equilibrium will favor the products. Similarly, equilibrium favors the reactants (i.e.  $K \gg 1$ ) if  $\Delta G_{rxn}$  is large and *positive*, in which case the reactants have a lower energy state. We'll use this relationship below.

Now we'll continue the discussion of rate constants.

## Transition State Theory

*Transition state theory* (also known as *activated complex theory*) describes how chemical reactions occur. Recall that chemical reactions involve the re-arrangement of atoms. TST is normally conceptualized by the pictures shown in Figs. 1 and 2.

Transition state theory is particularly useful in making certain kinds of predictions, particular those associated with reaction rates. It should be viewed as a theory, however, with limits to its applicability, rather than physical fact.

Consider the generic reaction:



The argument goes that when two reactants A and B collide with each other, they combine to form a high energy entity termed an *activated complex* or *transition state*. According to this theory, **this reaction is an equilibrium reaction**:



where the superscript  $\ddagger$  is customarily used for denoting the activated complex. This reaction has an equilibrium constant  $K^\ddagger$  such that

$$K^\ddagger = \frac{[AB^\ddagger]}{[A][B]} \quad (13)$$

The formation of products from this transition state

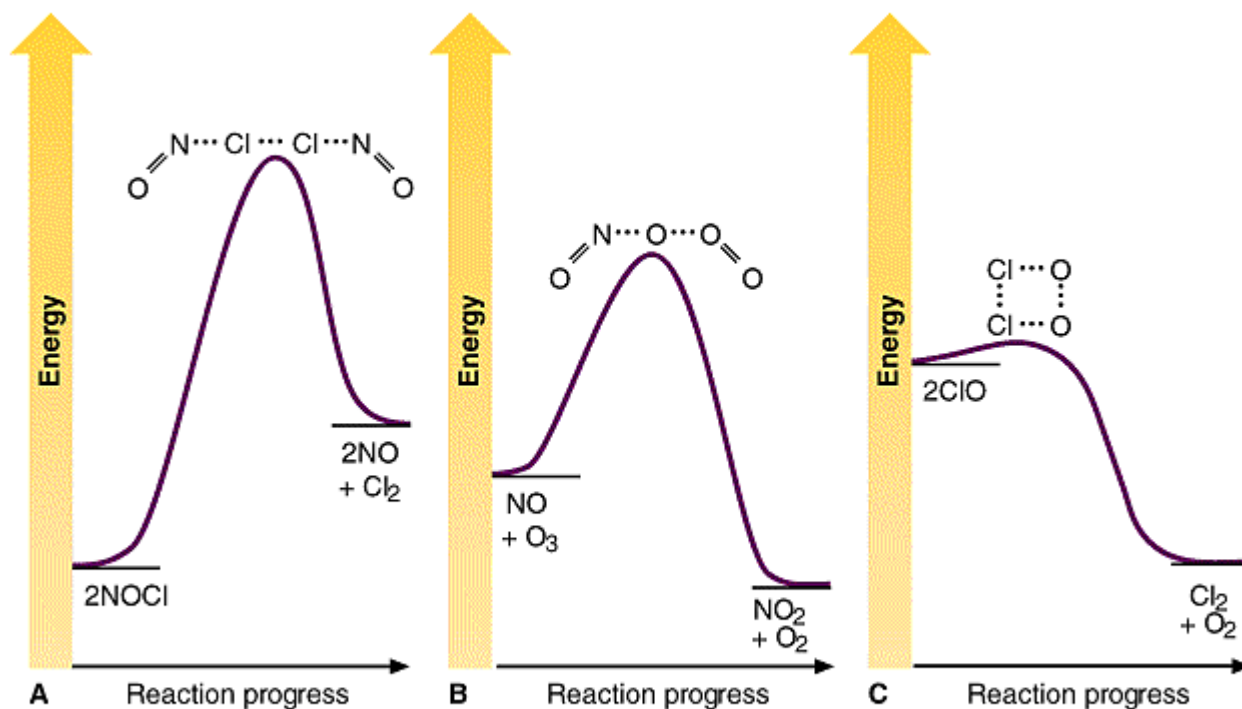


Figure 2: Energetics of three different reactions. At the peak of each energy curve is a molecular arrangement termed the transition state (or activated complex) for the reaction. You can see that its arrangement is in between those of the reactants and products. The energy barrier (which is related to the *rate* of reaction) is independent of the *net energy difference*, as illustrated by panels B and C. Also, the net energy difference can be positive (left panel), which is an *endothermic* reaction, or negative (middle and right panels), which is an *exothermic* reaction.



is **assumed to be irreversible** and therefore has a rate expression

$$\frac{d[\text{products}]}{dt} = k_{AB^\ddagger} [AB^\ddagger] \quad (15)$$

where it is generally assumed that the rate constant for the adduct to decay into products is:

$$k_{AB^\ddagger} = \frac{kT}{h} \quad (16)$$

where  $k$  is Boltzmann's constant and  $h$  is Planck's constant. The explanation for this requires statistical mechanics (if you want to see a derivation, see *Physical Chemistry: A Molecular Approach* by McQuarrie and Simon, 1997, Section 28-8). Substituting Eqs. 13 and 16 into Eq. 15 yields:

$$\frac{d[\text{products}]}{dt} = \frac{kT}{h} K^\ddagger [A][B] \quad (17)$$

and therefore the **overall rate constant** of our generic reaction Eq. 11 is (c.f. Eq. 8):

$$k_{AB} = \frac{kT}{h} K^\ddagger \quad (18)$$

Taking this one step further, recall Eq. 10:

$$\Delta G_{rxn} = -RT \ln K$$

which we can solve for  $K$  and substitute into Eq. 18 to yield:

$$k_{AB} = \frac{kT}{h} K^\ddagger = \frac{kT}{h} \exp\left(\frac{-\Delta G^\ddagger}{RT}\right) = \frac{kT}{h} \exp\left(\frac{-(\Delta H^\ddagger - T\Delta S^\ddagger)}{RT}\right)$$

yielding

$$k_{AB} = \frac{kT}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(\frac{-\Delta H^\ddagger}{RT}\right) \quad (19)$$

Physically, this says that the our generic reaction proceeds more slowly (smaller  $k_{AB}$ ) if the **creation of the activated complex** is associated with a *large negative change in entropy* and/or a *large positive change in enthalpy*, i.e. if the activated complex *is highly ordered* or has a *high energy state*, which makes sense.

## Arrhenius and Reaction Rate Dependence on Temperature

Arrhenius proposed that rate constants vary with temperature as:

$$k_{rxn} = A \exp\left(\frac{-E_a}{RT}\right) \quad (20)$$

where he defined  $E_a$  as the *activation energy* for the reaction and  $A$  is some pre-exponential factor thought to be independent of temperature. This was based on observations of various reactions.

Comparing Eqs. 20 and 19, transition state theory predicts that:

$$A = \frac{kT}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \text{ and } E_a = \Delta H^\ddagger$$

which in fact has some dependence on  $T$ , although it is not a strong effect since  $T$  tends not to vary by much in the course of most reactions. Arrhenius went further and proposed a rule of thumb where a doubling of the reaction rate occurs for every 10 K increase in temperature. From Eq. 20, this implies that around room temperature,  $E_a \sim 50$  kJ/mol, which is order of magnitude very reasonable.