Lecture 3, Class 3 (Lecture Notes):
Chemical Kinetics versus Equilibria (Chapter 1)

Spontaneity and Activation Energy

- Water is very stable – *e.g.* see the surface of the planet – suggesting that the reaction $2H_2 + O_2 \rightarrow 2H_2O$ has a significantly negative standard free energy of reaction (ΔG_r), which it does. However, if we mix hydrogen and oxygen together, they will not react until we provide a spark.
- This observation can be understood by postulating that reactant molecules must first attain the necessary activation energy (($\Delta G^{\#}$), to achieve a transition state, before they can "collapse" to products.
- Normally, in the chemistry laboratory we impart the activation energy to a few of the reacting molecules by heating the reaction mixture. After this, the release of free energy associated with product formation tends to sustain the reaction.
- Spontaneous reactions must, of course, have very low activation energies; while conversely, slow reactions have higher activation energies.
- Catalysts, which accelerate chemical reactions, work by lowering the activation energies of reactions. Enzymes (proteins, often oligomeric, often containing cofactors) are biological catalysts.
- Where the decomposition rate is comparable to or slower than the physical processes redistributing a particular contaminant in the environment, the chemical kinetics will be more important for transport and fate modeling than equilibrium considerations.

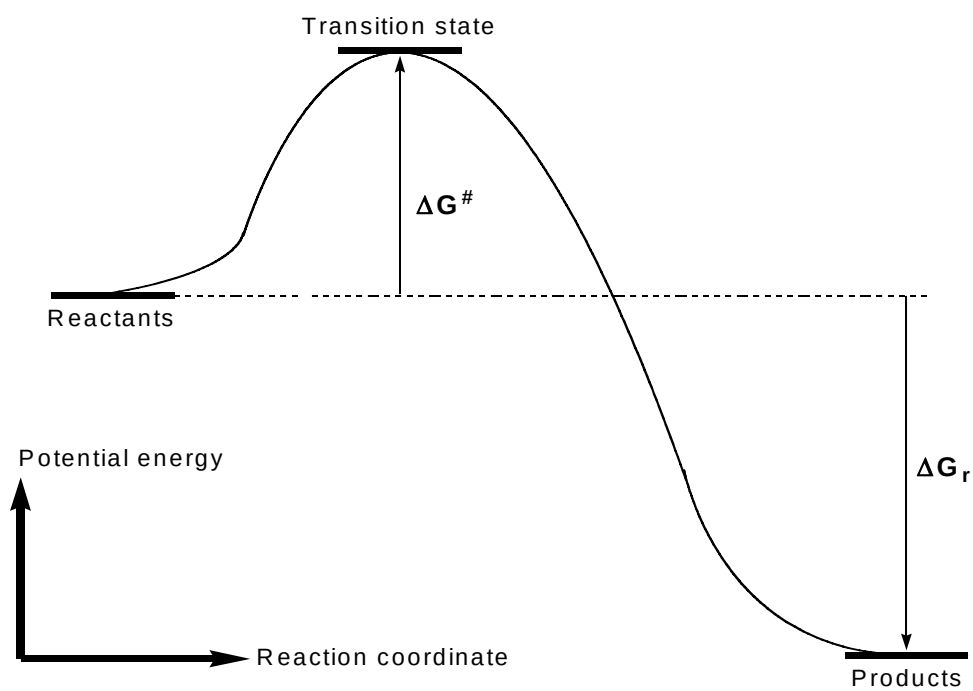

Figure 3.1 Difference between free energy of reaction and activation energy.

Dynamic Equilibria

- Chemical equilibria are dynamic, not static, so they too must have relatively low activation energies in both directions.
- Catalysts do not affect the equilibrium constant, but they do speed up the rate at which equilibrium is attained.
- Where the decomposition rate is faster than the physical processes redistributing a particular contaminant in the environment, consideration of the relevant equilibria will be more important for transport and fate modeling than the chemical kinetics.

Rate Law Equations

- Generally, you cannot deduce the rate law for a chemical reaction from its chemical equation, even if it is correctly balanced; both the rate constant(s) and the exponent(s) must be determined by experiment.

For the general chemical reaction:

$$aA + bB + cC + \ldots\ldots \rightleftharpoons pP + qQ + rR + \ldots\ldots$$

the rate law will be given by:

$$-dA/dt = k[A]^x[B]^y[C]^z\ldots\ldots$$

where the coefficients x, y, z,...etc. can take integer (including zero) and non-integer values.

For instance, the catalytic decay of phosphane on tungsten: $-d[PH_3]/dt = \mathbf{k_0}$

and the rate of HBr formation at high $[Br_2]$: $d[HBr]/dt = \mathbf{k_{3/2}[H_2][Br_2]^{1/2}}$

Scheme 3.2 General form of the rate law and some cautionary examples.

- However, in practice, most of the time you will be dealing with net first- or second-order processes and with some experience, you will often be able to correctly guess the form of the rate law and only need to establish the relevant rate constant(s).

First-order Reactions

- Radioactive decay is a classic example of a first-order process, which does not require intermolecular collisions to proceed: $\boldsymbol{dC/dt = -k_1 \bullet C}$; where C is the concentration of the parent compound and the units of the first-order rate constant (k_1) are s^{-1}.
- The half-life of a first order process is obtained from the rearranged and integrated form of the rate equation:

$$dC/dt = -k_1C \quad \Rightarrow \quad dC/C = -k_1dt$$

$$\int_{C_0}^{C_t} dC/C = -\int_0^t k dt \qquad \{N.B.\ \int (1/x).dx = \ln x + constant\}$$

$$[\ln C]_{C_0}^{C_t} = -kt \quad \Rightarrow \quad \ln[C] - \ln[C_0] = -k_1 t$$

$$\Rightarrow \quad \ln[C] = \ln[C_0] - k_1 t \quad \Rightarrow \quad C = C_0 e^{-kt} \quad \text{(exponential decay)}$$

Additionally, if $C_t/C_0 = 0.5$, then $\ln(0.5) = -k_1 t_{1/2} \Rightarrow \boldsymbol{t_{1/2} = 0.693/k_1}$

Ex. 1-9:

$$k_1 = 0.693/1900 = 3.6 \times 10^{-4}/\text{day}$$
$$C_t = 10\exp-\{(3.6 \times 10^{-4}/\text{day})(53 \text{ years})(365 \text{ days/year})\}$$

Second-order Reactions

- Most reaction mechanisms involve a series of second-order processes, as trimolecular collisions are quite unlikely. If a reaction of molecularity two is rate-limiting, the rate law is of the form: $\boldsymbol{-dA/dt = -dB/dt = -k_2 \bullet A \bullet B}$ and the rate constant has units $M^{-1}s^{-1}$.
- The order of the reaction reflects the number of discreet molecules involved in the rate-determining step of the mechanism, for instance:

$$NO + O_3 \rightarrow NO_2 + O_2; \quad -d[NO]/dt = k_2[NO][O_3]$$
$$2NO_2 + F_2 \rightarrow 2NO_2F; \quad -d[NO_2]/dt = k_2[NO_2][F_2]$$

- In some cases, such as hydrolyses in water, second-order reactions exhibit pseudo-first-order kinetics: $\boldsymbol{-dC/dt} = -k_2 \bullet [H_2O] \bullet C = -k_2 \bullet 55.4 \bullet C = \boldsymbol{-k_1' \bullet C}$ where the constant concentration of water has been combined with k_2 to generate the new (pseudo-first order) rate constant (k_1').

Pressure and Temperature

- Both pressure and temperature significantly influence rate constants, but pressure effects (which are very important in gas phase reactions in closed systems, such as in many industrial plants) are not usually of concern in an environmental setting.
- If the rate constants are known at two temperatures, then the rate constants for that same reaction at all other temperatures may (in principle) be calculated from the Arrhenius equation: $\boldsymbol{k = A \bullet \exp(-\Delta G^{\#}/RT)}$ where A is the pre-exponential factor (an empirical constant) and the other parameters are as defined earlier.
- There is a useful "rule of thumb" concerning rate constants: for every 10 °C rise in temperature there is an approximate doubling of the rate constant.

Ex. 1-10 (variation):

$$\Delta G^{\#} = 47.5 \text{ kJ/mol} \Rightarrow A = 0.046\exp\{(47{,}500)/[(8.3)(293)]\} = 1.4 \times 10^7/\text{day}$$
$$\text{At } 10\ °C,\ k = (1.4 \times 10^7)\exp\{-(47{,}500)/[(8.3)(283)]\} = 0.023/\text{day}$$

Sections in Text: 1.66

Next Time: 1.7 to conclusion of Chapter 1